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Key Points:

- In situ analysis in planktic foraminifers reveals that the C-isotope excursion (CIE) marking the onset of the PETM is at least 4.6 per mille for surface ocean DIC
- CIE magnitudes registered by surface ocean dissolved inorganic carbon and terrestrial substrates are highly congruent at the PETM onset
- The C-isotope composition of diagenetic calcite indicates that many planktic foraminifer records of the CIE are attenuated by diagenesis

Supporting Information:

- Supporting Information S1

Correspondence to:
R. Kozdon,
rkozdon@ldeo.columbia.edu

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Diagenetic Attenuation of Carbon Isotope Excursion Recorded by Planktic Foraminifers During the Paleocene-Eocene Thermal Maximum

Reinhard Kozdon[1], D. Clay Kelly[2], and John W. Valley[2,3]

[1]Lamont-Doherty Earth Observatory, Columbia University, Palisades, NY, USA, [2]Department of Geoscience, University of Wisconsin-Madison, Madison, WI, USA, [3]WiscSIMS, Department of Geoscience, University of Wisconsin-Madison, Madison, WI, USA

Abstract Earth surface temperatures warmed by ~5 °C during an ancient (~56 Ma) global warming event referred to as the Paleocene-Eocene thermal maximum (PETM). A hallmark of the PETM is a carbon isotope excursion (CIE) signaling the release of massive amounts of ^{13}C-depleted carbon into the ocean-atmosphere system, but substrate-specific differences in the CIE magnitude are a source of uncertainty for estimating the mass of carbon emitted. Here we report that secondary ion mass spectrometry (SIMS)-based in situ measurements of δ^{13}C in minute (7 μm) domains of planktic foraminifer shells (Ocean Drilling Program Site 865, central Pacific Ocean) yield a CIE that is ~2‰ larger than that delineated by conventional "whole-shell" δ^{13}C values for this same PETM record. SIMS-based measurements on diagenetic crystallites yield δ^{13}C values (~2.8‰) that fall between those of pre-CIE and CIE planktic foraminifer shells, indicating that the crystallites are an amalgamated blend of pre-CIE and CIE carbonates. This suggests that diagenesis shifts the whole-shell δ^{13}C compositions of pre-CIE and CIE foraminifers found in samples straddling the base of the PETM interval toward the intermediate δ^{13}C composition of the crystallites, thereby dampening the amplitude of the isotopic excursion. The diagenetic process envisioned would be most consequential for carbonate-rich PETM records that have suffered chemical erosion of pre-CIE carbonate. Given that the domains targeted for SIMS analysis may not be pristinely preserved, we consider the 4.6‰ excursion in our SIMS-based δ^{13}C record to be a conservative estimate of the full CIE for surface ocean dissolved inorganic carbon.

1. Introduction

The Paleocene-Eocene thermal maximum (PETM) was the most prominent in a series of "thermal maxima" to have punctuated the greenhouse climate state that prevailed over much of the early Paleogene period (e.g., Cramer et al., 2003; Nicolo et al., 2007). This geologically brief (~200 ka) episode of global warming brought a close to the Paleocene epoch at ~56 Ma (Westerhold et al., 2017) and entailed a rapid ~5 °C increase in surface temperatures that perturbed the functional partitioning of Earth's biogeochemical systems (e.g., Bowen et al., 2004; Huber & Sloan, 2000; Zachos et al., 2003). The environmental changes wrought by PETM conditions profoundly impacted the global biosphere, altering the complexion of terrestrial and marine ecosystems (e.g., Gingerich, 2006; Thomas, 1990; Wing et al., 2005). Thus, the onset of PETM conditions left an indelible mark on the rock and fossil records, but its most widely recognized signature is a sharp decline in the carbon isotopic (δ^{13}C) compositions of marine and terrestrial materials (Kennett & Stott, 1991; Koch et al., 1992). This negative carbon isotope excursion (CIE) has been documented at numerous locations in various organic and inorganic substrates (e.g., Bowen et al., 2001; Cui et al., 2011; McCarren et al., 2008; Pagani et al., 2006); hence, its ubiquitous nature signals the release of massive quantities of isotopically light carbon into the ocean-atmosphere system (Dickens et al., 1995).

Delineating the CIE in the geologic record provides a chemostratigraphic framework for studying the dynamics of carbon cycling and climate change during the PETM, yet such critical aspects of the CIE as the source(s) of emitted carbon, mass of carbon input, and rate of carbon release are still debated (see Dickens, 2011). Criteria such as the δ^{13}C composition of the carbon source (Dickens et al., 1995; Higgins & Schrag, 2006), extent of carbonate dissolution in the oceans (Dickens et al., 1997; Zeebe et al., 2009), and degree of climatic warming (e.g., Zeebe et al., 2009) have all been used to assess the veracity of proposed carbon sources and constrain the mass of carbon released into the ocean-atmosphere system during the

PETM. The parameter most widely used to constrain the mass of carbon input is the magnitude of the CIE (e.g., Dickens et al., 1995; Gutjahr et al., 2017; Kirtland Turner & Ridgwell, 2016; Pagani et al., 2006; Svensen et al., 2004), but substrate-specific differences in the size of the excursion are a major source of uncertainty for this critical constraint (Bains et al., 2003). Such discrepancies are most evident between terrestrial and marine records that yield mean CIE magnitudes of ~4.7‰ and ~2.8‰ (McInerney & Wing, 2011), respectively. This disparity is puzzling since gas exchange across the air-sea interface is instantaneous on geologic time scales, so the CIE magnitude in marine records expressing the δ^{13}C of dissolved inorganic carbon (DIC) in the surface ocean (surface DIC) should be similar to that seen in terrestrial records expressing the δ^{13}C of atmospheric CO_2 (e.g., Böhm et al., 2002; Koch et al., 1992).

A number of processes and feedback mechanisms have been invoked to reconcile this interreservoir discrepancy, while only a handful of studies have given due consideration to the role that seafloor diagenesis may have played in attenuating the CIE recorded by marine carbonates (Bralower et al., 2014; Cohen et al., 2007; Handley et al., 2008; McCarren et al., 2008). This is especially true for CIE records based on the δ^{13}C of calcite in planktic foraminifer shells. And while the specter of diagenesis has been broached in the literature, its impact on CIE records remains poorly understood and quantitatively unconstrained. This shortcoming is both surprising and understandable. It is surprising from the standpoint that diagenesis is pervasive in seafloor sediments (e.g., Schrag et al., 1995) as evidenced by the paucity of pristinely preserved (glassy) foraminifer shells in the deep-sea sedimentary record (Pearson et al., 2001). On the other hand, it is understandable because the minute, micrometer scales over which this diagenetic alteration occurs within individual foraminifer shells (Sexton et al., 2006) prohibit the use of conventional gas-source mass spectrometry (GSMS) requiring acid digestion of whole foraminifer shells.

Here we quantify the effects of postdepositional diagenesis on the CIE using new δ^{13}C data acquired in situ by secondary ion mass spectrometry (SIMS) from minute ~7 μm domains within individual planktic foraminifer shells recovered at Ocean Drilling Program (ODP) Site 865. These $\delta^{13}C_{SIMS}$ data indicate that the CIE magnitude recorded by planktic foraminifer shells calcified in the oceanic mixed layer approaches ~5‰ and is therefore more congruous with the CIE magnitude measured from terrestrial materials and organic carbon. In addition, we present complementary $\delta^{13}C_{SIMS}$ data acquired from diagenetic crystallites that provide sorely needed insight into the mechanistic process by which diagenesis attenuates the magnitude of the CIE registered by planktic foraminifer $\delta^{13}C_{GSMS}$ records.

2. Materials and Methods

2.1. Study Site and Foraminifer Shells Selected for In Situ Analysis

Study materials are from two PETM records recovered at Site 865 (hole 865B: 18°26.415′N, 179°33.349′W, 1516.2-m water depth; hole 865C: 18°26.425′N, 179°33.339′W, 1517.4-m water depth), located atop Allison Guyot in the Mid-Pacific Mountains (Sager et al., 1993; Figure 1a). Benthic foraminifer assemblages indicate that both PETM sections were deposited at midbathyal (~1,300 m) water depths and paleolatitude projections place Site 865 near the equator during the late Paleocene (Sager et al., 1993). Previously published δ^{13}C records (Bralower, Zachos, et al., 1995) have constrained the PETM to a thin (~15–20 cm) stratigraphic interval in both study sections (Figure 1b). The two PETM sections are composed of weakly lithified, calcareous ooze from which foraminifer shells were gleaned by rinsing the sediment with pH buffered (~8.0), deionized water over a 63-μm sieve and oven dried at ~30 °C overnight.

Shells of the planktic foraminifer species *Morozovella velascoensis* and *Morozovella allisonensis* from the hole 865C section were targeted for $\delta^{13}C_{SIMS}$ analysis. Previous studies have shown that the stable isotopic signatures of these two species exhibit size-dependent trends that are similar to those of modern mixed layer-dwelling planktic foraminifers hosting algal symbionts (Kelly et al., 1998, 2001). At Site 865, the δ^{13}C compositions of *M. velascoensis* and *M. allisonensis* increase by ~0.75 to 1.0‰ over shell sizes ranging between ~150 and 355 μm (Kelly et al., 1998, 2001). To minimize the effects of such δ^{13}C/size variation, geochemical measurements were restricted to a narrow range (300–355 μm) of shell sizes (e.g., Bralower, Parrow, et al., 1995; Kelly et al., 1996, 1998). Accordingly, *M. velascoensis* was used for pre-CIE (104.00, 103.70, and 103.50 m below seafloor, mbsf) and post-CIE (102.00, 101.60, and 101.30 mbsf) samples, whereas the “excursion taxon” *M. allisonensis* was used for CIE samples (103.00 and 102.90 mbsf). We targeted the hole 865C record for study because a wealth of conventional, whole-shell stable isotope data has been published for

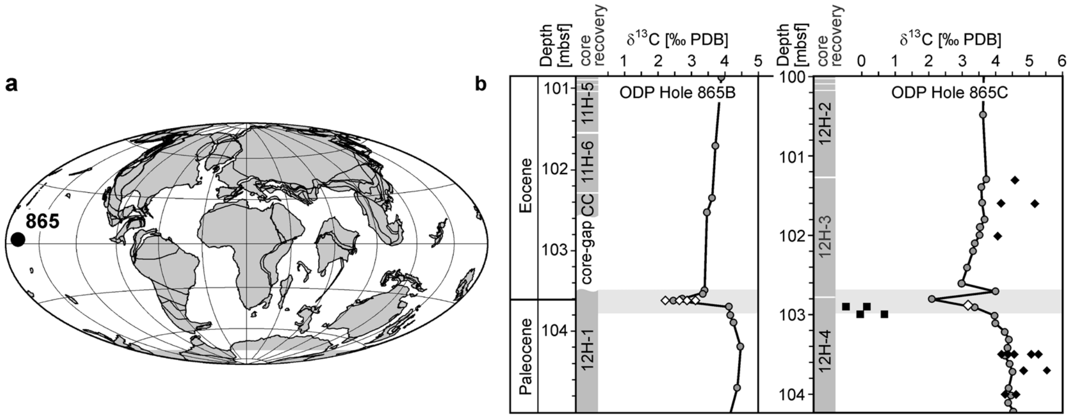

Figure 1. (a) Map showing early Eocene paleogeography (http://www.odsn.de) and location of Site 865. (b) Chemostratigraphic correlation of the hole 865B and 865C PETM sections using the carbon isotope excursion recorded by gas-source mass spectrometry of pooled, "multi-shell" samples (gray circles) of mixed layer-dwelling morozovellids (Bralower, Zachos, et al., 1995). Mean secondary ion mass spectrometry-based $\delta^{13}C$ values measured in situ from subdomains of individual shells of *M. velascoensis* (black diamonds) and *M. allisonensis* (black squares) plotted against the published carbon isotope excursion record for the hole 865C section. Note that diagenetic crystallites and calcite infilling chambers of *M. allisonensis* (open diamonds) are restricted to the carbon isotope excursion interval of holes 865B and 865C (gray bands) and that their $\delta^{13}C$ compositions are similar to those of correlative multi-shell samples measured by gas-source mass spectrometry. ODP = Ocean Drilling Program.

both *M. velascoensis* and *M. allisonensis* (300–355-μm size fraction) from this same PETM section (Bralower, Parrow, et al., 1995; Kelly et al., 1996, 1998). Added incentive for studying the Site 865 PETM records is provided by an earlier study (Kozdon et al., 2013) that found diagenetic crystallites (~500-μm diameter) composed of translucent crystals of calcite cementing numerous foraminifer shells and fragments in the neighboring hole 865B PETM section (Figure 2a). Thus, $\delta^{13}C_{SIMS}$ analyses were performed on the diagenetic crystallites for comparative purposes. In short, the CIE recorded by morozovellids from hole 865C was measured by performing 29 $\delta^{13}C_{SIMS}$ analyses in nine shells of pre-CIE *M. velascoensis*, 11 $\delta^{13}C_{SIMS}$ analyses in four shells of the CIE taxon *M. allisonensis*, and 11 $\delta^{13}C_{SIMS}$ analyses in four shells of post-CIE *M. velascoensis*. Additional 35 $\delta^{13}C_{SIMS}$ analyses were performed on four diagenetic crystallites recovered from the hole 865B PETM section (Figure 2a) as well as four $\delta^{13}C_{SIMS}$ analyses on a smaller crystallite found inside a shell of *M. allisonensis* from the hole 865C (Figures 2c and 2d).

2.2. In Situ Carbon Isotope Analysis by Ion Microprobe

Foraminifer shells and crystallites were cast with two grains of UW Calcite-3 (UWC-3) standard in epoxy and polished to midsection with a relief <1 μm (Kita et al., 2009). To minimize instrumental bias related to sample position, each epoxy mount was prepared such that all analytical pits were within 5 mm of the center of the mount (Kita et al., 2009). After scanning electron microscope (SEM) imaging using backscattered electron and secondary electron detectors to identify suitable domains near the base of muricae blades for in situ analysis (see Kozdon et al., 2011, 2013), samples were analyzed in two sessions (July and August 2012) by a CAMECA ims-1280 ion microprobe at WiscSIMS (Wisconsin Secondary Ion Mass Spectrometer Laboratory; Kita et al., 2009; Valley & Kita, 2009). In both sessions, the $^{133}Cs^+$ primary beam with an intensity of ~600 pA and a total accelerating voltage of 10 keV was focused to a diameter of ~7 μm on the sample surface. Sample charging was compensated by a conductive Au-coat of the sample mounts in combination with an electron flood gun. Tuning of the secondary optics was similar to Kita et al. (2009) and aimed to achieve high secondary ion transmission. Secondary C^- ions were detected simultaneously by a Faraday cup ($^{12}C^-$) and an electron multiplier ($^{13}C^-$). In the second session, $^{13}CH^-$ was included into the analytical protocol and measured simultaneously by a second electron multiplier. Typical $^{12}C^-$ count rates were between $\sim 5 \times 10^6$ and 6×10^6 counts per second. The total analytical time per spot was about 5 min including presputtering (1 min), automatic centering of the secondary ion image (~1 min), and analysis (20 cycles of 8 s each). The gain of the electron multiplier was monitored before the third analysis of each group of four standard analyses (about once every hour), and the applied high voltage was adjusted to compensate drift of the gain of the electron multiplier, if

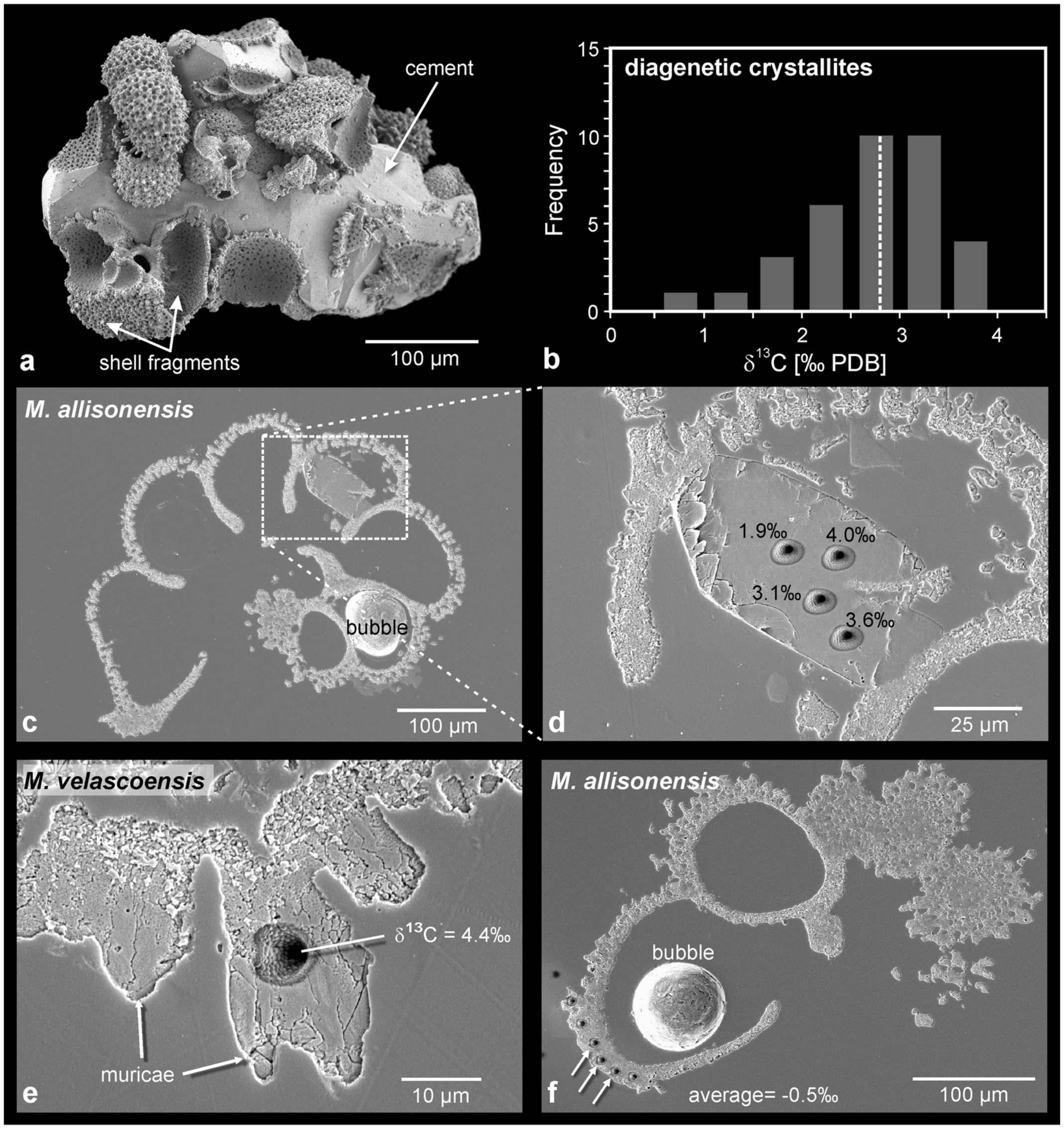

Figure 2. (a) Scanning electron microscope (SEM) image of diagenetic crystallite cementing foraminifer shells from the CIE interval (hole 865B, 103.60 m below seafloor (mbsf)). (b) Histogram showing frequency distribution of 35 in situ $\delta^{13}C$ measurements placed in four crystallites. Vertical dashed line denotes mean $\delta^{13}C$ composition of crystallites. (c) SEM image of a diagenetic crystallite (dashed box), polished to midsection, found inside the chamber of the PETM morphotype *M. allisonensis* (hole 865C, 102.86 mbsf). (d) Enlarged image of crystallite shown in panel c with 7-μm secondary ion mass spectrometry (SIMS) analysis pits and corresponding $\delta^{13}C$ values. (e) SEM image of cross section through the chamber wall of *M. velascoensis* (865C, 12–4, 70–72 cm, 103.50 mbsf) showing placement of SIMS analysis pit near base of muricae blade and corresponding $\delta^{13}C$ value. (f) SEM image of a cross section through a shell of *M. allisonensis* (865C, 12–4, 10–12 cm, 102.90 mbsf) showing six SIMS analysis pits in the final chamber. The average $\delta^{13}C$ of three measurements is −0.5‰ (pits marked by arrows); the other pits were placed in domains impregnated by epoxy and were not used.

required. Reproducibility of $\delta^{13}C$ of the bracketing standard analyses includes the drift of the gain of the electron multiplier.

Grains of UWC-3 ($\delta^{13}C = -0.91$‰ Vienna Pee Dee Belemnite (VPDB), Kozdon et al., 2009), mounted in the center of each epoxy mount, were measured in four spots before and after <13 sample analyses, and the resulting average value bracketing the samples was used for instrumental mass fractionation correction. Reproducibility of the individual spot analyses of UWC-3 standard (bracketing samples) is assigned as uncertainty of unknown samples and varies from 0.3‰ to 1.4‰ with an average of 0.7‰ (±2 standard deviation; 17 standard-sample-standard brackets were performed in total; see Table S1 in the supporting information). The first standard-sample-standard bracket of the August 2012 session features the highest standard deviation (1.4‰) due to some instability of the primary beam intensity that occurred after instrument startup. A total of 190 analyses was performed, including 100 UWC-3 measurements bracketing the samples. The complete data set and additional details of the methodology can be found in the supporting information (Table S1; see also Craig, 1957; Kita et al., 2009; Kozdon et al., 2009, 2011; Valley & Kita, 2009). Whenever possible, multiple $\delta^{13}C_{SIMS}$ measurements were taken in an individual shell. Replicate $\delta^{13}C_{SIMS}$ analyses within the same chamber are typically within analytical precision.

Several parameters and procedures were used to assess the quality of the data and to identify measurements of domains crosscutting unwanted secondary phases that need to be excluded from the data set. The secondary ion intensity ($^{12}C^{-}$ count rate in counts per second) of the sample analysis was compared to the average $^{12}C^{-}$ count rate of the eight bracketing standard analyses. Assuming a stable primary beam, only sample measurements with $^{12}C^{-}$ count rates between 90% and 105% of those of the bracketing standards were used (see Table S1 in the supporting information). Some measurements in crystallite #3 are slightly below the 90% threshold but considered as "robust" as the decrease in $^{12}C^{-}$ counts was caused by a minor drop in the primary beam intensity. In general, lower secondary count rates indicate analysis of porous domains, whereas higher $^{12}C^{-}$ count rates are mainly associated with epoxy (and/or other phases) overlapping the analysis pit.

In the second session (August 2012), we included the simultaneous measurement of $^{13}CH^{-}$ with $^{12}C^{-}$ and $^{13}C^{-}$ that provides an indication of water, organic matter content, and/or other H-bearing phases present in the SIMS pit that may compromise the quality of the data. The $^{13}CH/^{13}C$ ratio of each sample analysis is background corrected by subtraction of the average $^{13}CH/^{13}C$ of the eight bracketing UWC-3 standard analyses (see Table S1 in the supporting information). During this session, all background-corrected $^{13}CH/^{13}C$ ratios were clustered in a relatively narrow range (3.5×10^{-2} to 8.3×10^{-3}), and measured $\delta^{13}C$ is not correlated with $^{13}CH/^{13}C$. Thus, no data were excluded from the data set based on elevated $^{13}CH/^{13}C$ ratios.

After ion microprobe measurements, all SIMS analysis pits were imaged by SEM to verify their exact location and to identify "irregular" pits (Cavosie et al., 2005). Carbon isotope data from spots overlapping epoxy resin or areas of high porosity in the foraminifer chamber walls were not used.

3. Results

Comparison of published $\delta^{13}C$ values measured from pooled, multi-shell samples (multi-shell $\delta^{13}C_{GSMS}$) of *M. velascoensis* (Bralower, Parrow, et al., 1995) to those measured by $\delta^{13}C_{SIMS}$ analyses in shells of *M. velascoensis* and *M. allisonensis* (Table 1) shows that both data sets record the negative CIE in the hole 865C PETM section, but the magnitude of the CIE differs between the two parallel records (Figure 1b). The $\delta^{13}C_{SIMS}$ values acquired from shells of pre-CIE *M. velascoensis* are centered on ~4.7‰ (VPDB; $n = 9$ shells) and slightly higher than correlative multi-shell $\delta^{13}C_{GSMS}$ values. However, the sign of the difference between $\delta^{13}C_{SIMS}$ and multi-shell $\delta^{13}C_{GSMS}$ values is reversed within the CIE interval (~103.00–102.80 mbsf) where $\delta^{13}C_{SIMS}$ values for the PETM taxon *M. allisonensis* (~0.1‰ VPDB, $n = 4$ shells) are ~2‰ lower than corresponding multi-shell $\delta^{13}C_{GSMS}$ values for *M. velascoensis*. Within the overlying post-CIE interval (102.00–101.30 mbsf), both multi-shell $\delta^{13}C_{GSMS}$ and $\delta^{13}C_{SIMS}$ values of *M. velascoensis* (~4.5‰ VPDB, $n = 4$ shells) return to near pre-CIE values, and the original relation where $\delta^{13}C_{SIMS}$ values are higher than correlative multi-shell $\delta^{13}C_{GSMS}$ values for *M. velascoensis* is reestablished (Figure 1b). Thus, the mean magnitude of the excursion (~4.6‰) recorded by the $\delta^{13}C_{SIMS}$ data is ~2‰ larger than the CIE recorded by correlative multi-shell $\delta^{13}C_{GSMS}$ values, with the total range from highest to lowest $\delta^{13}C_{SIMS}$ values approaching ~6‰ (Figure 1b).

The differences between the SIMS and GSMS $\delta^{13}C$ data sets are further investigated by plotting the $\delta^{13}C_{SIMS}$ values against previously reported (Kelly et al., 1996, 1998) $\delta^{13}C_{GSMS}$ values measured from individual shells of *M. velascoensis* and *M. allisonensis* from within the CIE interval of hole 865C (Figure 3). We make this comparison because, unlike the multi-shell $\delta^{13}C_{GSMS}$ record, the "single-shell" $\delta^{13}C_{GSMS}$ record includes values measured from individual shells of the PETM taxon, *M. allisonensis*. Hence, we are able to directly compare the $\delta^{13}C_{SIMS}$ and single-shell $\delta^{13}C_{GSMS}$ values for *M. allisonensis*. Yet despite the inclusion of single-shell $\delta^{13}C_{GSMS}$ values for *M. allisonensis*, the results of this comparison are similar to those described above for

Table 1
In Situ δ^{13}C Analyses by Ion Microprobe in Morozovellid Species and Diagenetic Crystallites From ODP Site 865, Central Pacific

In situ δ^{13}C analyses of foraminifera shells

Hole, core section, interval	MBSF (m)	Event	Species	Size fraction (μm)	Shell/analysis number	Individual δ^{13}C analysis (‰ PDB)	± 2 SD [a]	δ^{13}C, mean of each shell (‰ PDB)
865C, 12–3, 0–2 cm	101.30	Post-CIE	*M. velascoensis*	300–355	Shell 80-1	5.42	1.02	4.57
					Shell 80-2	4.35	1.02	
					Shell 80-3	3.93	1.02	
865C, 12–3, 30–32 cm	101.60	Post-CIE	*M. velascoensis*	300–355	Shell 117-1	3.65	0.66	4.16
					Shell 117-2	4.66	0.66	
					Shell 115-1	3.45	0.53	5.13
					Shell 115-2	6.45	0.53	
					Shell 115-4	4.59	0.53	
					Shell 115-5	4.87	0.53	
					Shell 115-7	6.27	0.53	
865C, 12–3, 70–72 cm	102.00	Post-CIE	*M. velascoensis*	300–355	Shell 68-1	4.05	0.33	4.05
865C, 12–4, 10–12 cm	102.90	CIE	*M. allisonensis*	300–355	Shell 51-2	−0.19	0.45	−0.47
					Shell 51-3	−0.96	0.45	
					Shell 51-4	−0.25	0.45	
					Shell 52-1	−0.62	0.47	0.17
					Shell 52-2	1.41	0.47	
					Shell 52-3	0.13	0.47	
					Shell 52-4	−0.22	0.47	
					Shell 52-5	0.16	0.47	
865C, 12–4, 20–22 cm	103.00	CIE	*M. allisonensis*	300–355	Shell 17-1	0.69	0.47	0.69
					Shell 18-1	−0.78	0.47	−0.05
					Shell 18-2	0.68	0.47	
865C, 12–4, 70–72 cm	103.50	Pre-CIE	*M. velascoensis*	300–355	Shell 12-1	5.43	0.59	4.52
					Shell 12-2	5.07	0.59	
					Shell 12-3	3.07	0.59	
					Shell 13-1	3.57	0.59	4.18
					Shell 13-3	4.79	0.59	
					Shell 14-1	4.23	0.55	4.37
					Shell 14-2	4.55	0.55	
					Shell 14-3	4.29	0.55	
					Shell 14-4	5.06	0.55	
					Shell 14-5	3.75	0.55	
					Shell 15-1	5.48	0.55	5.27
					Shell 15-2	4.92	0.55	
					Shell 15-4	5.40	0.55	
					Shell 16-1	4.41	0.55	5.03
					Shell 16-2	5.65	0.81	
865C, 12–4, 90–92 cm	103.70	Pre-CIE	*M. velascoensis*	300–355	Shell 129-1	3.89	1.43	4.81
					Shell 129-2	5.67	1.43	
					Shell 129-3	4.87	1.43	
					Shell 127-1	6.10	1.43	5.51
					Shell 127-3	5.45	1.43	
					Shell 127-4	4.99	1.43	
865C, 12–4, 120–122 cm	104.00	Pre-CIE	*M. velascoensis*	300–355	Shell 100-1	3.71	0.36	4.27
					Shell 100-2	3.84	0.36	
					Shell 100-3	5.23	0.36	
					Shell 100-4	4.30	0.36	
					Shell 103-1	2.37	0.36	4.60
					Shell 103-2	4.74	0.36	
					Shell 103-3	5.83	0.36	
					Shell 103-4	5.45	0.36	

Table 1 *(continued)*

In situ $\delta^{13}C$ analyses of diagenetic crystallites and chamber infilling

Hole, core section, interval	Mbsf (m)	Event	Species	Size fraction (μm)	Crystallite # and analysis number	Individual $\delta^{13}C$ analysis (‰ PDB)	± 2 SD [a]	$\delta^{13}C$, mean of each crystallite (‰ PDB)
865B, 12H-1, 10–12 cm	103.60	CIE			Crystallite #3, 1	1.91	0.79	2.23
					Crystallite #3, 2	1.81	0.79	
					Crystallite #3, 3	2.93	0.79	
					Crystallite #3, 4	2.85	0.79	
					Crystallite #3, 5	2.16	0.79	
					Crystallite #3, 6	3.48	0.79	
					Crystallite #3, 7	1.77	0.79	
					Crystallite #3, 8	2.52	0.79	
					Crystallite #3, 9	1.63	0.79	
					Crystallite #3, 10	2.62	0.79	
865B, 12H-1, 10–12 cm	103.60	CIE			Crystallite #5, 1	2.59	0.81	2.92
					Crystallite #5, 2	3.08	0.81	
					Crystallite #5, 3	2.87	0.81	
					Crystallite #5, 4	3.14	0.81	
865B, 12H-1, 10–12 cm	103.60	CIE			Crystallite #6, 1	2.75	0.60	2.64
					Crystallite #6, 2	3.06	0.60	
					Crystallite #6, 3	2.91	0.60	
					Crystallite #6, 4	3.23	0.60	
					Crystallite #6, 5	0.77	0.60	
					Crystallite #6, 6	2.78	0.60	
					Crystallite #6, 7	3.15	0.60	
					Crystallite #6, 8	2.46	0.60	
865B, 12H-1, 10–12 cm	103.60	CIE			Crystallite #7, 1	3.56	1.15	3.12
					Crystallite #7, 2	3.13	1.15	
					Crystallite #7, 3	3.16	1.15	
					Crystallite #7, 4	2.68	1.15	
					Crystallite #7, 5	3.37	1.15	
					Crystallite #7, 6	2.95	1.15	
					Crystallite #7, 7	2.26	1.15	
					Crystallite #7, 8	2.40	1.15	
					Crystallite #7, 9	3.77	1.15	
					Crystallite #7, 10	3.14	1.15	
					Crystallite #7, 11	2.71	1.15	
					Crystallite #7, 12	3.73	1.15	
					Crystallite #7, 13	3.74	1.15	
865C, 12–4, 6–8 cm	102.87	CIE	*M. allisonensis*	300–355	Shell 60, infilling, 1	1.88	1.04	3.16
					Shell 60, infilling, 2	3.13	1.04	
					Shell 60, infilling, 3	3.97	1.04	
					Shell 60, infilling, 4	3.64	1.04	

[a] Reproducibility, defined as the spot-to-spot reproducibility of the eight standard analyses bracketing each block of sample analyses. ODP = Ocean Drilling Program; MBSF = m below seafloor; SD = standard deviation; CIE = carbon isotope excursion.

the comparison to multi-shell $\delta^{13}C_{GSMS}$ values. Namely, the CIE interval is characterized by a reversal in the sign of the relation between in situ $\delta^{13}C_{SIMS}$ and single-shell $\delta^{13}C_{GSMS}$ values registered by *M. allisonensis*, with the CIE magnitude delimited by the single-shell $\delta^{13}C_{GSMS}$ values still being ~2‰ smaller than the mean CIE magnitude recorded by $\delta^{13}C_{SIMS}$ values (Figure 3).

The $\delta^{13}C_{SIMS}$ values of the diagenetic crystallites are centered on ~2.8‰ (Figure 2b) and similar to the multi-shell $\delta^{13}C_{GSMS}$ values of *M. velascoensis* samples from within the CIE interval of hole 865B (Figure 1b). In contrast, the mean $\delta^{13}C_{SIMS}$ composition of the diagenetic crystallites falls between the single-shell $\delta^{13}C_{GSMS}$ values of pre-CIE and CIE morozovellid shells (Figure 3). We also note that the mean $\delta^{13}C_{SIMS}$ composition of these blocky crystallites (~2.8‰ VPDB, *n* = 4 crystallites) is comparable to that of a smaller crystallite (~3.2‰ VPDB) found inside an *M. allisonensis* shell from the CIE interval (102.86 mbsf) of hole 865C (Figures 2b–2d).

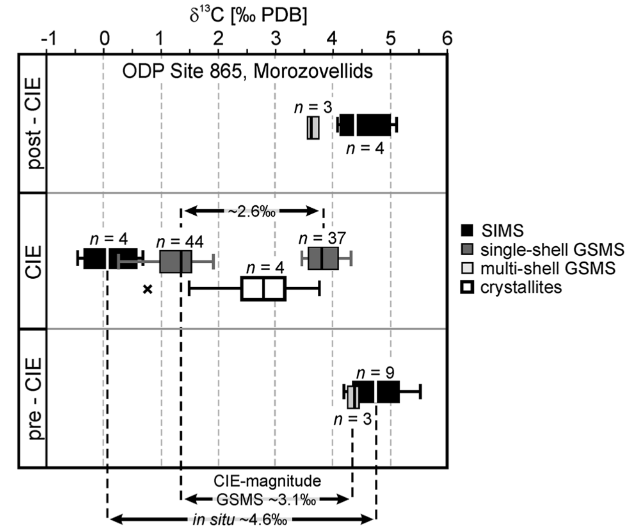

Figure 3. Box and whisker plot summarizing differences in the magnitude of the carbon isotope excursion (CIE) between mean secondary ion mass spectrometry (SIMS) δ^{13}C values of individual morozovellid shells and conventional gas-source mass spectrometer (GSMS) analyses of pooled (multi-shell) and individual (single-shell) morozovellid samples. Boxes denote the first and third quartiles, with the vertical line inside the box being the median value and whiskers delimiting the minimum and maximum of all δ^{13}C values for each data set from the pre-CIE, CIE, and post-CIE intervals. Multi-shell δ^{13}C values (Bralower, Zachos, et al., 1995) are from same pre-CIE and post-CIE core samples as SIMS δ^{13}C values, all single-shell GSMS δ^{13}C values (Kelly et al., 1996) are from samples within CIE interval. Bimodal distribution of single-shell GSMS δ^{13}C values within CIE interval reflects sediment mixing. Note that SIMS-based CIE (4.6‰) is larger than that measured by GSMS analyses of multi-shell (~3.1‰) and single-shell (2.6‰) samples. SIMS δ^{13}C values for diagenetic cements (crystallites) from CIE interval are intermediate (δ^{13}C = 2.8‰) between mean GSMS δ^{13}C values of individual pre-CIE and CIE shells. Unusually low δ^{13}C value from an individual SIMS pit in a crystallite denoted by "x." Number (*n*) of multi-shell samples analyzed by GSMS, individual shells analyzed by SIMS or GSMS, and diagenetic crystallites analyzed by SIMS noted above/below corresponding boxes.

4. Discussion

The integrity of PETM records recovered from the deep-sea sedimentary archive has been questioned on the grounds that the stratigraphies have been distorted and/or rendered incomplete by the combined effects of such processes as carbonate dissolution (Zachos et al., 2005), sediment mixing (Ridgwell, 2007), and varying sedimentation rates (Kirtland Turner & Ridgwell, 2013). In addition, environmental change wrought by the PETM induced biotic responses that involved faunal change and physiological ("vital") effects, which further complicate δ^{13}C records of the CIE (e.g., Bralower & Self-Trail, 2016; Thomas, 2003; Uchikawa & Zeebe, 2010). The combined effects of these processes are undoubtedly responsible for some of the disparities seen between the CIE magnitudes of terrestrial and marine sedimentary records (McInerney & Wing, 2011). Of particular interest to this study is the CIE magnitude (~3–4‰) returned by planktic foraminifers (e.g., Gutjahr et al., 2017; Nunes & Norris, 2006; Zachos et al., 2003), which is ~2‰ smaller than that recorded by terrestrial organic and inorganic carbon (e.g., Bowen et al., 2001; Handley et al., 2008; Pagani et al., 2006). Moreover, the magnitude of the CIE delimited by $\delta^{13}C_{GSMS}$ values of mixed layer-dwelling planktic foraminifers varies spatially. For instance, the CIE compiled from published $\delta^{13}C_{GSMS}$ data approaches ~3‰ at Site 865 (Bralower, Parrow, et al., 1995; Kelly et al., 1996), while it is ~4‰ at Sites 689 and 690 in the South Atlantic (Kennett & Stott, 1991; Zachos et al., 2007). To a degree, such variability may reflect spatial differences in primary productivity (i.e., biological pump) and sedimentation rates that affect the stratigraphic expression of the CIE (e.g., Kirtland Turner & Ridgwell, 2013; Sluijs et al., 2007; Thomas & Shackleton, 1996). Still, the size of the CIE recorded by "whole-shell" $\delta^{13}C_{GSMS}$ measurements of planktic foraminifers from Site 865 falls at the lower end of the spectrum and is substantially smaller than the CIE reported for terrestrial records. Below, we use the δ^{13}C data at hand to assess the potential of the aforementioned mechanisms to mask the full size of the CIE at Site 865 and, by the same token, arrive at the conclusion that postdepositional diagenesis is the most parsimonious explanation for the smaller CIE previously reported from Site 865.

Sediment-mixing processes such as winnowing by bottom-water currents and bioturbation have long been recognized as a means of smoothing marine chemostratigraphies, and the time-averaging effects of sediment mixing are especially problematic for multi-shell $\delta^{13}C_{GSMS}$ records compiled from measurements of aggregate (pooled) samples consisting of multiple foraminifer shells (e.g., Kirtland Turner & Ridgwell, 2013). The bimodal distribution of the single-shell $\delta^{13}C_{GSMS}$ values within the CIE interval of hole 865C (Kelly et al., 1996) attests to how sediment mixing has thoroughly blended this condensed PETM stratigraphy (Figure 3). On the other hand, these same single-shell $\delta^{13}C_{GSMS}$ data can be used to reduce the effects of sediment mixing because the δ^{13}C signatures of individual shells clearly distinguish reworked pre-CIE shells with high δ^{13}C values from CIE shells with anomalously low δ^{13}C values. The efficacy of this "taphonomic filter" is evidenced by previous studies that have used single-shell $\delta^{13}C_{GSMS}$ values to show that none of the shells belonging to the thermocline-dwelling genus *Subbotina* spp. return a CIE value at Site 865 (Kelly et al., 1996, 1998). This finding indicates that the vast majority of subbotinid shells found within the CIE interval at Site 865 are displaced contaminants from older sediments and is why a complementary $\delta^{13}C_{SIMS}$ record for this thermocline-dwelling group was not generated in this study. Additionally, this same series of single-shell $\delta^{13}C_{GSMS}$ analyses revealed that the PETM taxon *M. allisonensis* (*n* = 44 shells) invariably yields anomalously low values, thereby confirming that this distinctive morphotype lived only during the CIE (Kelly et al., 1996). Hence, single-shell $\delta^{13}C_{GSMS}$ values of planktic foraminifers—especially those of

M. allisonensis—mitigate the effects of sediment mixing, yet these same single-shell $\delta^{13}C_{GSMS}$ values still yield a CIE magnitude of only ~2.6‰ (see Figure 3).

Another potential mechanism for attenuating the CIE is changing ocean pH. Culturing experiments have shown that the stable isotope composition of modern planktic foraminifer shells is influenced by seawater pH, with $\delta^{13}C$ values increasing at lower pH levels (Spero et al., 1997). This revelation has fueled speculation that ocean acidification may have increased the $\delta^{13}C$ of planktic foraminifer shells during the PETM, thereby reducing the size of the recorded excursion (Pagani et al., 2006). Modeling of this pH effect indicates that the $\delta^{13}C$ of mixed layer-dwelling morozovellids may have been increased by as much as ~0.9‰ during the PETM (Uchikawa & Zeebe, 2010). However, if pH was the main driver in attenuating the CIE magnitude recorded by planktic foraminifers, then the $\delta^{13}C_{SIMS}$ and single-shell $\delta^{13}C_{GSMS}$ values for the excursion taxon *M. allisonensis* should be roughly the same, yet this is clearly not the case (Figure 3). This observation contradicts the notion that the difference between SIMS- and GSMS-based $\delta^{13}C$ values is due to changing ocean pH, but it does not preclude the possibility that a pH-induced increase in planktic foraminifer $\delta^{13}C$ compositions may have dampened the overall amplitude of the CIE recorded by our $\delta^{13}C_{SIMS}$ analyses. Taking this provision into account suggests that the actual size of the CIE in the surface DIC reservoir may have been on the order of ~5–6‰. We therefore consider the ~4.6‰ excursion seen in our $\delta^{13}C_{SIMS}$ record to be a conservative estimate of the full CIE for the surface DIC reservoir.

Virtually all deep-sea PETM records feature a decline in sedimentary calcite that typically manifests as a clay-rich layer coincident with the CIE onset (e.g., Zachos et al., 2005). This drop in the amount of sedimentary calcite signals a transient increase in carbonate dissolution in response to carbon input during the initial stages of the PETM (Dickens et al., 1997). Detailed study of PETM sections arrayed along a bathymetric transect has shown that resultant shoaling of the calcite compensation depth (CCD) truncated the basal stratigraphies of these PETM records, which in turn reduced the magnitude of the CIE (e.g., McCarren et al., 2008; Zachos et al., 2005). Thus, it has been argued that carbonate dissolution has rendered many deep-sea PETM records incomplete (Pagani et al., 2006). This same line of reasoning has been used to explain the larger CIEs (~6–8‰) returned by bulk carbonate $\delta^{13}C_{GSMS}$ records generated for PETM sections deposited in neritic settings that presumably remained well above the CCD and were not strongly affected by carbonate dissolution (Zhang et al., 2017). Although a clay-rich dissolution layer is not observed at Site 865, we assume a priori that both PETM records at Site 865 have been truncated by carbonate dissolution given the global extent of ocean acidification (Penman et al., 2014; Zeebe et al., 2009) and absence of intermediate (transitional) values in the single-shell $\delta^{13}C_{GSMS}$ data set (Kelly et al., 1996). We therefore have good reason to suspect that the stratigraphies of the Site 865 PETM records do not capture the full CIE, which is yet another reason to consider our SIMS-based excursion to be a minimum estimate of the true CIE magnitude. This said, we do not consider dissolution to be the cause of the observed differences between the $\delta^{13}C_{SIMS}$ and single-shell $\delta^{13}C_{GSMS}$ values because none of the shells examined/analyzed in this study show signs of significant dissolution.

Having evaluated the feasibility of these alternative mechanisms, we examine the $\delta^{13}C$ data through the lens of postdepositional diagenesis. All planktic foraminifer shells analyzed in this study appear “frosty” (opaque, stark white) under reflected light and possess protuberances (muricae) on the exterior surface of their shells that have been thickened into blade-like structures (see Figures 2e and 2f). These are the telltale signs of diagenesis (Sexton et al., 2006). Moreover, SEM imaging of planktic foraminifer shells has confirmed that carbonate recrystallization is pervasive throughout the entirety of the early Paleogene section recovered at Site 865 (Edgar et al., 2015; Pearson & Burgess, 2008; Sexton et al., 2006). In short, the morozovellid shells analyzed in this study feature a strong diagenetic overprint.

In an effort to reduce the effects of diagenesis, an earlier study used in situ $\delta^{18}O_{SIMS}$ measurements on isolated domains within individual morozovellid shells from the Site 865 PETM section (Kozdon et al., 2013). These ultrahigh resolution (~3-μm analysis pits) $\delta^{18}O_{SIMS}$ analyses revealed that the relatively nonporous domain located at the base of muricae is better preserved than the rest of the shell and that this same domain, at the very least, partially retains the original chemistry of the biogenic calcite (Kozdon et al., 2013). Thus, by targeting these same domains with $\delta^{13}C_{SIMS}$ analyses (Figures 2e and 2f), we were able to prescribe a “biogenic” endmember $\delta^{13}C$ value of 0.1‰ for *M. allisonensis* shells. This biogenic endmember $\delta^{13}C$ value was used, in combination with the diagenetic endmember $\delta^{13}C$ value of 2.8‰ measured from the crystallites as well as published $\delta^{18}O_{SIMS}$ data acquired from similar domains within *M. allisonensis* shells and the

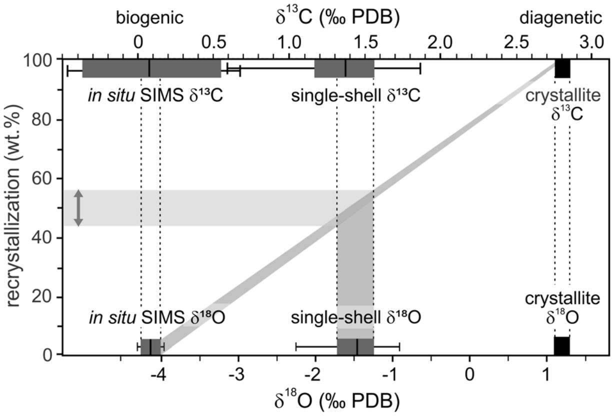

Figure 4. Four-endmember mass balance quantifying the degree of recrystallization for planktic foraminifer shells in the PETM records at Site 865. Mean values for secondary ion mass spectrometry (SIMS)-based $\delta^{13}C$ and $\delta^{18}O$ compositions of crystallites represent the diagenetic endmembers, while the range and median of SIMS-based $\delta^{13}C$ and $\delta^{18}O$ values measured in situ from individual shells of the PETM morphotype *M. allisonensis* delimit the "biogenic" endmembers. Note that $\delta^{13}C$ and $\delta^{18}O$ values for individual shells of *M. allisonensis* (Kelly et al., 1996), as determined by conventional gas-source mass spectrometry, fall between the diagenetic and biogenic endmember values, indicating that the whole-shell isotope compositions are a mixture of the two carbonate phases. SIMS-based $\delta^{18}O$ values for *M. allisonensis* shells are from Kozdon et al. (2011); SIMS-based $\delta^{18}O$ values for the diagenetic crystallites are from Kozdon et al. (2013).

diagenetic crystallites (Kozdon et al., 2011, 2013), to construct a self-consistent mass balance for both carbon and oxygen isotopes (Figure 4). The differences between the single-shell GSMS values and SIMS in situ measurements of both the biogenic and diagenetic compositional endmembers indicate that morozovellid shells from the hole 865C PETM section comprise about 45–55 wt.% diagenetic calcite, either through partial recrystallization of the shell or the addition of diagenetic cements. This degree of alteration closely matches earlier models for diagenesis in deep-sea sediments that estimate ~30 wt.% recrystallization and/or cementation (Schrag, 1999; Schrag et al., 1995; Tripati et al., 2003) as well as an earlier mass balance based solely on $\delta^{18}O$ measurements (Kozdon et al., 2011). The results of our mass balance calculations support the view that the foraminifer shells analyzed in this study are an aggregate mixture of both biogenic and diagenetic calcites and that the subdomains targeted by SIMS are better preserved than the rest of the shell. Given the degree of alteration and that the two carbonate phases formed under very different geochemical conditions, we posit that postdepositional diagenesis is the primary agent for attenuating the CIE recorded by $\delta^{13}C_{GSMS}$ analyses of whole planktic foraminifer shells.

A highly relevant aspect of the $\delta^{13}C$ data is the reversal of the $\delta^{13}C_{SIMS}$ versus $\delta^{13}C_{GSMS}$ relation across the CIE interval (Figures 1b and 3), which contradicts the view that the offsets in $\delta^{13}C$ reflect a systematic bias between the two analytical techniques. One possibility is that $\delta^{13}C$ offsets between SIMS and GSMS analyses are due to a combination of intrashell $\delta^{13}C$ variation and the differing amounts of material analyzed by the two techniques. For instance, $<$1 ng of material is analyzed with a 7-μm SIMS spot, whereas a whole-shell GSMS measurement carried out on an individual shell (300–355 μm in diameter) typically analyzes ~20 μg of calcite. Thus, the $\delta^{13}C$ offsets could be due to the measurement of ^{13}C-depleted juvenile chambers by whole-shell GSMS analyses that are excluded from SIMS analyses entailing in situ $\delta^{13}C$ measurements in isolated subdomains of a shell. This explanation is plausible for the pre-CIE and post-CIE intervals where $\delta^{13}C_{SIMS}$ values are higher than correlative $\delta^{13}C_{GSMS}$ values, but it does not account for the reversal in the SIMS versus GSMS relation registered by *M. allisonensis* shells within the CIE interval (Figure 3). To address this inconsistency, we consider an auxiliary hypothesis positing that the loss of algal photosymbionts hosted by many planktic foraminifer species (i.e., symbiont bleaching) led to a transient loss of the $\delta^{13}C$/size relation within *M. allisonensis* during the PETM (e.g., Si & Aubry, 2018). In essence, symbiont bleaching would result in a breakdown of the $\delta^{13}C$/size relation, thereby reducing interchamber $\delta^{13}C$ variation within a shell by removing the ^{13}C-enriched signal associated with larger, adult chambers. Symbiont bleaching warrants consideration owing to the extreme environmental conditions of the PETM, but we do not favor this interpretation because GSMS-based stable isotope analyses of size-segregated samples have shown that the PETM taxon, *M. allisonensis*, retains this $\delta^{13}C$/size relation at Site 865 (Kelly et al., 1998). In addition, a loss of the $\delta^{13}C$/size relation would amplify—not attenuate—the CIE, which would suggest that the negative excursion observed in planktic foraminifer $\delta^{13}C$ records overestimates the true size of the CIE. Hence, symbiont bleaching does not address the problem at hand; that being, why is the CIE in planktic foraminifer records smaller relative to that of terrestrial records? Finally, a reduction in intrashell $\delta^{13}C$ variability should bring the in situ $\delta^{13}C_{SIMS}$ and whole-shell $\delta^{13}C_{GSMS}$ values into agreement. Yet to the contrary, $\delta^{13}C_{SIMS}$ values are 1.2‰ lower than single-shell $\delta^{13}C_{GSMS}$ values for *M. allisonensis* within the CIE interval (Figure 3).

To gain insight into the reversal of the $\delta^{13}C_{SIMS}$ versus $\delta^{13}C_{GSMS}$ relation, we turn our attention back to the $\delta^{13}C_{SIMS}$ values measured from the diagenetic crystallites. The mean $\delta^{13}C_{SIMS}$ composition of these crystallites (2.8‰ VPDB) is comparable to that measured from the crystallite (3.2‰) found inside a *M. allisonensis* shell from the hole 865C section (Figures 2b–2d), so we assume that the $\delta^{13}C$ composition of the crystallites is representative of the $\delta^{13}C$ of the secondary calcite overprinting foraminifer shells within the CIE interval.

More importantly, the average $\delta^{13}C_{SIMS}$ value of the crystallites is centered between single-shell $\delta^{13}C_{GSMS}$ values returned by pre-CIE and CIE morozovellids (Figure 3). The intermediate $\delta^{13}C$ values of the crystallites suggest that postdepositional diagenesis increases the whole-shell $\delta^{13}C_{GSMS}$ values of CIE foraminifers. We therefore posit that the addition of diagenetic calcite increased whole-shell $\delta^{13}C_{GSMS}$ values of CIE *M. allisonensis* making them ^{13}C enriched relative to corresponding in situ $\delta^{13}C_{SIMS}$ values ($\delta^{13}C_{SIMS} < \delta^{13}C_{GSMS}$). The end result would be the observed reversal in $\delta^{13}C_{SIMS}$ versus $\delta^{13}C_{GSMS}$ values within the CIE interval (Figure 3) and the attenuation of the CIE by a diagenetic process that shifted the whole-shell $\delta^{13}C$ compositions of CIE foraminifers toward the intermediate $\delta^{13}C$ composition of the crystallites. An interesting corollary is that post-depositional diagenesis has the potential to alter the whole-shell $\delta^{13}C$ compositions of all planktic foraminifers (i.e., pre-CIE and CIE shells) preserved within the CIE interval. Hence, it is likely that postdepositional diagenesis attenuates the CIE magnitude not only by increasing the $\delta^{13}C$ compositions of CIE shells but also by decreasing the $\delta^{13}C$ compositions of pre-CIE shells that were reworked upsection into the CIE interval prior to cementation.

The stratigraphic distribution of the crystallites is restricted to the CIE interval of hole 865B, suggesting that their formation was penecontemporaneous with sediment deposition/mixing during the PETM (Kozdon et al., 2013). Based on current understanding of carbonate saturation history for the PETM, the stratigraphic distribution of crystallites reflects the precipitation of secondary carbonate that overprinted the PETM section during the later (i.e., recovery) stages of the CIE. Initial carbon input resulted in carbonate undersaturation, which fueled dissolution of previously deposited pre-CIE calcite with high $\delta^{13}C$ compositions both on the seafloor and within the upper part of the sediment column, as well as the remineralization of biogenic calcite with low $\delta^{13}C$ compositions that precipitated during the earliest stages of the CIE (e.g., Bralower et al., 2014; Dickens, 2000; Zachos et al., 2005). This short-lived episode of "chemical erosion" was followed by a period of carbonate oversaturation driven by the enhancement of such negative feedbacks as silicate mineral weathering reactions during the recovery phase of the CIE (e.g., Kelly et al., 2005; Penman et al., 2016). Thus, the CIE recovery is typified by CCD subsidence to water depths in excess of the bathymetric position it held prior to carbon input and the widespread preservation of sedimentary calcite on the seafloor (e.g., Penman et al., 2016). We therefore argue that the crystallites formed during the CIE recovery as the carbonate saturation state of the ocean increased. Further, we posit that this "overshoot" in carbonate saturation fostered crystallite formation through the reprecipitation of inorganic carbon dissolved within sedimentary pore fluids. Thus, the intermediate $\delta^{13}C$ values of the crystallites (~2.8‰) indicate that these diagenetic cements are an amalgamated blend of two carbonate phases with distinctly different $\delta^{13}C$ compositions—pre-CIE "donor" carbonate and ambient CIE carbonate dissolved in bottom waters—that reprecipitated to overprint the PETM record at Site 865 (Kozdon et al., 2013). This view is supported by the similar $\delta^{13}C$ compositions of the crystallites and correlative pooled, multi-shell samples as the latter are themselves mixtures of foraminifer shells with pre-CIE and CIE $\delta^{13}C$ compositions (Figure 1b).

Although we consider our revised CIE magnitude of ~4.6‰ to be a conservative estimate of the full CIE in the surface DIC reservoir, it is congruent with the mean CIE magnitude compiled from terrestrial records. To a first approximation, mass balance calculations (McInerney & Wing, 2011) using a CIE of 4.6‰ for surface DIC requires the release of either ~4,300 Pg of C from marine sedimentary methane hydrates ($\delta^{13}C = -60$‰), ~10,000 Pg of C from thermogenic methane or Antarctic permafrost ($\delta^{13}C = -30$‰), or the oxidation of ~15,400 Pg of organic matter ($\delta^{13}C = -22$‰). A total release of ~4,300 Pg of methane carbon ($\delta^{13}C = -60$‰) is grossly similar to that used to reproduce observed patterns of carbonate dissolution in global ocean during the PETM (Zeebe et al., 2009). When viewed within the context of model simulations run for a range of carbon input durations (Kirtland Turner & Ridgwell, 2016), our revised CIE is most consistent with scenarios entailing shorter ($\leq$5 kyr) carbon input durations sourced by biogenic methane ($\delta^{13}C = -60$‰) and/or organic matter ($\delta^{13}C = -22$‰). However, we note that such estimates for mass and rate of carbon input are deemed provisional and are meant to motivate future modeling studies. This is especially the case in light of recently reported evidence suggesting that the CIE was caused by igneous activity related to the North Atlantic Igneous Province (e.g., Storey et al., 2007) and that the CIE reflects a more sustained (~55 kyr) release of even greater amounts (~10,200–12,200 Pg C) of isotopically heavier carbon ($\delta^{13}C = -11$‰ to -17‰) sourced by mantle CO_2 outgassing and thermal combustion of organic matter (Gutjahr et al., 2017).

5. Conclusions

SIMS-based in situ measurements of δ^{13}C in minute (~7-μm diameter) domains within individual shells of mixed layer-dwelling planktic foraminifers yield a CIE magnitude (~4.6‰) that is ~2‰ larger than that registered by conventional whole-shell GSMS measurements of the same planktic foraminifer species in the PETM record recovered at Site 865. The transient reversal in the sign of the SIMS versus GSMS δ^{13}C relation within the CIE interval, where $\delta^{13}C_{SIMS}$ values are lower than those of correlative $\delta^{13}C_{GSMS}$ measurements, indicates that the larger CIE returned by SIMS analyses is not an artifact of a systematic analytical bias. Moreover, the intermediate δ^{13}C composition of crystallites found within the CIE interval suggests that the composition of these cements is an amalgamated blend of pre-CIE and CIE inorganic carbon; hence, postdepositional diagenesis has the potential to decrease and increase whole-shell $\delta^{13}C_{GSMS}$ values measured from pre-CIE and CIE foraminifers, respectively. We therefore attribute the smaller magnitude of the CIE recorded by whole-shell $\delta^{13}C_{GSMS}$ values to postdepositional diagenesis shifting both pre-CIE and CIE whole-shell $\delta^{13}C_{GSMS}$ values toward the intermediate δ^{13}C composition of the diagenetic calcite. The “dual effects” of this diagenetic process are most applicable to carbonate-rich PETM records that have suffered chemical erosion of preexisting (pre-CIE) sedimentary calcite. Despite being ~2‰ larger than the CIE measured by GSMS, we consider our SIMS-based CIE of ~4.6‰ to be a conservative estimate of the full CIE in the surface DIC reservoir for two reasons. First, the domains targeted for in situ analysis may not be pristinely preserved, so our $\delta^{13}C_{SIMS}$ record likely underestimates the actual size of the CIE. Second, other processes not accounted for in this study such as a pH effect on foraminifer δ^{13}C compositions and truncation of the CIE stratigraphy by carbonate dissolution have likely conspired with postdepositional diagenesis to attenuate the CIE at Site 865. Nevertheless, we consider the larger excursion returned by SIMS δ^{13}C analysis to be a more accurate measure of the actual size of the CIE in the surface ocean, and we note that it is congruent with the mean CIE compiled from terrestrial PETM records reflecting the δ^{13}C of atmospheric CO_2. Similar studies geared toward constructing new SIMS-based δ^{13}C records of the CIE using other foraminifer taxa (i.e., mixed layer-dwelling acarininids, thermocline-dwelling subbotinids, and deep-sea benthics) from different deep-sea PETM sections are underway. Whether the diagenetic model herein envisioned played a role in attenuating the CIEs marking other hyperthermal climate states entailing intensified carbonate dissolution is presently unknown.

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References

Bains, S., Norris, R. D., Corfield, R. M., Bowen, G. J., Gingerich, P. D., & Koch, P. L. (2003). Marine-terrestrial linkages at the Paleocene-Eocene boundary. *Geological Society of America Special Papers*, *369*, 1–9.

Böhm, F., Haase-Schramm, A., Eisenhauer, A., Dullo, W. C., Joachimski, M., Lehnert, H., & Reitner, J. (2002). Evidence for preindustrial variations in the marine surface water carbonate system from coralline sponges. *Geochemistry, Geophysics, Geosystems*, *3*(3), 1–13. https://doi.org/10.1029/2001GC000264

Bowen, G. J., Beerling, D. J., Koch, P. L., Zachos, J. C., & Quattlebaum, T. (2004). A humid climate state during the Palaeocene/Eocene thermal maximum. *Nature*, *432*(7016), 495–499. Retrieved from http://www.nature.com/nature/journal/v432/n7016/suppinfo/nature03115_S1.html

Bowen, G. J., Koch, J., Gingerich, P. D., Norris, R. D., Bains, S., & Corfield, R. M. (2001). Refined isotope stratigraphy across the continental Paleocene-Eocene boundary on polecat bench in the northern Bighorn Basin. In P. D. Gingerich (Ed.), *Paleocene Eocene stratigraphy and biotic change in the Bighorn and Clarks Fork Basins, Wyoming* (pp. 73–88). Ann Arbor: University of Michigan Papers on Paleontology.

Bralower, T. J., Meissner, K. J., Alexander, K., & Thomas, D. J. (2014). The dynamics of global change at the Paleocene-Eocene thermal maximum: A data-model comparison. *Geochemistry, Geophysics, Geosystems*, *15*, 3830–3848. https://doi.org/10.1002/2014GC005474

Bralower, T. J., Parrow, M., Thomas, E., & Zachos, J. C. (1995). Data report: Stable isotopic stratigraphy of the Paleogene pelagic cap at Site 865. In *Allison guyot*. *Rep* (pp. 581–586). College Station: Ocean Drilling Program.

Bralower, T. J., & Self-Trail, J. M. (2016). Nannoplankton malformation during the Paleocene-Eocene thermal maximum and its paleoecological and paleoceanographic significance. *Paleoceanography*, *31*, 1423–1439. https://doi.org/10.1002/2016PA002980

Bralower, T. J., Zachos, J. C., Thomas, E., Parrow, M., Paull, C. K., Kelly, D. C., et al. (1995). Late Paleocene to Eocene paleoceanography of the equatorial Pacific Ocean: Stable isotopes recorded at Ocean Drilling Program Site 865, Allison Guyot. *Paleoceanography*, *10*(4), 841–865. https://doi.org/10.1029/95PA01143

Cavosie, A. J., Valley, J. W., Wilde, S. A., & E. I. M. F (2005). Magmatic δ^{18}O in 4400–3900 Ma detrital zircons: A record of the alteration and recycling of crust in the Early Archean. *Earth and Planetary Science Letters*, *235*(3–4), 663–681. https://doi.org/10.1016/j.epsl.2005.04.028

Cohen, A. S., Coe, A. L., & Kemp, D. B. (2007). The Late Palaeocene–Early Eocene and Toarcian (Early Jurassic) carbon isotope excursions: A comparison of their time scales, associated environmental changes, causes and consequences. *Journal of the Geological Society*, *164*(6), 1093–1108. https://doi.org/10.1144/0016-76492006-123

Craig, H. (1957). Isotopic standards for carbon and oxygen and correction factors for mass-spectrometric analysis of carbon dioxide. *Geochimica et Cosmochimica Acta*, *12*(1–2), 133–149. https://doi.org/10.1016/0016-7037(57)90024-8

Cramer, B. S., Wright, J. D., Kent, D. V., & Aubry, M. P. (2003). Orbital climate forcing of δ13C excursions in the late Paleocene–early Eocene (chrons C24n–C25n). *Paleoceanography*, *18*(4), 1097. https://doi.org/10.1029/2003PA000909

Cui, Y., Kump, L. R., Ridgwell, A. J., Charles, A. J., Junium, C. K., Diefendorf, A. F., et al. (2011). Slow release of fossil carbon during the Palaeocene-Eocene thermal maximum. *Nature Geoscience*, *4*(7), 481–485. Retrieved from http://www.nature.com/ngeo/journal/v4/n7/abs/ngeo1179.html#supplementary-information

Dickens, G. R. (2000). Methane oxidation during the late Palaeocene thermal maximum. *Bulletin de la Societe Geologique de France*, *171*(1), 37–49.

Dickens, G. R. (2011). Down the Rabbit Hole: Toward appropriate discussion of methane release from gas hydrate systems during the Paleocene-Eocene thermal maximum and other past hyperthermal events. *Climate of the Past*, *7*(3), 831–846. https://doi.org/10.5194/cp-7-831-2011

Dickens, G. R., Castillo, M. M., & Walker, J. C. G. (1997). A blast of gas in the latest Paleocene: Simulating first-order effects of massive dissociation of oceanic methane hydrate. *Geology*, *25*(3), 259–262. https://doi.org/10.1130/0091-7613(1997)025%3C0259:abogit%3E2.3.co;2

Dickens, G. R., O'Neil, J. R., Rea, D. K., & Owen, M. (1995). Dissociation of oceanic methane hydrate as a cause of the carbon isotope excursion at the end of the Paleocene. *Paleoceanography*, *10*(6), 965–971. https://doi.org/10.1029/95PA02087

Edgar, K. M., Anagnostou, E., Pearson, P. N., & Foster, G. L. (2015). Assessing the impact of diagenesis on δ^{11}B, δ^{13}C, δ^{18}O, Sr/Ca and B/Ca values in fossil planktic foraminiferal calcite. *Geochimica et Cosmochimica Acta*, *166*, 189–209. https://doi.org/10.1016/j.gca.2015.06.018

Gingerich, P. D. (2006). Environment and evolution through the Paleocene-Eocene thermal maximum. *Trends in Ecology & Evolution*, *21*(5), 246–253. https://doi.org/10.1016/j.tree.2006.03.006

Gutjahr, M., Ridgwell, A., Sexton, P. F., Anagnostou, E., Pearson, P. N., Pälike, H., et al. (2017). Very large release of mostly volcanic carbon during the Palaeocene-Eocene thermal maximum. *Nature*, *548*(7669), 573–577. https://doi.org/10.1038/nature23646

Handley, L., Pearson, P. N., McMillan, I. K., & Pancost, R. D. (2008). Large terrestrial and marine carbon and hydrogen isotope excursions in a new Paleocene/Eocene boundary section from Tanzania. *Earth and Planetary Science Letters*, *275*(1–2), 17–25. https://doi.org/10.1016/j.epsl.2008.07.030

Higgins, J. A., & Schrag, D. P. (2006). Beyond methane: Towards a theory for the Paleocene–Eocene thermal maximum. *Earth and Planetary Science Letters*, *245*(3–4), 523–537. https://doi.org/10.1016/j.epsl.2006.03.009

Huber, B. T., & Sloan, L. C. (2000). Climatic responses to tropical sea surface temperature changes on a "greenhouse" Earth. *Paleoceanography*, *15*(4), 443–450. https://doi.org/10.1029/1999PA000455

Kelly, D. C., Bralower, T. J., & Zachos, J. C. (1998). Evolutionary consequences of the latest Paleocene thermal maximum for tropical planktonic foraminifera. *Palaeogeography Palaeoclimatology Palaeoecology*, *141*(1-2), 139–161. https://doi.org/10.1016/S0031-0182(98)00017-0

Kelly, D. C., Bralower, T. J., & Zachos, J. C. (2001). On the demise of the early Paleogene *Morozovella velascoensis* lineage: Terminal progenesis in the planktonic foraminifera. *Palaois*, *16*(5), 507–523. https://doi.org/10.1669/0883-1351(2001)016%3C0507:OTDOTE%3E2.0.CO;2

Kelly, D. C., Bralower, T. J., Zachos, J. C., Silva, I. P., & Thomas, E. (1996). Rapid diversification of planktonic foraminifera in the tropical Pacific (ODP Site 865) during the late Paleocene thermal maximum. *Geology*, *24*(5), 423–426. https://doi.org/10.1130/0091-7613(1996)024%3C0423:RDOPFI%3E2.3.CO;2

Kelly, D. C., Zachos, J. C., Bralower, T. J., & Schellenberg, S. A. (2005). Enhanced terrestrial weathering/runoff and surface ocean carbonate production during the recovery stages of the Paleocene-Eocene thermal maximum. *Paleoceanography*, *20*, PA4023. https://doi.org/10.1029/2005PA001163

Kennett, J. P., & Stott, L. D. (1991). Abrupt deep-sea warming, palaeoceanographic changes and benthic extinctions at the end of the Paleocene. *Nature*, *353*(6341), 225–229. https://doi.org/10.1038/353225a0

Kirtland Turner, S., & Ridgwell, A. (2013). Recovering the true size of an Eocene hyperthermal from the marine sedimentary record. *Paleoceanography*, *28*, 700–712. https://doi.org/10.1002/2013PA002541

Kirtland Turner, S., & Ridgwell, A. (2016). Development of a novel empirical framework for interpreting geological carbon isotope excursions, with implications for the rate of carbon injection across the PETM. *Earth and Planetary Science Letters*, *435*, 1–13. https://doi.org/10.1016/j.epsl.2015.11.027

Kita, N. T., Ushikubo, T., Fu, B., & Valley, J. W. (2009). High precision SIMS oxygen isotope analysis and the effect of sample topography. *Chemical Geology*, *264*(1–4), 43–57. https://doi.org/10.1016/j.chemgeo.2009.02.012

Koch, P. L., Zachos, J. C., & Gingerich, P. D. (1992). Correlation between isotope records in marine and continental carbon reservoirs near the Palaeocene/Eocene boundary. *Nature*, *358*(6384), 319–322. https://doi.org/10.1038/358319a0

Kozdon, R., Kelly, D. C., Kita, N. T., Fournelle, J. H., & Valley, J. W. (2011). Planktonic foraminiferal oxygen isotope analysis by ion microprobe technique suggests warm tropical sea surface temperatures during the Early Paleogene. *Paleoceanography*, *26*, PA3206. https://doi.org/10.1029/2010PA002056

Kozdon, R., Kelly, D. C., Kitajima, K., Strickland, A., Fournelle, J. H., & Valley, J. W. (2013). In situ δ^{18}O and Mg/Ca analyses of diagenetic and planktic foraminiferal calcite preserved in a deep-sea record of the Paleocene-Eocene thermal maximum. *Paleoceanography*, *28*, 517–528. https://doi.org/10.1002/palo.20048

Kozdon, R., Ushikubo, T., Kita, N. T., Spicuzza, M., & Valley, J. W. (2009). Intratest oxygen isotope variability in the planktonic foraminifer *N. pachyderma:* Real vs. apparent vital effects by ion microprobe. *Chemical Geology*, *258*(3-4), 327–337. https://doi.org/10.1016/j.chemgeo.2008.10.032

McCarren, H., Thomas, E., Hasegawa, T., Röhl, U., & Zachos, J. C. (2008). Depth dependency of the Paleocene-Eocene carbon isotope excursion: Paired benthic and terrestrial biomarker records (Ocean Drilling Program Leg 208, Walvis ridge). *Geochemistry, Geophysics, Geosystems*, *9*, Q10008. https://doi.org/10.1029/2008GC002116

McInerney, F. A., & Wing, S. L. (2011). The Paleocene-Eocene thermal maximum: A perturbation of carbon cycle, climate, and biosphere with implications for the future. *Annual Review of Earth and Planetary Sciences*, *39*(1), 489–516. https://doi.org/10.1146/annurev-earth-040610-133431

Nicolo, M. J., Dickens, G. R., Hollis, C. J., & Zachos, J. C. (2007). Multiple early Eocene hyperthermals: Their sedimentary expression on the New Zealand continental margin and in the deep sea. *Geology*, *35*(8), 699–702. https://doi.org/10.1130/g23648a.1

Nunes, F., & Norris, R. D. (2006). Abrupt reversal in ocean overturning during the Palaeocene/Eocene warm period. *Nature*, *439*(7072), 60–63. https://doi.org/10.1038/nature04386

Pagani, M., Pedentchouk, N., Huber, M., Sluijs, A., Schouten, S., Brinkhuis, H., et al. (2006). Arctic hydrology during global warming at the Palaeocene/Eocene thermal maximum. *Nature*, *442*(7103), 671–675. Retrieved from http://www.nature.com/nature/journal/v442/n7103/suppinfo/nature05043_S1.html

Pearson, P. N., & Burgess, C. E. (2008). Foraminifer test preservation and diagenesis: Comparison of high latitude Eocene sites. In W. E. N. Austin & R. H. James (Eds.), *Biogeochemical controls on palaeoceanographic environmental proxies*, *Special Publications* (pp. 59–72). London: Geological Society.

Pearson, P. N., Ditchfield, P. W., Singano, J., Harcourt-Brown, K. G., Nicholas, C. J., Olsson, R. K., et al. (2001). Warm tropical sea surface temperatures in the Late Cretaceous and Eocene epochs. *Nature*, *413*(6855), 481–487. https://doi.org/10.1038/35097000

Penman, D. E., Hönisch, B., Zeebe, R. E., Thomas, E., & Zachos, J. C. (2014). Rapid and sustained surface ocean acidification during the Paleocene-Eocene thermal maximum. *Paleoceanography*, *29*, 357–369. https://doi.org/10.1002/2014PA002621

Penman, D. E., Turner, S. K., Sexton, P. F., Norris, R. D., Dickson, A. J., Boulila, S., et al. (2016). An abyssal carbonate compensation depth overshoot in the aftermath of the Palaeocene-Eocene thermal maximum. *Nature Geoscience*, *9*(8), 575–580. https://doi.org/10.1038/ngeo2757

Ridgwell, A. (2007). Interpreting transient carbonate compensation depth changes by marine sediment core modeling. *Paleoceanography*, *22*, PA4102. https://doi.org/10.1029/2006PA001372

Sager, W. W., Winterer, E. L., & Firth, J. V. (1993). Proceedings of the ocean drilling program. Initial report 143.

Schrag, D. P. (1999). Effects of diagenesis on the isotopic record of late Paleogene tropical sea surface temperatures. *Chemical Geology*, *161*(1–3), 215–224. https://doi.org/10.1016/s0009-2541(99)00088-1

Schrag, D. P., DePaolo, D. J., & Richter, F. M. (1995). Reconstructing past sea surface temperatures: Correcting for diagenesis of bulk marine carbonate. *Geochimica et Cosmochimica Acta*, *59*(11), 2265–2278. https://doi.org/10.1016/0016-7037(95)00105-9

Sexton, P. F., Wilson, P. A., & Pearson, P. N. (2006). Microstructural and geochemical perspectives on planktic foraminiferal preservation: "Glassy" versus "frosty". *Geochemistry, Geophysics, Geosystems*, *7*, Q12P19. https://doi.org/10.1029/2006GC001291

Si, W., & Aubry, M.-P. (2018). Vital effects and ecologic adaptation of photosymbiont-bearing planktonic foraminifera during the Paleocene-Eocene thermal maximum, implications for paleoclimate. *Paleoceanography and Paleoclimatology*, *33*, 112–125. https://doi.org/10.1002/2017PA003219

Sluijs, A., Brinkhuis, H., Schouten, S., Bohaty, S. M., John, C. M., Zachos, J. C., et al. (2007). Environmental precursors to rapid light carbon injection at the Palaeocene/Eocene boundary. *Nature*, *450*(7173), 1218–1221. Retrieved from http://www.nature.com/nature/journal/v450/n7173/suppinfo/nature06400_S1.html

Spero, H. J., Bijma, J., Lea, D. W., & Bemis, B. E. (1997). Effect of seawater carbonate concentration on foraminiferal carbon and oxygen isotopes. *Nature*, *390*(6659), 497–500. https://doi.org/10.1038/37333

Storey, M., Duncan, R. A., & Swisher, C. C. (2007). Paleocene-Eocene thermal maximum and the opening of the Northeast Atlantic. *Science*, *316*(5824), 587–589. https://doi.org/10.1126/science.1135274

Svensen, H., Planke, S., Malthe-Sorenssen, A., Jamtveit, B., Myklebust, R., Rasmussen Eidem, T., & Rey, S. S. (2004). Release of methane from a volcanic basin as a mechanism for initial Eocene global warming. *Nature*, *429*(6991), 542–545. https://doi.org/10.1038/nature02566

Thomas, E. (1990). Late Cretaceous-early Eocene mass extinctions in the deep sea. In V. L. Sharpton & P. D. Ward (Eds.), *Global catastrophes in Earth history: An interdisciplinary conference on impacts, volcanism, and mass mortality*, *Special Papers* (pp. 481–495). America: Geological Society.

Thomas, E. (2003). Benthic foraminiferal record across the initial Eocene thermal maximum, Southern Ocean Site 690, Causes and consequences of globally warm climates in the Early Paleogene. *Geological Society of America Special Papers*, *369*, 319. https://doi.org/10.1130/0-8137-2369-8.319

Thomas, E., & Shackleton, N. J. (1996). *The Palaeocene-Eocene benthic foraminiferal extinction and stable isotope anomalies*, *Special Publication* (Vol. 4, p. 9). London: Geological Society.

Tripati, A. K., Delaney, M. L., Zachos, J. C., Anderson, L. D., Kelly, D. C., & Elderfield, H. (2003). Tropical sea-surface temperature reconstruction for the early Paleogene using Mg/Ca ratios of planktonic foraminifera. *Paleoceanography*, *18*(4), 1101. https://doi.org/10.1029/2003PA000937

Uchikawa, J., & Zeebe, R. E. (2010). Examining possible effects of seawater pH decline on foraminiferal stable isotopes during the Paleocene-Eocene thermal maximum. *Paleoceanography*, *25*, PA2216. https://doi.org/10.1029/2009PA001864

Valley, J. W., & Kita, N. T. (2009). *In situ* oxygen isotope geochemistry by ion microprobe. In M. Fayek (Ed.), *MAC short course, vol. 41: Secondary ion mass spectrometry in the Earth sciences* (pp. 16–63). Toronto, Ontario.

Westerhold, T., Röhl, U., Frederichs, T., Agnini, C., Raffi, I., Zachos, J. C., & Wilkens, R. H. (2017). Astronomical calibration of the Ypresian timescale: Implications for seafloor spreading rates and the chaotic behavior of the solar system? *Climate of the Past*, *13*(9), 1129–1152. https://doi.org/10.5194/cp-13-1129-2017

Wing, S. L., Harrington, G. J., Smith, F. A., Bloch, J. I., Boyer, D. M., & Freeman, K. H. (2005). Transient floral change and rapid global warming at the Paleocene-Eocene boundary. *Science*, *310*(5750), 993–996. https://doi.org/10.1126/science.1116913

Zachos, J. C., Bohaty, S. M., John, C. M., McCarren, H., Kelly, D. C., & Nielsen, T. (2007). The Palaeocene–Eocene carbon isotope excursion: Constraints from individual shell planktonic foraminifer records. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, *365*(1856), 1829–1842. https://doi.org/10.1098/rsta.2007.2045

Zachos, J. C., Röhl, U., Schellenberg, S. A., Sluijs, A., Hodell, D. A., Kelly, D. C., et al. (2005). Rapid acidification of the ocean during the Paleocene-Eocene thermal maximum. *Science*, *308*(5728), 1611–1615. https://doi.org/10.1126/science.1109004

Zachos, J. C., Wera, M. W., Bohaty, S., Delaney, M. L., Petrizzo, M. R., Brill, A., et al. (2003). A transient rise in tropical sea surface temperature during the Paleocene-Eocene thermal maximum. *Science*, *302*(5650), 1551–1554. https://doi.org/10.1126/science.1090110

Zeebe, R. E., Zachos, J. C., & Dickens, G. R. (2009). Carbon dioxide forcing alone insufficient to explain Palaeocene-Eocene thermal maximum warming. *Nature Geoscience*, *2*(8), 576–580. https://doi.org/10.1038/NGEO578

Zhang, Q., Wendler, I., Xu, X., Willems, H., & Ding, L. (2017). Structure and magnitude of the carbon isotope excursion during the Paleocene-Eocene thermal maximum. *Gondwana Research*, *46*, 114–123. https://doi.org/10.1016/j.gr.2017.02.016

Erratum

In the originally published version of this paper, the third Key Point was published as "lanktic foraminifer." This has since been changed to "planktic foraminifer." This version may be considered the authoritative version of record.