Geochemistry
Geophysics
Geosystems
G3
AN ELECTRONIC JOURNAL OF THE EARTH SCIENCES
Published by AGU and the Geochemical Society

Article
Volume 9, Number 10
16 October 2008
Q10008, doi:10.1029/2008GC002116
ISSN: 1525-2027

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Depth dependency of the Paleocene-Eocene carbon isotope excursion: Paired benthic and terrestrial biomarker records (Ocean Drilling Program Leg 208, Walvis Ridge)

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[1] The Paleocene Eocene Thermal Maximum (PETM) coincided with a negative carbon isotope excursion (CIE) in carbonate and organic matter, in terrestrial and marine records. Consequently the PETM global warming of 5–6°C has been attributed to the rapid emission of a large amount of isotopically light carbon into the ocean-atmosphere system, and the magnitude of the CIE has been used to estimate the amount of carbon greenhouse gas emitted. However, there are large discrepancies between the magnitude of the CIE in marine and in terrestrial material, in different types of marine carbonate records (bulk carbonate, planktic and benthic foraminiferal carbonate), and in marine carbonate records from different locations. The marine carbonate record of the CIE may be incomplete in most deep-sea (bathyal-abyssal) locations because of ocean acidification and widespread dissolution of seafloor carbonates. We demonstrate that the CIE in benthic foraminiferal stable isotope records is relatively abrupt and not as gradual as portrayed in bulk carbonate records along the Walvis Ridge depth transect (SE Atlantic). The benthic CIE is about −1.5‰ at 3600 m paleodepth, in contrast to about −3.5‰ at 1500 m paleodepth, consistent with depth-dependent truncation by carbonate dissolution. Strong covariance between the benthic record and the stable carbon isotope values of terrestrial n-alkanes isolated from the same core (i.e., Site 1263) supports a relatively rapid excursion of at least −3.5‰ but no more than −5.0‰.

Components: 6336 words, 4 figures.

Keywords: Paleocene/Eocene thermal maximum; abrupt/rapid climate change; geochemical tracers; paleoceanography; stable isotope chemistry; ODP.

Index Terms: 4948 Paleoceanography: Paleocene/Eocene thermal maximum; 4901 Paleoceanography: Abrupt/rapid climate change (1605); 1041 Geochemistry: Stable isotope geochemistry (0454, 4870).

Received 3 June 2008; **Revised** 17 August 2008; **Accepted** 26 August 2008; **Published** 16 October 2008.

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

1. Introduction

[2] The Paleocene Eocene Thermal Maximum (PETM; ~55 Ma) has received much attention due to its similarities to expected future global warming forced by the emission of greenhouse gases from fossil fuel burning. The PETM was characterized by ~5–6°C warming of the deep sea [*Kennett and Stott*, 1991; *Norris and Röhl*, 1999; *Thomas et al.*, 1999; *Thomas and Shackleton*, 1996; *Tripati and Elderfield*, 2005] massive and widespread dissolution of seafloor carbonates [*Thomas*, 1998; *Thomas and Shackleton*, 1996; *Zachos et al.*, 2005; *Zeebe and Zachos*, 2007] and a large negative carbon isotope excursion (CIE). Carbonate dissolution in combination with a CIE can be explained by the rapid release of thousands of Gigatons (Gt) of isotopically depleted carbon to the ocean/atmosphere [e.g., *Dickens*, 2003]. Several possible sources for this carbon have been suggested, including methane hydrates [*Dickens et al.*, 1995], burning of terrestrial biomass [*Kurtz et al.*, 2003], thermal combustion of organic matter [*Svensen et al.*, 2004], an impacting comet [*Cramer and Kent*, 2005], and flood basalt volcanism [*Storey et al.*, 2007].

[3] The average global magnitude of the CIE can be used to constrain the source, isotopic signature, and mass of carbon released [e.g., *Pagani et al.*, 2006a], but a problem with such calculations is that the observed magnitude of the CIE varies by type and location of record. Some species of planktonic foraminifera represent the surface ocean reservoir, whereas bulk carbonate and other planktonic foraminifera record conditions in the deeper thermocline. Furthermore, these records may be influenced by local productivity and surface water stratification. Bulk carbonate and planktonic foraminiferal records show excursions between 2.0‰ to 4‰. The CIE magnitude in benthic foraminifera averages 2‰ to 3‰ in many deep-sea sections [*Nunes and Norris*, 2006; *Thomas and Shackleton*, 1996] but reaches ~4–5‰ in a New Jersey shelf record [*Cramer and Kent*, 2005; *John et al.*, 2008; *Zachos et al.*, 2006]. An even greater inconsistency exists between marine and terrestrial carbon isotope records (e.g., organic matter, soil carbonate nodules, herbivore teeth), the latter showing excursions of 5–6‰ [e.g., *Bowen et al.*, 2006].

[4] This discrepancy has been attributed to overestimates of the magnitude of the CIE in the terrestrial record caused by changes in humidity, precipitation patterns, and/or changes in isotope discrimination during photosynthesis at high CO_2 levels and/or changes in plant community composition [e.g., *Pagani et al.*, 2006a, 2006b; *Schouten et al.*, 2007; *Smith et al.*, 2007]. However, the marine record (especially bulk carbonate material) may underestimate the magnitude of the CIE because of damping (e.g., by bioturbation) and truncation (by dissolution) of the carbonate records [e.g., *Pagani et al.*, 2006b; *Zachos et al.*, 2005; *Zeebe and Zachos*, 2007].

[5] Constraining the rate and magnitude of the CIE in the largest ocean-atmosphere carbon reservoir, the dissolved inorganic carbon in the deep ocean, is of great importance for evaluation of the globally averaged magnitude of the CIE. Dramatic shoaling of the carbonate compensation depth (CCD) caused dissolution of carbonate deposited before the PETM event (“burn-down”), as well as during the initial stages of the event. The fidelity of the benthic deep-sea isotope reconstructions is also compromised by the severe extinction and mass migration of benthic foraminifera [e.g., *Thomas*, 1998, 2007]. Directly after the extinction, assemblages were dominated by minuscule, thin-walled species, and species commonly used for isotope

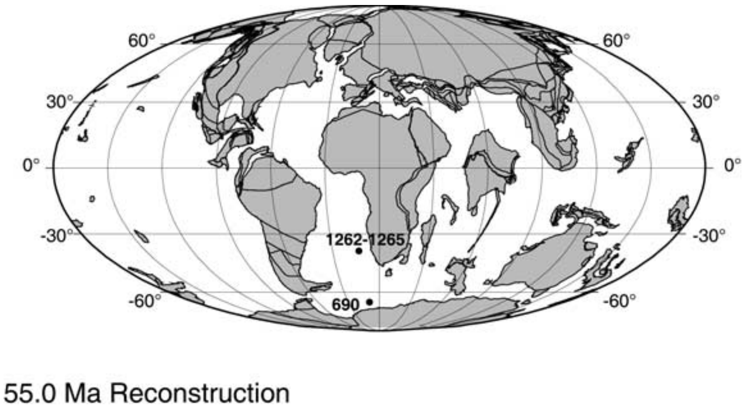

Figure 1. Paleogeographic reconstruction 55 Ma showing sites included in this study (http://www.odsn.de/odsn/services/paleomap/paleomap.html).

analysis were rare, very small, or absent in the "peak-CIE," even at locations little affected by dissolution such as Site 690 [e.g., *Thomas*, 2003] and Shatsky Rise sites [e.g., *Takeda and Kaiho*, 2007]. Because of these problems, most deep-sea carbonate carbon isotope records suffer from a gap in data across the early part of the CIE, so that the most extreme values may not be represented in these records. Many shallower marine records also show severe dissolution [*Thomas*, 1998], e.g., section Zumaya, Spain [*Schmitz et al.*, 1997] at paleodepth of about 1000 m, as well as middle eastern sections at shelf depths [e.g., *Dupuis et al.*, 2003].

[6] In order to evaluate the influence of dissolution on the deep-sea CIE, we studied three sites along a depth transect on Walvis Ridge in the SE Atlantic, over a paleodepth range including 1500 m (Site 1263), 1850 m (Site 1265), and 3600 m (Site 1262) (Figure 1) [*Zachos et al.*, 2004]. As the Atlantic Basin widened by ocean spreading, hot spot volcanism created the Walvis Ridge [*Rabinowitz and Simpson*, 1984]. A simple thermal subsidence model applied to this aseismic mid ocean ridge indicates approximately 1.1 km of subsidence since the Maastrichtian, providing the basis for paleodepth estimates [*Moore et al.*, 1984; *Zachos et al.*, 2004]. Previous drilling in the same region at DSDP Site 525 (~1250 m paleo water depth) provided one data point with an extremely low δ^{13}C value [*Thomas and Shackleton*, 1996]. These data suggested a correlation between depth and CIE magnitude but lacked geographically constrained sites with which to compare and contrast. The CIE is characterized by a clay layer that increases in thickness with water depth [*Zachos et al.*, 2005]. We compare our benthic data with recently published δ^{13}C data of *n*-alkanes derived from terrestrial leaf waxes extracted from Site 1263 cores [*Hasegawa et al.*, 2006]. Together, these records provide a unique opportunity to evaluate the variability of the CIE magnitude with depth and across different proxies.

2. Methods

[7] The PETM was continuously sampled in cores recovered at Sites 1262 (4759 m depth), 1263 (2717 m), and 1265 (3083 m), and divided into sample slices of 1 cm thickness [*Zachos et al.*, 2005]. Long-term Paleogene sedimentation rates along Walvis Ridge average 12–15 m/Ma [*Zachos et al.*, 2002], providing a temporal resolution of ~1.5–3.0 ka. Samples were washed and sieved, then the >63 μm fraction was picked for specimens of *Nuttallides truempyi* and *Oridorsalis umbonatus*, long ranging species that survived the benthic foraminiferal extinction event. Small, thin-walled individuals of these species were present in the low-carbonate samples deposited during the CIE. The most clay-rich samples were barren of benthic and planktonic foraminifera, with sampling gaps from roughly 139.76–140.14 m composite depth (mcd) at Site 1262 (38 cm) to 335.58–335.71 mcd at Site 1263 (13 cm). It is possible in some cases to obtain isolated specimens of calcareous fossils from layers of sediment containing low carbonate concentrations (<1 wt% $CaCO_3$). Weight percent carbonate measurements are made with a comparatively small amount of sample (1g or less), that is statistically unlikely to contain one of few foraminifera contained in the 10 cc total sample volume. Stable isotope analyses of bulk material from horizons with low carbonate content are similarly problematic, requiring a greater volume of material

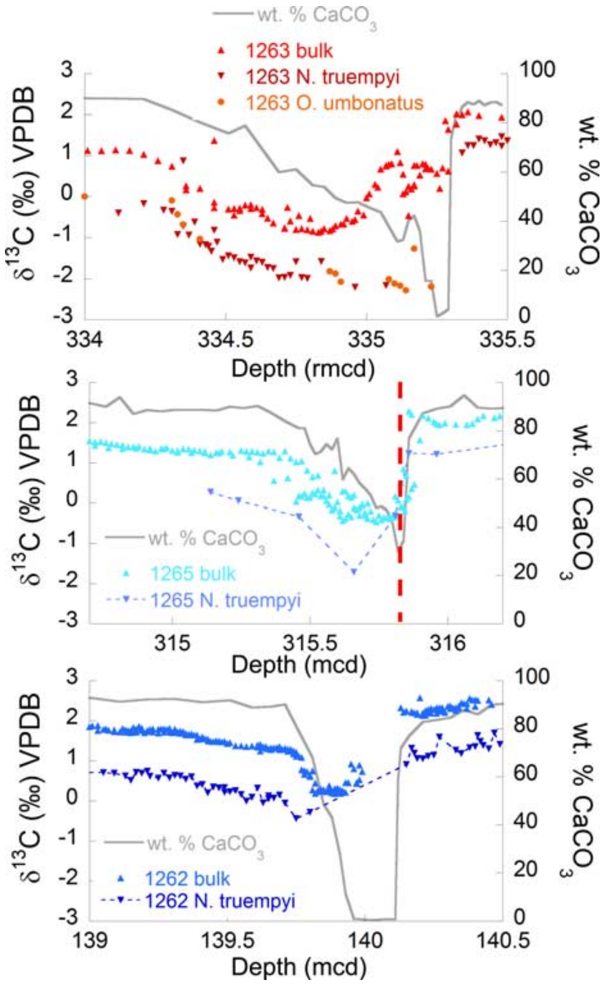

Figure 2. The δ^{13}C and weight percent calcium carbonate (wt. % $CaCO_3$) data for ODP Leg 208 Sites 1263, 1265, and 1262 plotted versus depth. Bulk isotopes and wt. % $CaCO_3$ are from *Zachos et al.* [2005]. Dashed red line indicates unconformity at Site 1265.

to conduct the analysis. Stable isotope analyses of multispecimen and a few single specimen samples were performed on an Autocarb coupled to a PRISM mass spectrometer at the UCSC SIL facilities. All values are reported relative to the VPDB standard. Analytical precision based on replicate analyses of in-house standard Carrara Marble (n = 59) and NBS-19 (n = 8) averages 0.04‰ (1σ) for δ^{13}C and 0.07‰ (1σ) for δ^{18}O. *O. umbonatus* stable isotope values were adjusted to allow for direct comparison to *N. truempyi* using the relative offset [*O. umbonatus* +0.42] for δ^{13}C and [(*O. umbonatus* −0.36)/0.79] for δ^{18}O [*Katz et al.*, 2003].

[8] Single specimen analyses are especially useful when attempting to characterize environmental variability across small spatial and bathymetric gradients, for example in tracing the source and progression of methane gas release [*Thomas et al.*, 2002]. However, in this study, multispecimen analyses of monospecific samples proved more desirable for two reasons. First, in order to isolate an average, global value for the PETM CIE, it was important that data points must reflect an average value, eliminating bias from small-scale ocean chemistry variability or sediment diagenesis. Second, and most importantly, the majority of analyses have been conducted on very small specimens of *N. truempyi* or *O. umbonatus* that simply did not contain sufficient mass to analyze singly. This is especially relevant across the PETM event where the foraminifera appear to have had difficulty calcifying and/or the sediments have been subject to dissolution post deposition. In the interest of consistency, stable isotope analyses are almost exclusively conducted on multispecimen samples throughout this study. In several samples (seven) at Site 1263, however, a large (>5 μg) single specimen was found and analyzed. These particular samples fall outside the plotted depth range of Figure 2 but are indicated on Table S1 in the auxiliary material[1] with italics.

[9] The long-chain *n*-alkane carbon isotope data (*n*-C_{29}, *n*-C_{31}, and *n*-C_{33}) were generated on thirteen 5 cm long quarter-round samples taken across the PETM section of core recovered from Site 1263. See *Hasegawa et al.* [2006] for detailed descriptions of preparation and analytical techniques employed during terrestrial biomarker analysis.

[10] Advanced X-ray fluorescence (XRF) scanning of cores from Leg 208 and Site 690 have provided high resolution Fe and Ba data, suitable for detailed cyclostratigraphy [*Röhl et al.*, 2007]. The high-fidelity age model produced by *Röhl et al.* [2007] has been used in this study to generate ages relative to the onset of the CIE. We have then converted relative sample ages to absolute age, assigning an age of 55.53 Ma to the base of the CIE. This age number is one of three options resulting from orbital calibration of Fe and color cycles in the Leg 208 cores [*Westerhold et al.*, 2007], and is close to a CIE age derived from terrestrial sediments [*Wing et al.*, 2000]. As accurate absolute ages still cannot be provided (see discussions in the work of *Kuiper et al.* [2008] and *Westerhold et al.*

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[1] Auxiliary materials are available in the HTML. doi:10.1029/2008GC002116.

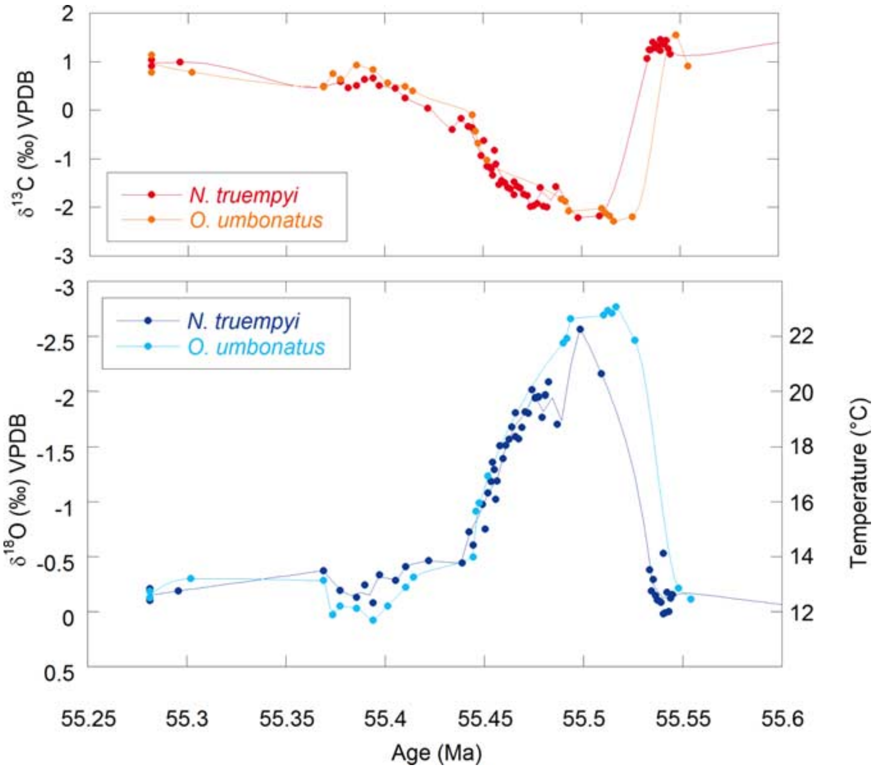

Figure 3. Site 1263 δ^{13}C and δ^{18}O from two species of benthic foraminifera, *Nuttallides truempyi* and *Oridorsalis umbonatus*. Temperature estimates are based on the adjusted δ^{18}O values using equations of *Bemis et al.* [1998], assuming an ice free world ($\delta^{18}O_{SMOW} = -1.0$‰). Age model from *Röhl et al.* [2007].

[2007, 2008]), the absolute number might change in the future, but we are confident that the internal structure and relative relationships of the PETM are robust [*Röhl et al.*, 2007].

[11] XRF scanning data of cores from Site 1265 together with stable isotope data provided conclusive evidence for the presence of a small unconformity at the base of the PETM clay layer. A characteristic spike in Ba concentrations at the PETM can be used as a stratigraphic tool for evaluating the relative completeness of sediment sections across this time interval [*Röhl et al.*, 2007]. The basal Ba spike is present at sites 690, 1263, and 1262, but not at Site 1265 [*Röhl et al.*, 2007]. The Ba profiles for the remainder of the CIE and recovery intervals are consistent between all sites [*Röhl et al.*, 2007].

3. Results

[12] Benthic foraminifera at all three sites record the CIE across the clay rich layer. However, marked gaps are present in each record due to the absence of specimens within the carbonate-free layer. The thickness of the clay layers, and of the gaps, increases with depth from 5 cm at 1263 to 30 cm at 1262. Foraminifera are absent over 13 cm at 1263 and 38 cm at 1262. The magnitude of the benthic CIE is depth-dependent, decreasing with increasing depth (Figure 2). The deepest Site 1262 shows a CIE of −1.5‰, the shallowest Site 1263 a CIE of −3.5‰,with absolute values (minima) of δ^{13}C during the CIE of −0.4‰ δ^{13}C at Site 1262 and −2.2‰ δ^{13}C at Site 1263, and intermediate values at Site 1265 (Table S1).

[13] The benthic δ^{18}O records show excursions from −0.6‰ at Site 1262 to −2.4‰ at Site 1263, with minima of δ^{18}O from −0.8‰ at Site 1262 to −2.7‰ at Site 1263 (Table S1); the latter would correspond to a temperature increase of about 10°C in the absence of salinity and ice volume effects (Figure 3). These minimum carbon and oxygen isotope values at Site 1263 are the lowest observed at any deep-sea site, and are markedly more extreme than those observed at Site 690, which has considerably less carbonate dissolution (Figure 4).

[14] Though *n*-alkanes could be detected at all the sites, only at Site 1263 were abundances sufficient

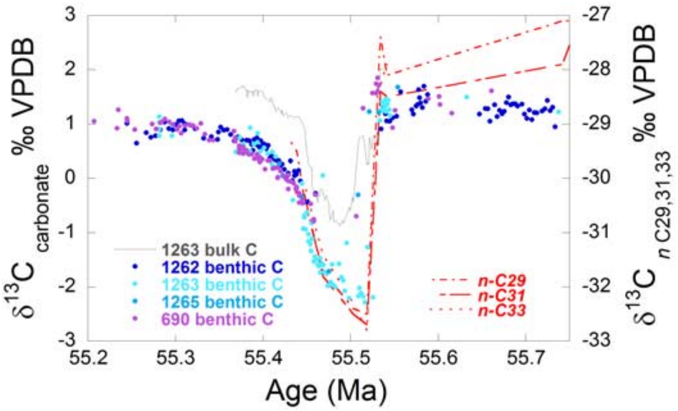

Figure 4. Leg 208 benthic $\delta^{13}C$ and *n*-alkane $\delta^{13}C$ records versus age along with benthic carbon isotope data from Site 690 [*Kennett and Stott*, 1991; *Kelly et al.*, 2005]. Site 690 data were generated using multispecimen samples of *N. truempyi*. Age model from *Röhl et al.* [2007].

for isotope measurements [*Hasegawa et al.*, 2006]. The magnitude of the CIE measured from *n*-C_{29}, *n*-C_{31}, and *n*-C_{33} was −5.1‰, −4.3‰, and −4.9‰ respectively (Table S2). As in the benthic records, the onset of the CIE spans the interval between 335.42 and 335.94 mcd.

4. Discussion

[15] Our isotope records show, as expected, increased truncation of the CIE record with greater depth, and thus confirm the incomplete nature of the pelagic carbonate record of the PETM, even at the least affected (shallowest) Site 1263. On the other hand, these records also indicate that differences between various records might not be due to truncation alone. The magnitude of the benthic CIE, with a minimum of −2.29‰ at the shallowest Site 1263, is 1.0‰ greater than that at Site 690 (Figure 4). Owing to high carbonate accumulation rates, Site 690 is often recognized as having one of the most complete marine records of the PETM [*Bains et al.*, 1999; *Röhl et al.*, 2000, 2007]. Still, its benthic isotope record is incomplete because only reworked specimens of *N. truempyi* are present in an interval over 20 cm above the benthic extinction horizon. A few analyses of the diminutive species *B. ovula* (renamed *B. kugleri* [*Thomas*, 2003]) from this interval show a minimum $\delta^{13}C$ value not much lower than that measured in *N. truempyi* (lowest value −1.55‰ [*Thomas et al.*, 2000]). These *B. ovula* data points probably still undersample the excursion, which is ~4.0‰ in planktonic foraminifera, because of the low sample resolution. The benthic foraminiferal $\delta^{13}C$ value at Site 1263 is lower than those in all records compiled by *Nunes and Norris* [2006], although a value at equatorial Atlantic Site 1258 with a similar paleodepth as 1263 is close (−2.06‰).

[16] If the record of Site 1263 better approximates the "true" globally averaged magnitude of the CIE in dissolved inorganic carbon in the deep-sea reservoir, the CIE cannot have been completely sampled in most bathyal-abyssal records. This deficiency is primarily the result of severe dissolution (as at Site 1262), combined with the ecological absence of benthic foraminifera used in analysis, as at Site 690 [e.g., *Thomas*, 2003]. This assertion is supported by records from shallow marine sections. Benthic foraminifera in shallow neritic environments, preserved in New Jersey sections with unusually high sedimentation rates, record a CIE of similar, though slightly greater magnitude than that at Site 1263 [*Cramer and Kent*, 2005; *John et al.*, 2008; *Zachos et al.*, 2006]. In addition, nearly all pelagic sediment cores are affected to some degree by carbonate dissolution, as indicated by the presence of a clay layer (low carbonate), decreased concentration of $CaCO_3$, or partial dissolution and etching of microfaunas [*Thomas*, 1998]. The clear relation between the magnitude of the CIE and water depth/dissolution intensity at the sites on the Walvis Ridge depth transect confirms that dissolution strongly contributes to truncation of the CIE [*Zeebe and Zachos*, 2007]. If the actual minimum values of the benthic foraminiferal CIE are not represented in deep-sea records, benthic $\delta^{13}C$ cannot be used to reconstruct deep-water circulation during the peak of the CIE [*Nunes and Norris*, 2006].

[17] If the average global magnitude of the deep sea CIE was at least −3.5‰, simple mass balance calculations demand the release of a minimum of 2300 GtC ($\delta^{13}C = -60$‰) from hydrates to account for the total CIE, and upwards of 3300 GtC with a CIE as extreme as −5‰. A much greater mass would be required if released from isotopically heavier sources (for example, organic matter at −27 ± 2‰ [see *Archer*, 2007; *Buffett and Archer*, 2004; *Higgins and Schrag*, 2006; *Pagani et al.*, 2006b]). Several proposed PETM triggers could have worked in concert to force the cumulative magnitude of the CIE. For example, an initial pulse of greenhouse gas emissions from the interaction of magma and carbon rich sediments during the emplacement of massive flood basalts [*Storey et al.*, 2007; *Svensen et al.*, 2004] or from the flood basalts themselves [*Eldholm and Thomas*, 1993], could help explain why the CIE is so much larger than that of later, otherwise similar hyperthermal events [e.g., *Lourens et al.*, 2005]. A recent model-data comparison study has suggested that a volume of 6800 Gt of −22‰ carbon, accounting for a 4‰ CIE, is most consistent with observed trends in carbonate distribution and dissolution [*Panchuk et al.*, 2008].

[18] On geologic timescales (>10^3 years), the magnitude of the CIE of the atmosphere should closely match that of the ocean. It is possible that the *n*-alkane record is biased, amplifying the excursion as recorded in organic biomarkers. Strong odd carbon preference, as measured in *n*-alkanes from Site 1263, indicates production by terrestrial plants as leaf waxes [*Eglinton and Hamilton*, 1967]. The carbon preference index for n-C_{29-33} at Site 1263 ranges from 4.9 to 12.5 [*Hasegawa et al.*, 2006]. Documented differences in isotopic fractionation between gymnosperms and angiosperms at the PETM [*Schouten et al.*, 2007; *Smith et al.*, 2007] complicate interpretation of the CIE as recorded in terrestrial biomarkers. Analyses of compound specific carbon isotopes in terrestrial organic matter from an Arctic core show a CIE of 3‰ in gymnosperms at the PETM, but upwards of 6‰ change in angiosperm $\delta^{13}C$ [*Schouten et al.*, 2007]. Without palynological data for Walvis Ridge cores, or even Africa, such artifacts cannot be constrained in the record from Site 1263. Studies of coincident floral macrofaunas and *n*-alkane $\delta^{13}C$ in terrestrial records in the Bighorn Basin (Wyoming, USA) [*Smith et al.*, 2007] demonstrate an exaggerated CIE at the peak of the PETM, most likely due to the complete collapse of conifer (gymnosperm) populations [*Smith et al.*, 2007]. A similar pattern of floral change in west south Africa would bias the Walvis Ridge record toward a larger CIE, suggesting that the ∼5‰ excursion in terrestrial biomarkers at Site 1263 represents a maximum value.

[19] The possibility of a diagenetic overprint to explain the low benthic values at Site 1263 during the CIE seems unlikely given that (1) the shells are free of secondary overgrowths, and (2) there is no indication of isotopically depleted diagenetic carbonate in the bulk carbonate carbon isotope record, despite the very low carbonate content in the excursion layer. Is it possible that the benthic CIE at Site 1263 is partly influenced by a local bottom water signal? The $\delta^{13}C$ values were similar to coeval values at Site 690 (Figure 4), and many other sites [*Nunes and Norris*, 2006] prior to the CIE, and over the upper portion of the excursion where the records overlap. Unless there is a chronostratigraphic correlation error, one would thus have to assume that the bottom waters at Site 1263 became unusually ^{12}C enriched and negatively offset only during the peak of the CIE. This would require the temporary appearance of a more nutrient rich, possibly low-oxygen water mass in this region of the south Atlantic.

[20] High relative abundances of benthic foraminifera of the genus *Bulimina* may indicate a high food supply to the seafloor, or the occurrence of suboxic to dysoxic environments in bottom waters [*Jorissen et al.*, 2007; *Kaiho*, 1994]. At Site 1263 (but not at Site 1262) the relative abundance of buliminid species increased within the CIE, suggesting an increased food supply or lowered oxygenation of bottom waters at the shallower site [e.g., *Thomas*, 2007]. Relative abundances of other species and estimates of benthic foraminiferal accumulation rates argue against an increased food supply, thus suggesting that the water mass at Site 1263 may have been relatively low in oxygen, and possibly warmer than Sites 1262 and 1265 in view of the observed oxygen isotope values.

[21] Such a water mass may have been derived from a North Atlantic source of water, rich in isotopically light carbon. This water mass could reflect slow input of methane derived carbon or organically derived carbon somewhere in the northern Atlantic basin [e.g., *Katz et al.*, 1999; *Svensen et al.*, 2004]. Alternatively, intermediate depths could be infiltrated by "old" water, supplied by a source area in the northern Pacific Ocean [e.g., *Bice and Marotzke*, 2002]. Both these possibilities would be consistent with the overall gradient in carbonate corrosivity of deep ocean water

masses, with more corrosive waters in the Atlantic than in the Pacific [*Zeebe and Zachos*, 2007]. However, modeling of high rates of subaqueous hydrothermal methane release at the PETM in the North Atlantic suggests that methane would reach the atmosphere without being oxidized or dissolved in the water column due to bubble formation [*Svensen et al.*, 2004; *Zhang*, 2003]. If the water mass was derived from the northern Pacific, it may have taken an unusual route, reaching Site 1263 from the north (between the two American continents), since it did not leave a distinct geochemical fingerprint in the southern ocean (i.e., Sites 689 and 690). Further, the lack of an obvious offset in δ^{13}C during the recovery interval where records from separate basins overlap, suggests that this warm, O_2 depleted mass, if present at all, was only present during the most extreme conditions of the PETM.

5. Summary and Conclusions

[22] The benthic foraminiferal CIE at three Ocean Drilling Program sites (1262, 1263, and 1265) along the Walvis Ridge transect shows that deep-sea records are commonly truncated by dissolution, with increasing truncation at greater depth. Nonetheless, the most complete record at the shallowest location, Site 1263 ($\sim$1500 m paleowater depth), shows the greatest magnitude of the CIE observed to date in deep-sea benthic records (-3.5‰), as well as the most extreme δ^{13}C for benthic foraminiferal carbonate (-2.2‰). The larger magnitude of the benthic CIE might reflect the temporary appearance in the south Atlantic of an intermediate water mass with low δ^{13}C values, high temperatures, and possibly low oxygenation. Such a water mass might have been derived from lower latitudes triggered by a transient switch in deep-water circulation, though additional evidence is required to test this. Finally, the onset of the CIE at Site 1263 as recorded by benthic foraminifera is more abrupt than that recorded by the bulk carbonate implying that the more gradual pattern of the CIE in the latter is an artifact of dissolution and reworking. This assertion is supported by strong covariance of the benthic record with a carbon isotope record of terrestrial n-alkanes extracted from the same section.

Acknowledgments

[23] This research used sediment samples provided by the Ocean Drilling Program (ODP). ODP is sponsored by the U.S. National Science Foundation (NSF) and participating countries under management of Joint Oceanographic Institutions (JOI), Inc. Funding for this research was provided by a Schlanger Ocean Drilling Fellowship, which is part of the NSF sponsored U.S. Science Support Program (USSSP), a U.S. National Science Foundation Biocomplexity Grant (EAR-0120727) to J. Zachos and E. Thomas, and by the Deutsche Forschungsgemeinschaft (DFG) to U. Röhl. We are grateful to J. Dickens and D. C. Kelly for their thoughtful comments on an earlier version of this manuscript, as well as to Louis Derry and Paul Wilson for their careful reviews.

References

Archer, D. (2007), Methane hydrate stability and anthropogenic climate change, *Biogeosciences*, *4*, 521–544.

Bains, S., R. M. Corfield, and R. D. Norris (1999), Mechanisms of climate warming at the end of the Paleocene, *Science*, *285*, 724–727, doi:10.1126/science.285.5428.724.

Bemis, B. E., H. J. Spero, J. Bijma, and D. W. Lea (1998), Reevaluation of the oxygen isotopic composition of planktonic foraminifera: Experimental results and revised paleotemperature equations, *Paleoceanography*, *13*, 150–160, doi:10.1029/98PA00070.

Bice, K. L., and J. Marotzke (2002), Could changing ocean circulation have destabilized methane hydrate at the Paleocene/Eocene boundary?, *Paleoceanography*, *17*(2), 1018, doi:10.1029/2001PA000678.

Bowen, G. J., et al. (2006), Eocene hyperthermal event offers insight into greenhouse warming, *Eos Trans. AGU*, *87*(17), 165–169.

Buffett, B., and D. Archer (2004), Global inventory of methane clathrate: Sensitivity to changes in the deep ocean, *Earth Planet. Sci. Lett.*, *227*, 185–199, doi:10.1016/j.epsl.2004.09.005.

Cramer, B. S., and D. V. Kent (2005), Bolide summer: The Paleocene/Eocene thermal maximum as a response to an extraterrestrial trigger, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *224*, 144–166, doi:10.1016/j.palaeo.2005.03.040.

Dickens, G. R. (2003), Rethinking the global carbon cycle with a large, dynamic and microbially mediated gas hydrate capacitor, *Earth Planet. Sci. Lett.*, *213*, 169–183, doi:10.1016/S0012-821X(03)00325-X.

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

Dupuis, C., M. P. Aubry, E. Steurbaut, W. A. Berggren, K. Ouda, R. Magioncalda, B. S. Cramer, D. V. Kent, R. P. Speijer, and C. Heilmann-Clausen (2003), The Dababiya Quarry section: Lithostratigraphy, clay mineralogy, geochemistry and paleontology, *Micropaleontology*, *49*, 41–59, doi:10.2113/49.Suppl_1.41.

Eglinton, G., and R. J. Hamilton (1967), Leaf epicuticular waxes, *Science*, *156*, 1322–1335, doi:10.1126/science.156.3780.1322.

Eldholm, E., and E. Thomas (1993), Environmental impact of volcanic margin formation, *Earth Planet. Sci. Lett.*, *117*(3-4), 319–329, doi:10.1016/0012-821X(93)90087-P.

Hasegawa, T., S. Yamamoto, and L. M. Pratt (2006), Data report: Stable carbon isotope fluctuation of long-chain n-alkanes from Leg 208 Hole 1263A across the Paleocene/Eocene boundary, *Proc. Ocean Drill. Program Sci. Results*, *208*, 1–11.

Higgins, J. A., and D. P. Schrag (2006), Beyond methane: Towards a theory for the Paleocene-Eocene Thermal Maximum, *Earth Planet. Sci. Lett.*, *245*, 523–537, doi:10.1016/j.epsl.2006.03.009.

John, C., S. Bohaty, J. Zachos, A. Sluijs, S. J. Gibbs, H. Brinkhuis, and T. J. Bralower (2008), North American continental margin records of the Paleocene-Eocene thermal maximum: Implications for global carbon and hydrological cycling, *Paleoceanography*, *23*, PA2217, doi:10.1029/2007PA001465.

Jorissen, F. J., C. Fontanier, and E. Thomas (2007), Paleoceanographical proxies based on deep-sea benthic foraminiferal assemblage characteristics, in *Proxies in Late Cenozoic Paleoceanography, Part 2, Biological Tracers and Biomarkers*, edited by C. Hillaire-Marcel and A. deVernal, pp. 263–326, Elsevier, New York.

Kaiho, K. (1994), Benthic foraminiferal dissolved-oxygen index and dissolved-oxygen levels in the modern ocean, *Geology*, *22*, 719–722, doi:10.1130/0091-7613(1994)022<0719:BFDOIA>2.3.CO;2.

Katz, M. E., D. K. Pak, G. R. Dickens, and K. G. Miller (1999), The source and fate of massive carbon input during the latest Paleocene thermal maximum, *Science*, *286*, 1531–1533, doi:10.1126/science.286.5444.1531.

Katz, M. E., D. R. Katz, J. D. Wright, K. G. Miller, D. K. Pak, N. J. Shackleton, and E. Thomas (2003), Early Cenozoic benthic foraminiferal isotopes: Species reliability and interspecies correction factors, *Paleoceanography*, *18*(2), 1024, doi:10.1029/2002PA000798.

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

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

Kuiper, K. F., A. Deino, F. J. Hilgen, W. Krijgsman, P. R. Renne, and J. R. Wijbrans (2008), Synchronizing rock clocks of Earth history, *Science*, *320*, 500–504, doi:10.1126/science.1154339.

Kurtz, A. C., L. R. Kump, M. A. Arthur, J. C. Zachos, and A. Paytan (2003), Early Cenozoic decoupling of the global carbon and sulfur cycles, *Paleoceanography*, *18*(4), 1090, doi:10.1029/2003PA000908.

Lourens, L. J., A. Sluijs, D. Kroon, J. C. Zachos, E. Thomas, U. Röhl, J. Bowles, and I. Raffi (2005), Astronomical pacing of late Palaeocene to early Eocene global warming events, *Nature*, *435*, 1083–1087, doi:10.1038/nature03814.

Moore, T. C., et al. (1984), Site report 527, *Initial Rep. Deep Sea Drill. Proj.*, *74*, 237–306.

Norris, R. D., and U. Röhl (1999), Carbon cycling and chronology of climate warming during the Palaeocene/Eocene transition, *Nature*, *401*, 775–778, doi:10.1038/44545.

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

Pagani, M., K. Caldeira, D. Archer, and J. C. Zachos (2006a), An ancient carbon mystery, *Science*, *314*, 1556–1557, doi:10.1126/science.1136110.

Pagani, M., N. Pedentchouk, M. Huber, A. Sluijs, S. Schouten, H. Brinkhuis, J. S. S. Damste, and G. R. Dickens (2006b), Arctic hydrology during global warming at the Palaeocene/Eocene thermal maximum, *Nature*, *442*, 671–675, doi:10.1038/nature05043.

Panchuk, K., A. Ridgwell, and L. R. Kump (2008), Sedimentary response to Paleocene-Eocene Thermal Maximum carbon release: A model-data comparison, *Geology*, *36*, 315–318, doi:10.1130/G24474A.1.

Rabinowitz, P. D., and E. S. W. Simpson (1984), Geophysical Site Survey Results on the Walvis Ridge, *Initial Rep. Deep Sea Drill. Proj.*, *74*, 795–825.

Röhl, U., T. J. Bralower, R. D. Norris, and G. Wefer (2000), New chronology for the late Paleocene thermal maximum and its environmental implications, *Geology*, *28*, 927–930, doi:10.1130/0091-7613(2000)28<927:NCFTLP>2.0.CO;2.

Röhl, U., T. Westerhold, T. J. Bralower, and J. C. Zachos (2007), On the duration of the Paleocene-Eocene thermal maximum (PETM), *Geochem. Geophys. Geosyst.*, *8*, Q12002, doi:10.1029/2007GC001784.

Schmitz, B., F. Asaro, E. Molina, S. Monechi, K. vonSalis, and R. P. Speijer (1997), High-resolution iridium, delta C-13, delta O-18, foraminifera and nannofossil profiles across the latest Paleocene benthic extinction event at Zumaya, Spain, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *133*, 49–68, doi:10.1016/S0031-0182(97)00024-2.

Schouten, S., M. Woltering, W. I. C. Rijpstra, A. Sluijs, H. Brinkhuis, and J. S. S. Damste (2007), The Paleocene-Eocene carbon isotope excursion in higher plant organic matter: Differential fractionation of angiosperms and conifers in the Arctic, *Earth Planet. Sci. Lett.*, *258*, 581–592, doi:10.1016/j.epsl.2007.04.024.

Smith, F. A., S. L. Wing, and K. H. Freeman (2007), Magnitude of the carbon isotope excursion at the Paleocene-Eocene thermal maximum: The role of plant community change, *Earth Planet. Sci. Lett.*, *262*, 50–65, doi:10.1016/j.epsl.2007.07.021.

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

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

Takeda, K., and K. Kaiho (2007), Faunal turnovers in central Pacific benthic foraminifera during the Paleocene-Eocene thermal maximum, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *251*, 175–197, doi:10.1016/j.palaeo.2007.02.026.

Thomas, D. J., T. J. Bralower, and J. C. Zachos (1999), New evidence for subtropical warming during the late Paleocene thermal maximum: Stable isotopes from Deep Sea Drilling Project Site 527, Walvis Ridge, *Paleoceanography*, *14*, 561–570, doi:10.1029/1999PA900031.

Thomas, D. J., J. C. Zachos, T. J. Bralower, E. Thomas, and S. Bohaty (2002), Warming the fuel for the fire: Evidence for the thermal dissociation of methane hydrate during the Paleocene-Eocene thermal maximum, *Geology*, *30*, 1067–1070, doi:10.1130/0091-7613(2002)030<1067:WTFFTF>2.0.CO;2.

Thomas, E. (1998), Biogeography of the Late Paleocene benthic foraminiferal extinction, in *Late Paleocene and Early Eocene Climatic and Biotic Events in the Marine and Terrestrial Records*, edited by M. P. Aubry et al., pp. 214–242, Columbia Univ. Press, New York.

Thomas, E. (2003), Extinction and food at the seafloor: A high-resolution benthic foraminiferal record across the initial Eocene thermal maximum, Southern Ocean Site 690, in *Causes and Consequences of Globally Warm Climates in* *the Early Paleogene*, edited by S. L. Wing et al., *Geol Soc. Am. Spec. Pap.*, *369*, 319–332.

Thomas, E. (2007), Cenozoic mass extinctions in the deep sea: What disturbs the largest habitat on Earth?, in *Large Ecosystem Perturbations: Causes and Consequences*, edited by S. Monechi et al., *Geol. Soc. Am. Spec. Pap.*, *424*, 1–23.

Thomas, E., and N. J. Shackleton (1996), The Paleocene-Eocene benthic foraminiferal extinction and stable isotope anomalies, in *Correlation of the Early Paleogene in Northwest Europe*, edited by R. W. O. Knox, R. M. Corfield, and R. E. Dunay, *Geol. Soc. London Spec. Publ.*, *101*, 401–441, doi:10.1144/GSL.SP.1996.101.01.20.

Thomas, E., J. C. Zachos, and T. J. Bralower (2000), Deep-sea environments on a warm Earth: Latest Paleocene - early Eocene, in *Warm Climates in Earth History*, edited by B. T. Huber et al., pp. 132–160, Cambridge Univ. Press, New York.

Tripati, A., and H. Elderfield (2005), Deep-sea temperature and circulation changes at the Paleocene-Eocene thermal maximum, *Science*, *308*, 1894–1898, doi:10.1126/science.1109202.

Westerhold, T., U. Röhl, J. Laskar, I. Raffi, J. Bowles, L. J. Lourens, and J. C. Zachos (2007), On the duration of magnetochrons C24r and C25n and the timing of early Eocene global warming events: Implications from the Ocean Drilling Program Leg 208 Walvis Ridge depth transect, *Paleoceanography*, *22*, PA2201, doi:10.1029/2006PA001322.

Westerhold, T., U. Röhl, I. Raffi, E. Fornaciari, S. Monechi, V. Reale, J. Bowles, and H. F. Evans (2008), Astronomical calibration of the Paleocene time, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *257*, 377–403.

Wing, S. L., H. M. Bao, and P. Koch (2000), An early Eocene cool period? Evidence for continental cooling during the warmest part of the Cenozoic, in *Warm Climates in Earth History*, edited by B. T. Huber et al., pp. 197–237, Cambridge Univ. Press, New York.

Zachos, J., D. Kroon, J. Baldauf, and P. Blum (2002), *Leg 208 Scientific Prospectus: Early Cenozoic Extreme Climates: The Walvis Ridge Transect*, Ocean Drill. Program, College Station, Tex.

Zachos, J., et al. (2004), *Leg 208 Initial Reports: Early Cenozoic Extreme Climates, The Walvis Ridge Transect*, Integrated Ocean Drill. Program, College Station, Tex.

Zachos, J. C., et al. (2005), Rapid acidification of the ocean during the Paleocene-Eocene thermal maximum, *Science*, *308*, 1611–1615, doi:10.1126/science.1109004.

Zachos, J. C., S. Schouten, S. Bohaty, T. Quattlebaum, A. Sluijs, H. Brinkhuis, S. J. Gibbs, and T. J. Bralower (2006), Extreme warming of mid-latitude coastal ocean during the Paleocene-Eocene Thermal Maximum: Inferences from TEX86 and isotope data, *Geology*, *34*, 737–740, doi:10.1130/G22522.1.

Zeebe, R. E., and J. C. Zachos (2007), Reversed deep-sea carbonate ion basin gradient during Paleocene-Eocene thermal maximum, *Paleoceanography*, *22*, PA3201, doi:10.1029/2006PA001395.

Zhang, Y. X. (2003), Methane escape from gas hydrate systems in marine environment, and methane-driven oceanic eruptions, *Geophys. Res. Lett.*, *30*(7), 1398, doi:10.1029/2002GL016658.