

# Assessing offsets between the $\delta^{13}\text{C}$ of sedimentary components and the global exogenic carbon pool across early Paleogene carbon cycle perturbations

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[1] Negative stable carbon isotope excursions (CIEs) across the Paleocene–Eocene thermal maximum (PETM;  $\sim 56$  Ma) range between 2‰ and 7‰, even after discounting sections with truncated records. Individual carbon isotope records differ in shape and magnitude from variations in the global exogenic carbon cycle through changes in (1) the relative abundance of mixed components with different  $\delta^{13}\text{C}$  within a measured substrate, (2) isotope fractionation through physiological change, and (3) the isotope composition of the carbon source. All three factors likely influence many early Paleogene  $\delta^{13}\text{C}$  records, especially across the PETM and other hyperthermal events. We apply these concepts to late Paleocene–early Eocene ( $\sim 58$ – $52$  Ma) records from Lomonosov Ridge, Arctic Ocean. Linear regression analyses show correlations between the  $\delta^{13}\text{C}$  of total organic carbon (TOC) and two proxies for the relative contribution of terrestrial organic components to sediment TOC: the branched and isoprenoid tetraether index and palynomorphs. We use these correlations to subtract the terrestrial component from  $\delta^{13}\text{C}_{\text{TOC}}$  and calculate marine organic matter  $\delta^{13}\text{C}$ . The results show that the magnitude of the CIE in  $\delta^{13}\text{C}_{\text{TOC}}$  across the PETM is exaggerated relative to the magnitude of the CIE in  $\delta^{13}\text{C}_{\text{MOM}}$  by  $\sim 3$ ‰ due to increased contributions of terrestrial organic carbon during the event. Collectively, all carbon isotope records across the PETM and other major climate–carbon cycle perturbations in Earth’s history are potentially biased through one or more of the above factors. Indeed, it is highly unlikely that any  $\delta^{13}\text{C}$  record shows the true shape and magnitude of the CIE for the global exogenic carbon cycle. For the PETM, we conclude that CIE in the exogenic carbon cycle is likely  $<4$ ‰, but it will take additional analyses and modeling to obtain an accurate value for this CIE.

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## 1. Introduction

[2] Earth’s surface, especially at high latitudes and in the deep sea, experienced warming from the late Paleocene through the early Eocene ( $\sim 59$ – $51$  Ma) [Zachos *et al.*, 2008]. Evidence for this warming comes from microfossil biogeography [e.g., Adams *et al.*, 1990; Thomas and Shackleton, 1996; Bujak and Brinkhuis, 1998] and sediment chemistry, such as foraminiferal  $\delta^{18}\text{O}$  or TEX<sub>86</sub> records [e.g., Zachos *et al.*, 2001; Pearson *et al.*, 2007; Bijl *et al.*, 2009]. The

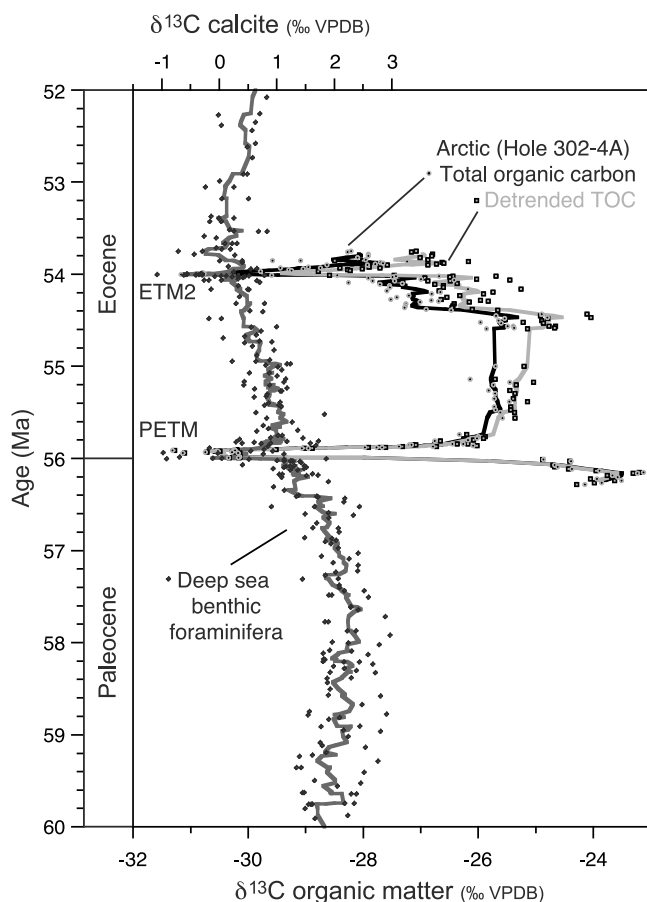
temperature increase broadly corresponded to a decrease in the  $\delta^{13}\text{C}$  of carbon-bearing phases (Figure 1) [Shackleton, 1986; Stein *et al.*, 2006; Hilting *et al.*, 2008; Zachos *et al.*, 2008; Zachos *et al.*, 2010], and a deepening of carbonate saturation horizons in the ocean [Hancock *et al.*, 2007; Leon-Rodriguez and Dickens, 2010]. Both suggest a large, multimillion-year rise in ocean and atmosphere carbon contents.

[3] Superimposed on these long-term trends were several “hyperthermals,” relatively brief ( $<200$  kyr) events characterized by significant additional warming [e.g., Bowen *et al.*, 2006; Sluijs *et al.*, 2007a]. The Paleocene–Eocene thermal maximum (PETM;  $\sim 56$  Ma) is the most prominent and best studied example, but at least six other episodes (e.g., Eocene thermal maximum 2, ETM2;  $\sim 54$  Ma) now clearly manifest in multiple sediment sequences from widespread locations [e.g., Cramer *et al.*, 2003; Lourens *et al.*, 2005; Nicolo *et al.*, 2007]. While their number and absolute ages remain uncertain, the hyperthermals each exhibit a negative stable carbon isotope excursion (CIE) in various sedimentary components (Figure 1), and dissolution of carbonate in deep ocean basins

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**Figure 1.** Comparison of deep-sea benthic foraminifer  $\delta^{13}\text{C}$  and Hole 302-4A  $\delta^{13}\text{C}_{\text{TOC}}$  records between 51 and 59 Ma. Left graph represents benthic foraminifer  $\delta^{13}\text{C}$  values compiled by Zachos *et al.* [2008], complemented with the *Cibicides* data for ETM2 from Lourens *et al.* [2005]. Lines are five-point moving averages. VPDB = Vienna Peedee belemnite. The Hole 302-4A  $\delta^{13}\text{C}_{\text{TOC}}$  record is detrended for global exogenic trends (gray line; see section 4.2) using the long-term trend in benthic foraminifer  $\delta^{13}\text{C}$ .

[e.g., Zachos *et al.*, 2005; Stap *et al.*, 2009]. These observations, along with the relative timing and magnitude of CIEs, are best explained by a series of geologically rapid and massive injections of  $^{13}\text{C}$ -depleted carbon from some carbon reservoir, or “carbon capacitor” [Dickens, 2000, 2003] into the exogenic carbon pool [Dickens *et al.*, 1997; Panchuk *et al.*, 2008; Zeebe *et al.*, 2009]. The latter, where carbon would cycle on geologically short ( $\sim 10^3$  years) time scales, would comprise the ocean, atmosphere, and terrestrial biosphere, including soil and humus [Kump and Arthur, 1999]. The capacitor would slowly store massive amounts of  $^{13}\text{C}$ -depleted carbon over relatively long ( $10^5$ – $10^6$  years) time scales but could release such carbon relatively quickly ( $< 10^5$  years) upon environmental change [Dickens, 2003]. Such systems might include seafloor gas hydrate systems [Dickens, 2003], peat [Kurtz *et al.*, 2003], or permafrost [DeConto *et al.*, 2012].

[4] The late Paleocene to early Eocene presents an especially intriguing interval for studying past climate change and carbon cycling [Zachos *et al.*, 2008]. A series of slow

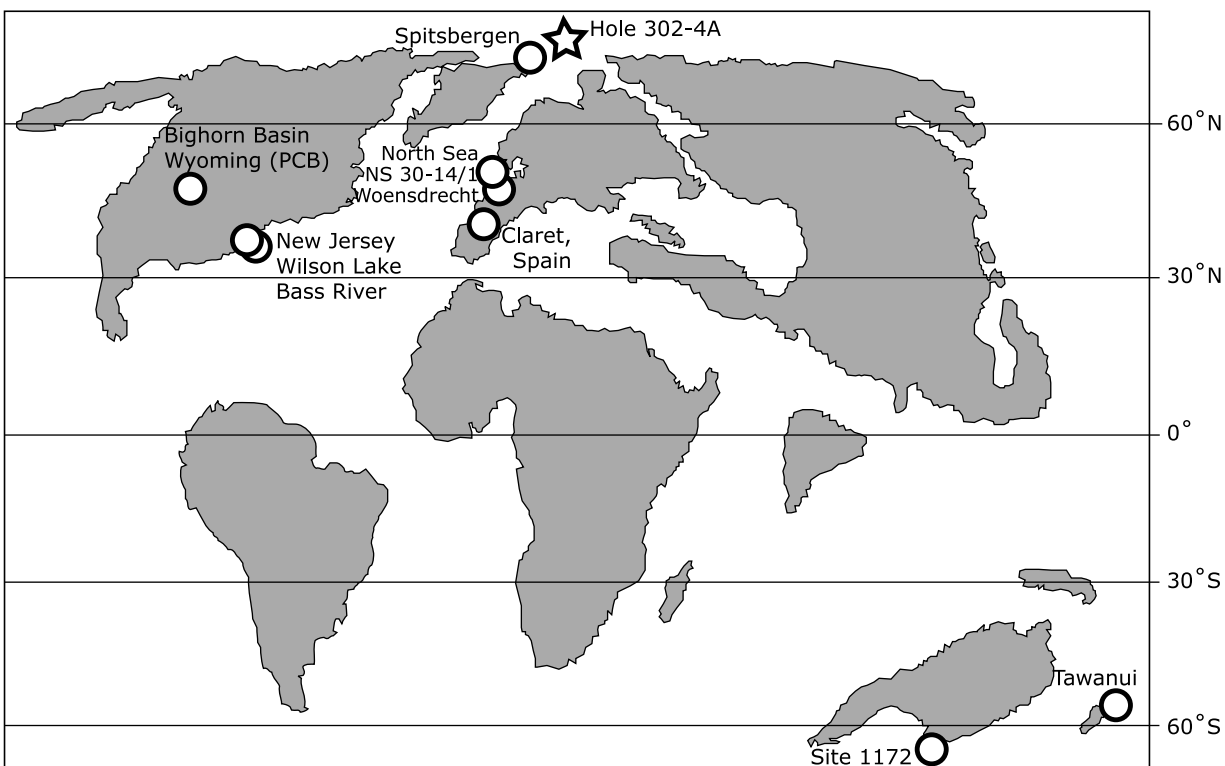
and fast net carbon inputs to the exogenic carbon cycle occurred and these additions coincided with a range of environmental responses [Adams *et al.*, 1990; Bujak and Brinkhuis, 1998; Bowen *et al.*, 2006; Sluijs *et al.*, 2007a; McInerney and Wing, 2011]. Furthermore, the superposition of the short-term injection events upon long-term changes implies different boundary states in which to examine the climate system and carbon cycling. Within this context, determining the magnitude and timing of changes in the  $\delta^{13}\text{C}$  of the exogenic carbon cycle becomes an important goal, because these constrain the size and source of the carbon injections from the inferred capacitor [e.g., Dickens *et al.*, 1997; Kump and Arthur, 1999; Dickens, 2001; Panchuk *et al.*, 2008; Zeebe *et al.*, 2009].

[5] Perhaps 100  $\delta^{13}\text{C}$  records, using a range of carbon substrates, have been generated across the PETM to date [McInerney and Wing, 2011]. Moreover,  $\delta^{13}\text{C}$  records are rapidly emerging across the other hyperthermals [Cramer *et al.*, 2003; Lourens *et al.*, 2005; Nicolo *et al.*, 2007; Sluijs *et al.*, 2009; Stap *et al.*, 2009, 2010; Clementz *et al.*, 2011; Abels *et al.*, 2012]. The shapes and magnitudes of CIEs in these records vary significantly [Bowen *et al.*, 2004; Stoll, 2005; Schouten *et al.*, 2007], which raises a provocative question: how do  $\delta^{13}\text{C}$  variations in any of these records relate to changes in the  $\delta^{13}\text{C}$  of the exogenic carbon cycle as a whole? We present and discuss mechanisms that may bias individual records and put these into a conceptual framework. We then discuss how  $\delta^{13}\text{C}$  records of total organic carbon ( $\delta^{13}\text{C}_{\text{TOC}}$ ) records may be corrected for changing organic matter composition across hyperthermal records, using published records from Integrated Ocean Drilling Program Hole 302-4A on Lomonosov Ridge, Arctic Ocean (Figure 2), as an example.

## 2. The Carbon Cycle Recording Problem

[6] For about two decades, it has been generally accepted that a prominent negative CIE marks the stratigraphic position of the PETM in sedimentary sections worldwide [Kennett and Stott, 1991; Koch *et al.*, 1992]. The CIE can be described, in a basic sense, as a major drop in  $\delta^{13}\text{C}$  over a fairly short interval of stratigraphic depth (time) followed by substantial rise in  $\delta^{13}\text{C}$  over a somewhat longer interval of stratigraphic depth (time). Although the exact timing remains controversial, all interpretations derived from multiple approaches indicate the entire CIE (onset and partial recovery) occurred within 220 kyr [Röhl *et al.*, 2007; Abdul Aziz *et al.*, 2008; Murphy *et al.*, 2010].

[7] The CIE is widely regarded to represent a massive input of  $^{13}\text{C}$ -depleted  $\text{CO}_2$  to the exogenic carbon cycle, followed by uptake of excess carbon into one or more reservoirs. This idea initially arose from considerations of the size, shape and approximate timing of the CIE [Dickens *et al.*, 1995; Thomas and Shackleton, 1996; Dickens *et al.*, 1997], as well as its occurrence in sediment records from different carbon reservoirs, notably the shallow and deep ocean [Kennett and Stott, 1991; Pak and Miller, 1992] and soils [Koch *et al.*, 1992]. The source of the  $\text{CO}_2$ , including whether it was oxidized  $\text{CH}_4$ , remains contentious [Dickens *et al.*, 1995; Kurtz *et al.*, 2003; Svensen *et al.*, 2004]. Nonetheless, confirmation for the general carbon injection hypothesis has come from the numerous  $\delta^{13}\text{C}$  records generated since [McInerney and Wing, 2011], as well from carbonate accumulation records in deep-



**Figure 2.** Locations of the discussed sites within a paleogeographic reconstruction of early Eocene times. Modified from *Scotese and Golanka* [1992].

sea sediment sequences, which show carbonate dissolution at the onset of the PETM, followed by very high carbonate preservation toward the end of the event [Kelly *et al.*, 2005; Zachos *et al.*, 2005]. These are expected geological expressions for a massive input of  $\text{CO}_2$  to the ocean, atmosphere or both [Dickens *et al.*, 1997].

[8] Theoretically, the magnitude and timing for such a global negative CIE should relate to a few basic parameters [e.g., Kump and Arthur, 1999; Dickens, 2001]: the mass and  $\delta^{13}\text{C}$  of the exogenic carbon cycle prior to the carbon injection, the size and  $\delta^{13}\text{C}$  of carbon fluxes into and out of the exogenic carbon reservoirs before the perturbation, and the changes in carbon fluxes during the event. Several issues arise, however, when one attempts to transfer this conceptual framework to the geological record. For example,  $\delta^{13}\text{C}$  records of various carbon-bearing phases in PETM sediment sections show a very large variation in the magnitude of the CIE, between 2‰ and 7‰, depending on location and analyzed substrate [McInerney and Wing, 2011]. In some sections, such variations result from brief hiatuses or core recovery problems at the onset of the event, which can lead to an absence of the recording substrate. Clearly, seafloor dissolution has truncated some marine carbonate  $\delta^{13}\text{C}$  records [McCarren *et al.*, 2009]. However, variations in the size of the CIE remain even after discounting sections with record gaps. For example, a  $\sim 2\%$  CIE manifests in bulk carbonate  $\delta^{13}\text{C}$  records across an expanded and continuous PETM section at Mead Stream, New Zealand [Hollis *et al.*, 2005a]. A similar change is found in a bulk carbonate  $\delta^{13}\text{C}$  record at Maud Rise, South Atlantic, where the record also appears

continuous [Bains *et al.*, 1999]. However, at this location, benthic foraminifera, thermocline dwelling foraminifera, and mixed layer dwelling foraminifera display CIEs of 2.5‰, 2‰, and 4.5‰, respectively [Kennett and Stott, 1991; Thomas *et al.*, 2002; Kelly *et al.*, 2005].

[9] The magnitude and timing of a negative  $\delta^{13}\text{C}$  excursion caused by a massive carbon input should show small variations between different pools of the exogenic carbon cycle [Dickens, 2000]. This is because  $\delta^{13}\text{C}$  changes along flow paths away from potential sites of carbon injection, a phenomenon that can be demonstrated using carbon cycle models that track the  $\delta^{13}\text{C}$  of the ocean, atmosphere, and biosphere [Walker and Kasting, 1992]. However, the wide range in CIEs recorded across the PETM lies far beyond that simulated in basic geochemical models [Dickens, 2000]. This raises two related questions [Bowen *et al.*, 2004; Diefendorf *et al.*, 2010; Dickens, 2011]: (1) What does the range in  $\delta^{13}\text{C}$  mean? (2) What is the correct value for the change in the  $\delta^{13}\text{C}$  of the entire exogenic carbon pool? Clearly, modeling a 2‰ or a 7‰ CIE in the exogenic carbon cycle makes an enormous difference to understanding causes and effects of a massive carbon input [Dickens *et al.*, 1997; Pagani *et al.*, 2006a; Zeebe *et al.*, 2009; Cui *et al.*, 2011].

[10] Other hyperthermal events of the early Paleogene have received far less attention than the PETM, in part because they were discovered relatively recently. Nonetheless, it is already clear that similar issues regarding  $\delta^{13}\text{C}$  records manifest for these events. For example, about 10  $\delta^{13}\text{C}$  records are presently available across ETM-2 and they show a variance in CIE of 1.4‰–3.8‰ [Cramer *et al.*, 2003; Lourens *et al.*, 2005;

*Nicolo et al.*, 2007; *Sluijs et al.*, 2009; *Stap et al.*, 2009, 2010; *Clementz et al.*, 2011; *Schoon et al.*, 2011; *Abels et al.*, 2012]. This range may increase with additional work using new locations and different substrates, as has been the case for the PETM.

[11] Furthermore, long-term carbon isotope records spanning the early Paleogene may deviate from one another. Planktonic and benthic foraminifer  $\delta^{13}\text{C}$  records from several locations exhibit a  $\sim 2\%$  decrease from the late Paleocene through the early Eocene ( $\sim 58\text{--}53$  Ma; Figure 1) [*Shackleton and Hall*, 1984; *Zachos et al.*, 2001; *Hilting et al.*, 2008]. Within this interval,  $\sim 1\%$  of the drop occurred between the PETM and ETM2. However, over the same time but in a sediment sequence from the Arctic, there is an  $\sim 4\%$  decrease in  $\delta^{13}\text{C}_{\text{TOC}}$  (Figure 1) [*Stein et al.*, 2006; *Sluijs et al.*, 2009]. Consequently, individual  $\delta^{13}\text{C}$  records seem to deviate from global exogenic trends on both long and short time scales.

### 3. Generic Causes

[12] The  $\delta^{13}\text{C}$  of a carbon-bearing phase (substrate) can be related to the  $\delta^{13}\text{C}$  of the exogenic carbon cycle through three basic equations:

$$\delta^{13}\text{C}_{\text{SUBSTRATE}} = X\% \cdot \delta^{13}\text{C}_X + Y\% \cdot \delta^{13}\text{C}_Y + Z\% \cdot \delta^{13}\text{C}_Z + \dots \quad (1)$$

$$\delta^{13}\text{C}_X = f + \delta^{13}\text{C}_{\text{LOCAL}} \quad (2)$$

$$\delta^{13}\text{C}_{\text{LOCAL}} = g + \delta^{13}\text{C}_{\text{EXOGENIC}} \quad (3)$$

where “substrate” denotes an analyzed carbon-bearing phase (e.g., bulk carbonate), X, Y, Z, etc., denote specific components of a substrate (e.g., foraminiferal and nannofossil carbonate), “local” denotes the carbon pool from which a substrate precipitates (e.g.,  $\text{HCO}_3^-$ ),  $f$  represents the offset in  $\delta^{13}\text{C}$  between the local pool and the substrate (e.g., fractionation factor [e.g., *Farquhar et al.*, 1989]), and  $g$  is the offset in  $\delta^{13}\text{C}$  between the local pool and the average of the global exogenic carbon pool. The third equation ultimately relates to a larger mass balance:

$$\delta^{13}\text{C}_{\text{EXOGENIC}} = (\delta^{13}\text{C}_{\text{LOCAL-A}} \cdot M_{\text{LOCAL-A}} + \delta^{13}\text{C}_{\text{LOCAL-B}} \cdot M_{\text{LOCAL-B}} + \dots) / (M_{\text{EXOGENIC}}) \quad (4)$$

where M is mass, A, B, C are different pools of carbon within the exogenic carbon cycle, and  $M_{\text{EXOGENIC}}$  is the sum of all local carbon reservoirs.

[13] Several factors might cause individual carbon isotope records to vary in shape and magnitude from that of the global exogenic carbon cycle during a carbon cycle perturbation [e.g., *Bowen et al.*, 2004; *Diefendorf et al.*, 2010; *Oehlert et al.*, 2011]. Collectively, there are three general possibilities, which relate to the above equations.

[14] First, most  $\delta^{13}\text{C}$  records comprise mixtures of several carbon sources (equation (1)). For example, bulk marine carbonate records are derived from agglomerations of many nannofossil and foraminifer taxa, and might also include authigenic carbonate; bulk organic carbon records constructed using marine sediments typically represent contributions from marine and terrestrial organic matter, as well as different taxa within the marine and terrestrial realms; higher-plant n-alkane

records may be derived from multiple species of gymnosperms, angiosperms and ferns. In many cases, we are unlikely aware of all contributors to the mixture. If the  $\delta^{13}\text{C}$  values of components (X, Y, Z, etc.) within the mixture differ significantly, any change in the relative abundance of the components over time will cause a deviation in  $\delta^{13}\text{C}$  [e.g., *Bralower*, 2002; *Stoll*, 2005; *Schouten et al.*, 2007]. The timing and magnitude of a CIE as recorded in a substrate can thus differ from that of the exogenic carbon pool as the proportion of components changes. This effect can be significant, as discussed below.

[15] An extension of this concept can occur with mixing of material of different age [*Leithold et al.*, 2006]. That is, the components (X, Y, Z, etc.) could represent an identical substrate, but formed at different times, such as before and during a CIE, and subsequently mixed. Bioturbation provides one obvious means for this to occur [*John et al.*, 2008; *Leon-Rodriguez and Dickens*, 2010; *Stap et al.*, 2010]; another is discussed below. In any case, mixing of components of different age would lead to a different expression of the CIE than that of the exogenic carbon cycle. Generally, it should dampen the magnitude by  $\sim 1\%$  and “smear” the CIE by at least several thousand years [*Stap et al.*, 2010; *Cui et al.*, 2011; *Sluijs et al.*, 2012].

[16] Second, the carbon isotope fractionation between the substrate and the local carbon pool can change (equation (2)). This is because many environmental conditions might change coincident with variations in global carbon cycling. For example, the carbon isotope fractionation between atmospheric  $\text{CO}_2$  and organic matter might change in terrestrial plants because of different water use efficiency [e.g., *Bowen et al.*, 2004; *Schouten et al.*, 2007]; the fractionation between DIC and producers of marine calcite might change because of different seawater pH [*Uchikawa and Zeebe*, 2010]. The net result may be an offset between the CIE as recorded in the substrate and the CIE of the local carbon source. Conceivably, such offsets can exceed  $1\%$ – $2\%$  [*Bowen et al.*, 2004; *Uchikawa and Zeebe*, 2010].

[17] Third, the  $\delta^{13}\text{C}$  of the local carbon pool from which a carbon-bearing phase precipitated could change relative to the exogenic carbon cycle (equation (3)). For example, during the hyperthermals and at the small scale, river inputs to some coastal regions appear to have increased significantly [e.g., *John et al.*, 2008; *Sluijs et al.*, 2008b]. Given the relationship between salinity and the  $\delta^{13}\text{C}$  of dissolved inorganic carbon (DIC) on shelves [*Spiker and Schemel*, 1979; *Chanton and Lewis*, 1999], excess river runoff, would have decreased the local  $\delta^{13}\text{C}$ , so that the negative  $\delta^{13}\text{C}$  excursion in neritic carbonate or organic carbon would be greater than expected. This effect may be significant because the  $\delta^{13}\text{C}_{\text{DIC}}$  of river water is typically approximately  $10\%$  lower than that of seawater [*Spiker and Schemel*, 1979], and has therefore been invoked as a cause for a  $-1.5\%$  amplification of marine  $\delta^{13}\text{C}$  records on the New Jersey margin across the PETM [*Dickens*, 2011]. Certain organisms may also have changed their habitat, and consequently incorporated C from different parts of the water column. As one possibility, planktonic foraminifera might migrate down in the water during extreme warming [e.g., *Handley et al.*, 2008]. Because of strong  $\delta^{13}\text{C}_{\text{DIC}}$  gradients with depth in many surface ocean regions (e.g., Global Ocean Data Analysis Project data [*Key et al.*, 2004]) the local  $\delta^{13}\text{C}$  would be lower, which would amplify the CIE relative

to that of the exogenic carbon cycle. This provides one means to reconcile the aforementioned 2.5‰ difference in the magnitude of the CIE between thermocline dwelling foraminifera and mixed layer dwelling foraminifera on Maud Rise across the PETM [Dickens, 2011].

[18] For constraining changes in the mass and flow of carbon in the exogenic carbon cycle, quantification of changes in  $f$  and  $g$  are desirable (equations (2) and (3)). This is because they represent offsets between sedimentary proxy carriers, individual carbon reservoirs, and the global exogenic carbon pool. We suspect that most, if not all,  $\delta^{13}\text{C}$  records across the PETM and other hyperthermals have strong potential for bias. It is highly unlikely that any particular  $\delta^{13}\text{C}$  record shows the true shape and magnitude of the CIE for the global exogenic carbon cycle.

[19] This issue becomes even more problematic (and intriguing) when one considers mass balance (equation (4)). In all likelihood, between 85 and 95% of the exogenic carbon cycle, by mass, has existed as dissolved  $\text{HCO}_3^-$  in ocean water below the mixed layer throughout the Phanerozoic. This necessarily implies that the  $\delta^{13}\text{C}$  of the deep ocean always dominates the overall  $\delta^{13}\text{C}$  composition of the entire exogenic carbon cycle. Even if  $\delta^{13}\text{C}$  excursions larger than 3.5‰ in magnitude were faithfully recording carbon isotope changes in shallow marine and atmospheric carbon reservoirs, they cannot be used to argue for such changes in the whole exogenic carbon cycle, unless such changes manifest in deep ocean records. Typically, thermocline dwelling and benthic foraminifer  $\delta^{13}\text{C}$  records in open ocean sections across the PETM do not exceed 3‰. Nonetheless, it is important to understand the range in  $\delta^{13}\text{C}$  across substrates during the early Paleogene and tease out the cause behind this variance, because such information may give us crucial insights to past processes during major environmental change.

## 4. Separating Substrate Effects From $\delta^{13}\text{C}_{\text{TOC}}$ Records

### 4.1. Background and Rationale

[20] To explore the conceptual ideas outlined above, we turn to carbon isotope records of total organic carbon ( $\delta^{13}\text{C}_{\text{TOC}}$ ) in marine sediment. At least 15 such records have now been generated across the PETM, and these show a large range in magnitude for the CIE [e.g., McInerney and Wing, 2011]. Some records, such as at Tawanui, New Zealand, show a CIE of  $\sim 2\%$  [Kaiho et al., 1996; Crouch et al., 2001], some, such as at ODP Site 1172 on the East Tasman Plateau, show a CIE of  $\sim 3\%$  [Shuijs et al., 2011], while some, such as in the Arctic and in the North Sea, show a CIE exceeding 5‰ [e.g., Shuijs et al., 2006, 2007b; Cui et al., 2011; Harding et al., 2011] (Figure 2). The variation in magnitude of the CIE clearly must reflect factors other than the change in  $\delta^{13}\text{C}$  of the exogenic carbon cycle, or even the atmosphere. Such differences might be attributed to potential hiatuses at the onset of the CIE [e.g., Hollis et al., 2005a; McCarren et al., 2009]. Alternatively, they might reflect variations in the composition of organic matter during the PETM, especially the relative portions of terrestrial and marine organic matter [Crouch et al., 2003; Shuijs et al., 2006].

[21] Marine organic matter (MOM) was much more depleted in  $^{13}\text{C}$  over long intervals of the Phanerozoic relative

to the Holocene. In their review, Hayes et al. [1999] indicated values between  $-26\%$  and  $-28\%$  for Paleocene–Eocene times, compared to approximately  $-20\%$  at present day. The difference likely results from high  $p\text{CO}_2$  in past ocean waters, which caused increased fractionation against  $^{13}\text{C}$  by the carboxylating enzyme Rubisco [Freeman and Hayes, 1992]. By contrast, sedimentary terrestrial organic matter  $\delta^{13}\text{C}$  was only slightly higher during the latest Paleocene to earliest Eocene, with values around  $-24\%$  [Magioncalda et al., 2004; Domingo et al., 2009]. Hence, site-specific variations in the relative supply of terrestrial and marine organic carbon should modify  $\delta^{13}\text{C}_{\text{TOC}}$  records in marine sediment across the hyperthermals.

[22] Sediment records from at least six passive continental margins suggest that global average sea level rose during the PETM [e.g., Sluijs et al., 2008a]. Concomitantly, the supply of sediment from rivers to the shelves, including organic matter, increased at many locations [e.g., Crouch et al., 2003; Hollis et al., 2005b; Giusberti et al., 2007; Sluijs et al., 2008b]. These two processes impact the supply of terrestrial material to a specific continental margin site differently, and wide deviations in the proportion of terrestrial and marine organic matter might be expected during the PETM. In particular, at Tawanui, the percentage of terrestrial palynomorphs increased during the PETM [Crouch et al., 2003]. This was attributed to greater riverine runoff and terrestrial discharge, and was offered as an explanation for why the CIE expressed by  $\delta^{13}\text{C}_{\text{TOC}}$  is relatively small at this location [Crouch et al., 2003]. Can the opposite effect, a greater percentage of marine organic carbon, explain the relatively large CIEs in  $\delta^{13}\text{C}_{\text{TOC}}$  records at locations such as the North Sea and the Arctic Ocean?

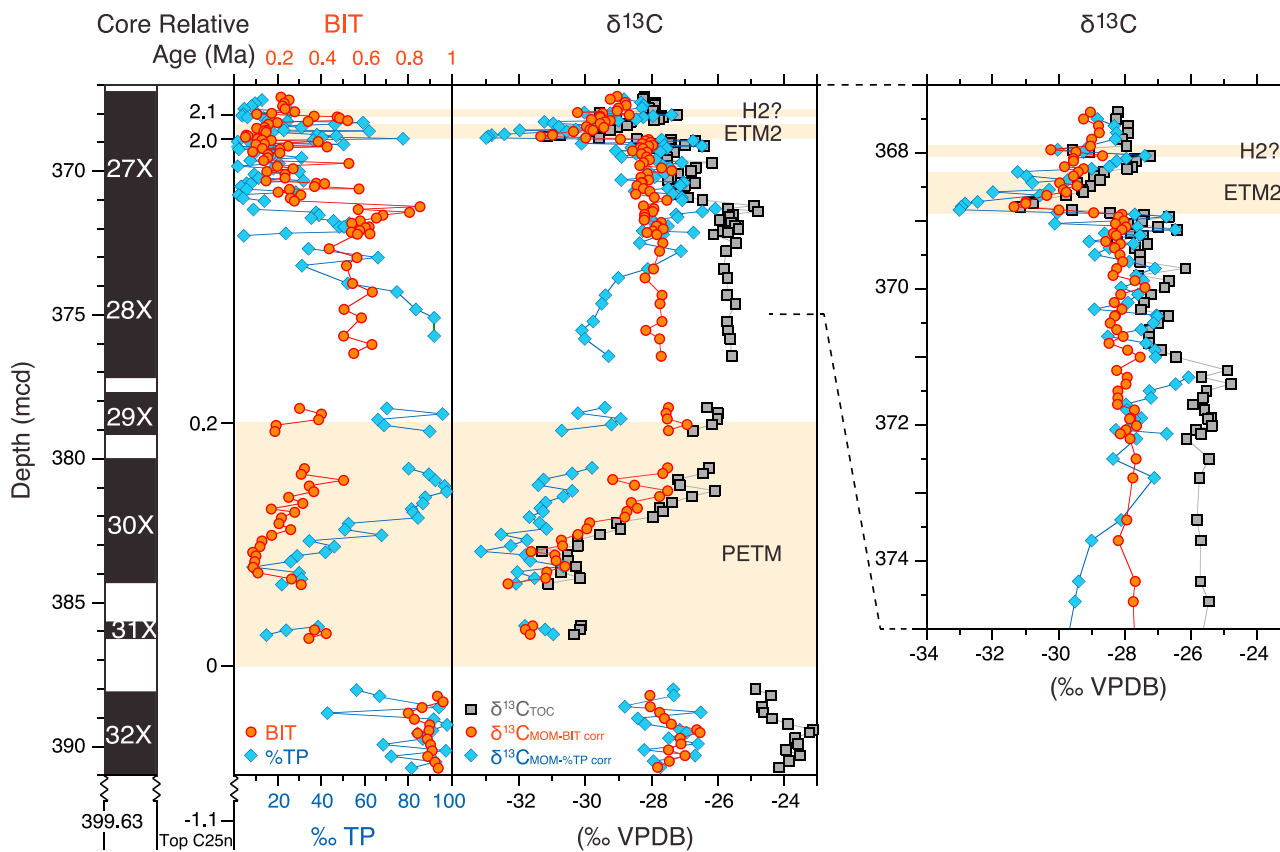
[23] The relative proportions of terrestrial and marine organic carbon might be disentangled with measurements of the branched and isoprenoid tetraether (BIT) index. This index describes the relative proportions of specific terrestrial and marine lipids known as glycerol dialkyl glycerol tetraethers (GDGTs); it is defined as [Hopmans et al., 2004]

$$\text{BIT} = [\text{I} + \text{II} + \text{III}] / [\text{I} + \text{II} + \text{III} + \text{IV}]$$

where I, II, and III are terrestrial GDGTs and IV is a marine GDGT. The terrestrial branched GDGTs are produced in soils by bacteria and transported to the ocean by rivers, while the marine isoprenoid GDGT, named crenarcheol, is predominantly produced in the ocean by planktonic archaea. The exact source of the terrestrial lipids remain unclear [Sinninghe Damsté et al., 2011], and absolute BIT values should be considered with care because interlaboratory comparisons show that analyses are not straightforward [Schouten et al., 2009]. In addition, organic carbon derived from soils may not scale linearly with the total abundance of terrestrial organic matter found in marine sediments [Weijers et al., 2009]. Regardless, the BIT index has emerged as a reliable proxy to quantify the relative amounts of terrestrial and marine organic matter in marine sediments on glacial-interglacial cycles [Ménnot et al., 2006] as well as deep time intervals, such as the hyperthermals [Shuijs et al., 2008a, 2011].

[24] The relative portions of terrestrial (pollen and spores) and marine (mostly dinoflagellate cysts) palynomorphs might also serve as a proxy for the relative abundances of terrestrial and marine organic matter. As for the BIT index, this approach

## IODP Expedition 302; Hole 4A



**Figure 3.** Geochemical and palynological records across the uppermost Paleocene and lower Eocene of IODP Site 4A, Lomonosov Ridge, Arctic Ocean. (left) The  $\delta^{13}\text{C}$  of total organic carbon (TOC) and  $\delta^{13}\text{C}$  of marine organic matter (MOM) reconstructed by subtracting the terrestrial component from the  $\delta^{13}\text{C}_{\text{TOC}}$  values using equations (8) and (9). (right) The BIT index and percentage terrestrial palynomorph (%TP) data used to calculate  $\delta^{13}\text{C}_{\text{MOM}}$ . Data are from *Sluijs et al.* [2008b].

has potential problems. In particular, species-specific pollen production and transport processes can affect the relationship between the percentage terrestrial palynomorphs (%TP) and the fraction of terrestrial organic matter in marine sediments.

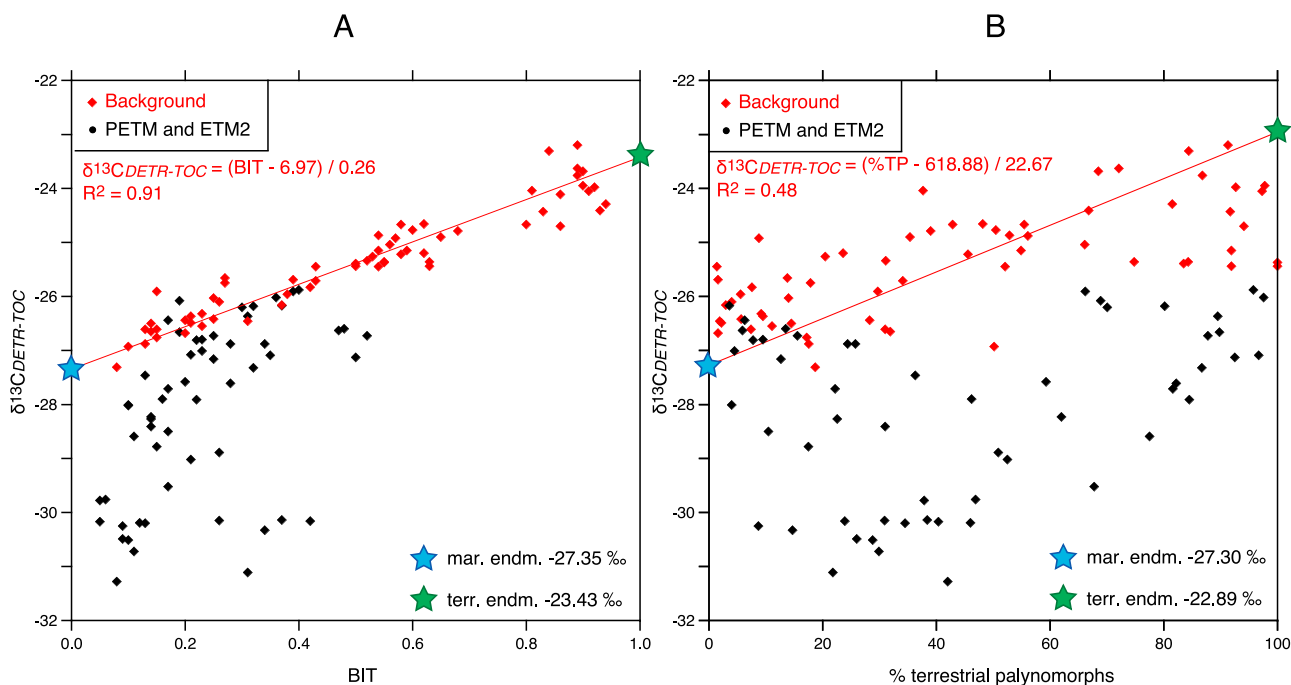
[25] Importantly, the BIT index and the %TP have different taphonomy, which is the pathway from biological origin to burial in sediment. Rivers can transport both GDGTs and terrestrial palynomorphs to the ocean. Branched GDGTs have not been observed in atmospheric dust [*Hopmans et al.*, 2004]. However, wind can transport terrestrial palynomorphs, particularly saccate pollen of gymnosperm plants. Moreover, the size of the material is much different: GDGTs are nominally a few nm, while terrestrial palynomorphs are typically between five and several tens of  $\mu\text{m}$ . Temporal records of the two proxies, when and where consistent, thus likely reflect past delivery of terrestrial organic matter to marine sediments.

#### 4.2. Material and Methods

[26] IODP Expedition 302 drilled Hole 4A on Lomonosov Ridge, central Arctic Ocean in 2004 (Figure 2) [*Backman et al.*, 2006]. Uppermost Paleocene–lowermost Eocene sediments in this hole (Cores 32X – 27X) were deposited at  $\sim 85^\circ\text{N}$ , and likely on the continental shelf [*O’Regan*

*et al.*, 2008], as indicated by generally high abundances of terrestrial components, including plant remains and abundant river-transported pollen and spores and terrestrial biomarkers [e.g., *Sluijs et al.*, 2008b]. The section lacks biogenic carbonate suitable for carbon isotope stratigraphy. However, both the PETM and ETM2 have been identified based on biostratigraphy and prominent CIEs in various organic components [*Pagani et al.*, 2006b]. Across the PETM, a large magnitude CIE of  $\sim 6\%$  appears in bulk organic carbon isotope records (Figure 1) [*Sluijs et al.*, 2006] and angiosperm-specific biomarkers yield a CIE of  $\sim 7\%$  [*Schouten et al.*, 2007]. However, the CIE is muted in other phases at this location, being 4.5%–5% in leaf wax n-alkanes [*Pagani et al.*, 2006b], and about 3% in gymnosperm specific biomarkers [*Schouten et al.*, 2007]. Clearly, various records at this site are affected by changes in the composition of the organic substrate (equation (1)).

[27] Records of  $\delta^{13}\text{C}_{\text{TOC}}$ , BIT and palynomorphs have been generated on 123 samples at Hole 302-4A that span the latest Paleocene and earliest Eocene (Figure 3) [*Sluijs et al.*, 2008b]. The  $\delta^{13}\text{C}_{\text{TOC}}$  records mark the negative CIEs associated with the PETM and ETM2 as well as a general



**Figure 4.** X-Y plot between  $\delta^{13}\text{C}_{\text{TOC}}$  (detrended for the long-term exogenic trend; see section 4.2) and (a) BIT index and (b) percentage terrestrial palynomorphs (%TP) at IODP Site 4A, Lomonosov Ridge, Arctic Ocean. Black data points represent samples from the PETM or ETM2. Correlations are calculated based on the samples from outside of these hyperthermals (Background), which are the red data points. Data are from *Sluijs et al.* [2008b].

decrease across the entire interval. These trends are generally mimicked by the BIT index and the percentage terrestrial palynomorphs (%TP) records, which show that the contribution of terrestrial organic matter varies significantly across the hyperthermals, and also over the long-term late Paleocene to early Eocene. This enables us to assess the relation between  $\delta^{13}\text{C}_{\text{TOC}}$  and organic matter origin. Moreover, this relation can be used to calculate the  $\delta^{13}\text{C}$  of the marine and terrestrial organic matter end-members. Ultimately, we use this result to correct  $\delta^{13}\text{C}_{\text{TOC}}$  records of the hyperthermals for the effect of changing contribution of marine and terrestrial organic carbon.

[28] To quantify the relation between organic matter origin and  $\delta^{13}\text{C}_{\text{TOC}}$ , exogenic trends must be excluded (equation (3)). Bulk carbonate, as well as surface, thermocline and deep ocean foraminifer  $\delta^{13}\text{C}$  records show a gradual decrease by  $\sim 2\%$  in several ocean basins during the late Paleocene to early Eocene (59–51 Ma) [Shackleton and Hall, 1984; Zachos et al., 2001; Hilting et al., 2008]. Within this trend, the interval from just before the PETM to just after ETM2 ( $\sim 56$ –54 Ma), yields a  $\sim 1\%$  negative shift (Figure 1). Because the same trend is seen in surface, intermediate and deep ocean records, we consider this value to be close to the global exogenic  $\delta^{13}\text{C}$  trend. To correct for this effect, we detrend the  $\delta^{13}\text{C}_{\text{TOC}}$  data ( $\delta^{13}\text{C}_{\text{DETR-TOC}}$ ) using the available age model [Sluijs et al., 2008b], using uppermost Paleocene values as the anchor point (Figure 1). Subsequently, we apply linear regression analyses to quantify the relation between  $\delta^{13}\text{C}_{\text{TOC}}$  and two proxies for the relative amount of terrestrial organic matter in uppermost Paleocene–lower Eocene sediments, BIT index and percent terrestrial palynomorphs of the total palynomorphs sum  $>15 \mu\text{m}$  (%TP).

### 4.3. Results and Discussion

[29] The collective data at Hole 302-4A show some important relationships. For samples “outside” the hyperthermal intervals, a strong linear relationship ( $R^2 = 0.91$ ) exists between the  $\delta^{13}\text{C}_{\text{TOC}}$  and the BIT index (Figure 4). This implies that varying proportions of terrestrial and marine organic matter impact the  $\delta^{13}\text{C}_{\text{TOC}}$  record throughout the studied interval.

[30] The correlation between  $\delta^{13}\text{C}_{\text{TOC}}$  and the percentage of terrestrial palynomorphs (%TP) is less strong ( $R^2 = 0.48$ ). This could mean that taphonomic processes, particularly transport from the continent into the marine basin, have blurred the correlation between  $\delta^{13}\text{C}_{\text{TOC}}$  and %TP. Indeed, bottom water energies across the late Paleocene–early Eocene interval at the ACEX drill site fluctuated considerably [Martinez et al., 2009; März et al., 2010], which might have differently affected BIT and %TP. In addition, transport of freshwater from the hinterland into the marine system might have (seasonally) increased due to changing precipitation patterns [Pagani et al., 2006b], which likely affected taphonomy of the various organic components differently.

[31] Selective preservation probably does not explain the marked differences in the organic biomarker and palynomorph assemblages [Sluijs et al., 2006]. First, the preservation of organic matter is also excellent outside the hyperthermals due to consistently low oxygen concentrations on the seafloor throughout the late Paleocene to early Eocene [Stein et al., 2006; Sluijs et al., 2008b]. Second, BIT and %TP compare the relative abundance of structurally similar organic components that are equally susceptible to oxidation. We tested for a relation between  $\delta^{13}\text{C}_{\text{TOC}}$  and %TOC for the same samples to

**Table 1.** Calculated Marine and Terrestrial Organic Matter  $\delta^{13}\text{C}$  End-Members and the Calculated Magnitudes of the CIEs Across the PETM, ETM2 and H2 in Marine Organic Matter

	Marine $\delta^{13}\text{C}$ End-Member	Terrestrial $\delta^{13}\text{C}$ End-Member	$\delta^{13}\text{C}_{\text{TOC}}$ Dependence of Terrestrial Organic Matter	CIE PETM	CIE ETM2	CIE ?H2?
Percentage terrestrial palynomorph correction	-27.30	-22.89	0.044‰/%TP	-3.86	-4.55	-0.93
BIT index correction	-27.35	-23.43	3.922‰/BIT-unit	-3.49	-2.60	-0.49
TOC				-5.87	-3.38	-1.51

further investigate a potential impact of preservation but we found no significant relationship ( $R^2 < 0.1$ ).

#### 4.3.1. The $\delta^{13}\text{C}$ of Terrestrial Organic Matter ( $\delta^{13}\text{C}_{\text{TER}}$ )

[32] The empirical linear relationships between  $\delta^{13}\text{C}_{\text{DETR-TOC}}$  and BIT or %TP (Figure 4) are described as follows:

$$\delta^{13}\text{C}_{\text{DETR-TOC}} = (\text{BIT} - 6.97)/0.26 \quad (5)$$

$$\delta^{13}\text{C}_{\text{DETR-TOC}} = (\%TP - 618.88)/22.67 \quad (6)$$

In these equations, the pure terrestrial end-member has BIT = 1 and %TP = 100. This implies that bulk terrestrial organic carbon has a  $\delta^{13}\text{C}$  of -23.4‰ according to the BIT equation, and -22.9‰ according to the %TP equation (Table 1).

[33] A compilation of published  $\delta^{13}\text{C}_{\text{TOC}}$  data (Figure 5) allows for comparison on an interregional scale. The  $\delta^{13}\text{C}_{\text{TOC}}$  in terrestrial early Paleogene sequences (per definition  $\delta^{13}\text{C}_{\text{TER}}$ ) from multiple continental locations exhibit average values between -23‰ and -25‰ [Collinson *et al.*, 2003; Carvajal-Ortiz *et al.*, 2009; Domingo *et al.*, 2009]. The calculated Arctic terrestrial end-member value is relatively high, but reasonably close to time-equivalent terrestrial deposits elsewhere, despite significant differences in vegetation, sedimentary conditions and preservation.

#### 4.3.2. The $\delta^{13}\text{C}$ of Marine Organic Matter ( $\delta^{13}\text{C}_{\text{MOM}}$ )

[34] Equations (5) and (6) also define a marine end-member, when BIT and %TP are set to zero. For samples exclusive of the hyperthermals,  $\delta^{13}\text{C}_{\text{MOM}}$  is approximately -27.3‰ using either the BIT or %TP equation (Table 1). This value is consistent with other  $\delta^{13}\text{C}$  measurements of Paleocene–Eocene marine organic carbon [Hayes *et al.*, 1999]. Early Paleogene  $\delta^{13}\text{C}_{\text{MOM}}$  was approximately 7‰ lower than Holocene marine organic matter. This was the case despite higher sea surface temperatures in the Arctic Ocean [Sluijs *et al.*, 2006] and elsewhere [Zachos *et al.*, 2008], which should increase  $\delta^{13}\text{C}_{\text{MOM}}$  values relative to present day due to temperature-dependent thermodynamic isotopic fractionation [e.g., Gruber *et al.*, 1999]. However, an early Paleogene  $\delta^{13}\text{C}_{\text{MOM}}$  of -27.3‰ is consistent with significantly higher past  $p\text{CO}_2$ , which, as noted previously, should result in increased  $^{13}\text{C}$  discrimination during carbon fixation [Freeman and Hayes, 1992].

#### 4.3.3. Calculating $\delta^{13}\text{C}_{\text{MOM}}$ From $\delta^{13}\text{C}_{\text{TOC}}$

[35] Changes in substrate composition are a major potential cause for differences in  $\delta^{13}\text{C}$  responses during hyperthermals (equation (1)). The correlations between  $\delta^{13}\text{C}_{\text{DETR-TOC}}$  and terrestrial components (Figure 4; equations (5) and (6)) allow corrections of each  $\delta^{13}\text{C}_{\text{TOC}}$  value at Hole 302-4A, including

those within the hyperthermals. These corrections account for the influence of different proportions of marine and terrestrial organic carbon upon  $\delta^{13}\text{C}_{\text{TOC}}$ , and can be expressed as “dependences” using BIT or %TP (Table 1):

$$\begin{aligned} \text{Dependence (BIT)} &= ((\delta^{13}\text{C}_{\text{TER}}) - (\delta^{13}\text{C}_{\text{MOM}}))/1 \\ &= (-23.42 + 27.35)/1 \\ &= 3.922\%/ \text{BIT unit} \end{aligned} \quad (7)$$

$$\begin{aligned} \text{Dependence (\%TP)} &= ((\delta^{13}\text{C}_{\text{TER}}) - (\delta^{13}\text{C}_{\text{MOM}}))/100 \\ &= (-22.89 + 27.30)/100 \\ &= 0.044\%/ \text{\%TP} \end{aligned} \quad (8)$$

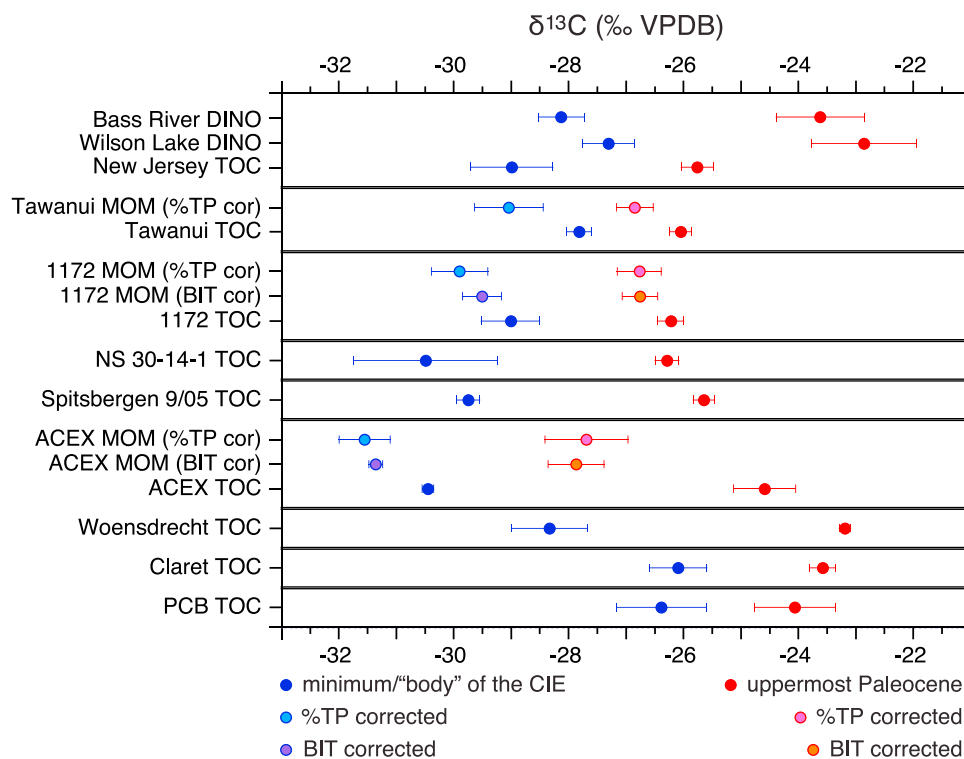
Following equations (5) and (6), the terrestrial organic matter contributions to  $\delta^{13}\text{C}_{\text{TOC}}$  of each sample can now be “removed,” leading to equations to calculate  $\delta^{13}\text{C}_{\text{MOM}}$ :

$$\begin{aligned} \delta^{13}\text{C}_{\text{MOM}} &= \delta^{13}\text{C}_{\text{TOC}} - \text{Dependence (BIT)} \cdot \text{BIT} \\ &= \delta^{13}\text{C}_{\text{TOC}} - 3.922 \cdot \text{BIT} \end{aligned} \quad (9)$$

$$\begin{aligned} \delta^{13}\text{C}_{\text{MOM}} &= \delta^{13}\text{C}_{\text{TOC}} - \text{Dependence (\%TP)} \cdot \%TP \\ &= \delta^{13}\text{C}_{\text{TOC}} - 0.044 \cdot \%TP \end{aligned} \quad (10)$$

[36] A long-term 4‰ decline in  $\delta^{13}\text{C}_{\text{TOC}}$  from approximately -24‰ to -28‰ occurred at Hole 302-4A between the upper Paleocene (circa 56 Ma) and the lower Eocene (circa 53 Ma; Figure 3). The magnitude of this shift is reduced to ~2‰ in calculated  $\delta^{13}\text{C}_{\text{MOM}}$  curves (Figure 3). This implies that the long-term (>3 Myr) decrease in the contribution of terrestrial organic matter to the depositional location, has affected the  $\delta^{13}\text{C}_{\text{TOC}}$  signal. As discussed above, another ~1‰ of the bulk  $\delta^{13}\text{C}_{\text{TOC}}$  signal can be explained by a change in the exogenic carbon cycle; such a drop has been observed in multiple marine calcite  $\delta^{13}\text{C}$  records (Figure 1) [Shackleton and Hall, 1984; Zachos *et al.*, 2001; Hilting *et al.*, 2008]. The residual ~1‰ shift in the long-term  $\delta^{13}\text{C}_{\text{MOM}}$  curve, from approximately -27‰ to -28‰, suggests a decrease in  $\delta^{13}\text{C}_{\text{MOM}}$  at this location, independent of changes in basic composition or the  $\delta^{13}\text{C}$  of the global exogenic carbon cycle. One possibility would be a change in the  $\delta^{13}\text{C}$  of local DIC pool relative to that of the exogenic carbon cycle (equation (3)). The BIT index and %TP decrease significantly over the long-term, consistent with a reduced supply of terrestrial organic carbon. One explanation for this pattern is greater distance to shore [Sluijs *et al.*, 2009], because Lomonosov Ridge was rifting away from the Eurasian shelf during the early Paleogene [O’Regan *et al.*, 2008]. However, given the relationship





**Figure 5.** Compilation of published organic carbon  $\delta^{13}\text{C}$  data across a virtual transect of outer shelf (top) to terrestrial (bottom) sites. Data points reflect averaged (with standard deviation error) upper Paleocene values in red, pink, and yellow and averaged early PETM values in blues and purple. Dark blue and red are  $\delta^{13}\text{C}_{\text{TOC}}$  values, and pink and orange reflect  $\delta^{13}\text{C}_{\text{MOM}}$  values as calculated using %TP and BIT index, respectively. Shown are dinoflagellate cyst (DINO)  $\delta^{13}\text{C}$  data [Sluijs *et al.*, 2007b] and  $\delta^{13}\text{C}_{\text{TOC}}$  data from the New Jersey Shelf [Kopp *et al.*, 2009]; Tawanui, New Zealand [Kaiho *et al.*, 1996]; ODP Site 1172, East Tasman Plateau [Sluijs *et al.*, 2011]; North Sea Site 30/14-1 [Sluijs *et al.*, 2007b]; Spitsbergen Core 9/05 [Cui *et al.*, 2011]; IODP Site 4A (Arctic Coring Expedition, ACEX) [Sluijs *et al.*, 2006]; Woensdrecht, Netherlands [Sluijs *et al.*, 2008a]; Claret, Spain [Domingo *et al.*, 2009]; and the Polecat Bench (PCB) Section in the Bighorn Basin, Wyoming [Magioncalda *et al.*, 2004].

between  $\delta^{13}\text{C}$  of DIC and coastal proximity [Spiker and Schemel, 1979; Chanton and Lewis, 1999], this effect should have increased Arctic  $\delta^{13}\text{C}_{\text{MOM}}$ , opposite to the record (Figure 3). A more satisfactory explanation is a change in the fractionation between marine MOM and the local DIC pool (equation (2)). In particular, there was a significant increase in  $p\text{CO}_2$  between 56 Ma and 53 Ma. This would be consistent with a concomitant long-term drop in the depth of the calcite compensation depth over the same time interval [Hancock *et al.*, 2007; Leon-Rodriguez and Dickens, 2010].

[37] As with the long-term trends, the  $\delta^{13}\text{C}_{\text{MOM}}$  and  $\delta^{13}\text{C}_{\text{TOC}}$  records display significant temporal differences relative to each other across the hyperthermals (Figure 3). The  $\delta^{13}\text{C}_{\text{MOM}}$  decreased from  $-27.5\text{‰}$  to  $-28\text{‰}$  during the uppermost Paleocene to  $-31\text{‰}$  to  $-31.5\text{‰}$  during the start of the PETM, using either the %TP or BIT correction (Table 1). The magnitude of the CIE is therefore  $-3.5\text{‰}$  to  $-4\text{‰}$  in marine organic carbon, compared to nearly  $-6\text{‰}$  in TOC. The simplest explanation is that the proportion of marine organic carbon increased on Lomonosov Ridge during the event, as expected for a rise in sea level and as recorded by drops in BIT and %TP values, exaggerating the CIE in  $\delta^{13}\text{C}_{\text{TOC}}$ .

[38] Across the onset of ETM2, the  $\delta^{13}\text{C}_{\text{MOM}}$ , as calculated using BIT, decreased from approximately  $-28.2\text{‰}$  to

$-30.8\text{‰}$ , implying a CIE of  $-2.6\text{‰}$  (Figure 3). By contrast, the CIE in  $\delta^{13}\text{C}_{\text{TOC}}$  is approximately  $-3.4\text{‰}$ . Again, ETM2 corresponds to a decrease in BIT, and the CIE in  $\delta^{13}\text{C}_{\text{MOM}}$  is probably smaller than in  $\delta^{13}\text{C}_{\text{TOC}}$  because of less terrestrial organic matter. Interestingly, however, the excursion in %TP-corrected  $\delta^{13}\text{C}_{\text{MOM}}$  is extremely large ( $-4.5\text{‰}$ ), because of an increase in the relative abundance of terrestrial palynomorphs (Figure 3). The discrepancy between BIT and %TP may reflect differences in the transport of soil biomarkers and pollen into the basin (see section 4.1). In addition, the  $R^2$  value between  $\delta^{13}\text{C}_{\text{TOC}}$  and %TP is only 0.5 implying a much larger uncertainty in the corrected magnitude of the CIE than using BIT. Because of the much higher  $R^2$ , we consider the BIT-corrected estimates of  $\delta^{13}\text{C}_{\text{MOM}}$  to be a more reliable proxy for terrestrial organic matter input than the %TP correction.

[39] The H2 event occurred  $\sim 100$  ka after ETM2 [Cramer *et al.*, 2003; Lourens *et al.*, 2005] and represents a hyperthermal with a relatively small negative CIE [Stap *et al.*, 2010]. Based on a  $\sim 1.5\text{‰}$  negative CIE in  $\delta^{13}\text{C}_{\text{TOC}}$ , the H2 event appears to occur in Hole 302-4A approximately 80 cm above the onset of ETM2 [Sluijs *et al.*, 2009] (Figure 3). However, marine biomarkers of primary producers, such as phytane, highly branched isoprenoid (HBI) alkenes from specific diatom genera and several hopanoids from

cyanobacteria do not show a negative CIE across H2 in these sediments [Schoon *et al.*, 2011]. The H2 CIE was potentially masked because of an increase in primary production [Schoon *et al.*, 2011], which would cause a local increase in  $\delta^{13}\text{C}_{\text{DIC}}$  and hence  $\delta^{13}\text{C}_{\text{MOM}}$  (equation (3)). Alternatively, the CIE as recorded in  $\delta^{13}\text{C}_{\text{TOC}}$ , does not reflect H2 at all but rather a change in the relative contributions of various sources of organic matter (equation (1)) [Schoon *et al.*, 2011]. The  $\delta^{13}\text{C}_{\text{MOM}}$  curves, however, show excursions of  $-0.5\text{‰}$  and  $-0.9\text{‰}$  following the BIT and %TP corrections, respectively. This CIE could reflect H2 and is, in fact, close to the reconstructed magnitude of the excursion in the deep ocean as recorded in benthic foraminifera ( $-0.8\text{‰}$  [Stap *et al.*, 2010]).

[40] How do the above estimates of the magnitude of the CIEs of the PETM and ETM2 in marine organic matter compare to estimates from the largest reservoir in the exogenic carbon pool, the deep sea? Proxy carriers from deep sea benthic foraminifera typically record a CIE of 2‰ to 3‰ for the PETM [McInerney and Wing, 2011], although one record shows a relatively large 3.5‰ CIE [McCarren *et al.*, 2009]. The latter record is from a relatively shallow deep ocean section and may stratigraphically complete because it was less affected by carbonate dissolution. The 3.5‰–4‰ CIE we find in  $\delta^{13}\text{C}_{\text{MOM}}$  is similar to or slightly larger than that recorded in deep sea benthic foraminifera. The CIE as recorded in single species deep ocean benthic foraminifera is approximately  $-1.4\text{‰}$  across the onset of ETM2 [Stap *et al.*, 2010]. Hence, similar to the PETM, the CIE as reflected in Arctic  $\delta^{13}\text{C}_{\text{MOM}}$  is exaggerated by  $\sim 1\text{‰}$  using the BIT correction, and  $\sim 3\text{‰}$  using the %TP correction.

[41] Because the patterns of climate change during the PETM and ETM2 in the Arctic [Sluijs *et al.*, 2009], and therefore the potential forcing factors for offsets between  $\delta^{13}\text{C}_{\text{MOM}}$  excursions and global exogenic trends, are similar, the potential explanations for the large CIE in  $\delta^{13}\text{C}_{\text{MOM}}$  across ETM2 are the same. Even ignoring global mass balance considerations (equation (4)), there are several issues. First, our corrections only partly address changes in substrate composition (equation (1)). Changes in marine biota, which evidently occurred during both the PETM and ETM2 [Sluijs *et al.*, 2008b, 2009], may have changed the relative proportions of different marine organic carbon components that contributed to total MOM. In any case, three effects should have accentuated the CIEs as recorded in Arctic marine organic matter relative to the CIEs of the entire exogenic carbon pool: (1) A rise in  $p\text{CO}_2$  would have increased carbon isotope fractionation by marine primary producers (equation (2)). Moreover, an increase in organic matter input (2) and river water supply (3) to the Arctic Ocean would have contributed to decreasing  $\delta^{13}\text{C}_{\text{DIC}}$  (equation (3)) [Spiker and Schemel, 1979; Chanton and Lewis, 1999; Fry, 2002]. This implies that the  $-3.5\text{‰}$  to  $-4\text{‰}$  shift in  $\delta^{13}\text{C}_{\text{MOM}}$  is likely exaggerated relative to the magnitude of the CIE of the global exogenic carbon pool.

#### 4.3.4. Comparison to Other $\delta^{13}\text{C}_{\text{TOC}}$ Records

[42] The  $\delta^{13}\text{C}_{\text{TOC}}$  records at Hole 302-4A appear impacted by significant mixing of terrestrial and marine organic carbon with different  $\delta^{13}\text{C}$ . Presumably, such mixing would affect other  $\delta^{13}\text{C}_{\text{TOC}}$  records in marine sediments emplaced

on early Paleogene continental margins, and this seems to be the case (Figure 5). Similar to Hole 302-4A, records from locations deposited close to the paleoshoreline, such as at Woensdrecht (North Sea) [Sluijs *et al.*, 2008a] have relatively high  $\delta^{13}\text{C}_{\text{TOC}}$  values (approximately  $-23\text{‰}$  outside the hyperthermals) for late Paleocene–early Eocene sediment. Indeed,  $\delta^{13}\text{C}_{\text{TOC}}$  values at these locations are close to those of  $\delta^{13}\text{C}_{\text{TER}}$  in continental sections at Claret (Spain,  $-23\text{‰}$  to  $-24\text{‰}$  [Domingo *et al.*, 2009]) and at Polecat Bench (Wyoming,  $-23\text{‰}$  to  $-25\text{‰}$  [Magioncalda *et al.*, 2004]). By contrast, sediment sections that accumulated further offshore during this time, such as at Site 30–14/1 (central North Sea [Sluijs *et al.*, 2007b]) or at Ocean Drilling Program Site 1172 (East Tasman Plateau [Sluijs *et al.*, 2011]), have intermediate  $\delta^{13}\text{C}_{\text{TOC}}$  values (approximately  $-26\text{‰}$ , Figure 5) suggestive of greater proportions of marine organic carbon.

[43] Several marine sequences with  $\delta^{13}\text{C}_{\text{TOC}}$  records have additional data that can be used to address marine and terrestrial contributions, as we have outlined for Hole 302-4A. At Site 1172, BIT and palynomorph assemblages have been determined for upper Paleocene and lower Eocene sediment; these records suggest significant sedimentary contributions from both terrestrial and marine sources [Sluijs *et al.*, 2011]. The evolution of  $\delta^{13}\text{C}_{\text{MOM}}$  can be assessed using the  $\delta^{13}\text{C}_{\text{TOC}}$  record, the BIT index and equation (9), which describes the relation between these variables at Hole 302-4A in the Arctic Ocean. Such correction lowers upper Paleocene  $\delta^{13}\text{C}_{\text{MOM}}$  to  $-26.7\text{‰}$ , very close to the Arctic value and the estimates of Hayes *et al.* [1999] (Figure 5).

[44] Unlike at Hole 302-4A or Site 1172,  $\delta^{13}\text{C}_{\text{TOC}}$  values at Tawanui (New Zealand) are relatively high ( $-26.1\text{‰}$ ) in upper Paleocene sediment, and show a small  $\sim 1.7\text{‰}$  CIE across the PETM [Kaiho *et al.*, 1996] (Figure 5). Also different: the PETM is marked by a significant increase in %TP, interpreted as reflecting greater riverine discharge [Crouch *et al.*, 2003]. Correction of the  $\delta^{13}\text{C}_{\text{TOC}}$  record for %TP (equation (8) from Hole 4A) results in upper Paleocene  $\delta^{13}\text{C}_{\text{MOM}}$  values of  $-26.9\text{‰}$ , again close to that estimated for Hole 4A. However, such a correction means that the CIE magnitude across the PETM is greater in  $\delta^{13}\text{C}_{\text{MOM}}$  ( $-2.1\text{‰}$ ). Thus, opposite to Hole 4A and Site 1172, an increase in terrestrial material dampened the magnitude of the CIE recorded by bulk organic carbon.

[45] The similarity in estimated  $\delta^{13}\text{C}_{\text{MOM}}$  values between early Paleogene records (pink and orange points in Figure 5) [Hayes *et al.*, 1999] is remarkable considering the variability in  $\delta^{13}\text{C}_{\text{MOM}}$  exhibited in the modern ocean [Goericke and Fry, 1994; Gruber *et al.*, 1999]. For the late Paleocene, the Arctic Ocean  $\delta^{13}\text{C}_{\text{MOM}}$  value of  $-27.3\text{‰}$  is only slightly lower than the  $\delta^{13}\text{C}_{\text{MOM}}$  records at other sites deposited at lower latitudes (Figure 5). Marine organic matter formed in modern oceans at high latitudes is generally depleted in  $^{13}\text{C}$  ( $\delta^{13}\text{C}_{\text{MOM}}$  = between  $-19\text{‰}$  and  $-26\text{‰}$ ) relative to that formed at lower latitudes ( $\delta^{13}\text{C}_{\text{MOM}}$  = between  $-18\text{‰}$  and  $-22\text{‰}$ ) [Goericke and Fry, 1994]. This is generally explained by higher concentrations of dissolved  $\text{CO}_2$  in cold polar waters and large seasonal shifts in nutrient availability, which together lead to higher fractionation [Rau *et al.*, 1989; Freeman and Hayes, 1992; Freeman, 2001]. The intriguing similarity of early Paleogene  $^{13}\text{C}_{\text{MOM}}$  values across latitudes may reflect past ocean conditions, specifically three key differences: (1) the meridional temperature gradient was almost assuredly much smaller [e.g., Bijl *et al.*, 2009; Huber and Caballero, 2011], (2) Arctic Ocean

productivity was likely higher [Knies *et al.*, 2008], and (3) ocean DIC concentrations were probably much higher [Panchuk *et al.*, 2008; Zeebe *et al.*, 2009]. All three factors would reduce global  $\delta^{13}\text{C}_{\text{MOM}}$  variability.

[46] Several substrates of organic matter were analyzed for  $\delta^{13}\text{C}$  across the upper Paleocene to lower Eocene deposits on the New Jersey Shelf. Uppermost Paleocene  $\delta^{13}\text{C}_{\text{TOC}}$  from a compilation of sites averages  $-25.8\text{‰}$  (Figure 5) [Kopp *et al.*, 2009], likely representing a mixture between dominant marine and some terrestrial organic matter. Surprisingly, two  $\delta^{13}\text{C}$  records of marine organic microfossils, dinoflagellate cysts from the New Jersey Shelf [Sluijs *et al.*, 2007b] show very high upper Paleocene values, close to the terrestrial end-member. Dinoflagellates often occur in intense blooms that may deplete the DIC pool and raise pH [Hansen, 2002] to the extent that seawater DIC becomes very rich in  $^{13}\text{C}$ . Alternatively, many dinoflagellates take up both  $\text{HCO}_3^-$  and  $\text{CO}_2$  for photosynthesis and several taxa dominantly acquire  $\text{HCO}_3^-$  [Rost *et al.*, 2006]. The  $\delta^{13}\text{C}$  of  $\text{HCO}_3^-$  is about 9‰ higher than that of dissolved  $\text{CO}_2$  [Mook *et al.*, 1974; Zeebe and Wolf-Gladrow, 2001]. These may be important mechanisms leading to high dinocyst  $\delta^{13}\text{C}$  values.

## 5. Broader Implications

[47] In principle, and for any substrate through any time interval, interpretations of  $\delta^{13}\text{C}$  records in regards to global carbon cycling are subject to three parameters: (1) the abundance of constituent end-members, (2) carbon isotope fractionation relative to the local source of carbon, and (3) the offset in carbon isotope composition between the local carbon source and the exogenic carbon cycle (equations (1)–(3)). Under steady state conditions, individual records may very well provide quantitatively precise information on exogenic carbon cycling. However, when environmental conditions change in the time domain, and these changes impact relationships between “carbon isotope recorders” and the exogenic carbon cycle, interpretations become complicated and intriguing. This particularly holds for episodes of extreme environmental change and major perturbations in global carbon cycling, such as the PETM and other early Paleogene hyperthermals. Multiple factors should have impacted  $\delta^{13}\text{C}$  records differently; this applies to records constructed using different substrates, those constructed at different locations, or both.

[48] For example, Cui *et al.* [2011] measured a  $-4.2\text{‰}$  CIE in bulk TOC across the PETM in a marginal marine sequence in Spitsbergen, and suggested that this change represents that within the entire exogenic carbon cycle. First, it remains difficult to support this inference from a mass balance perspective (equation (4)), as no  $\delta^{13}\text{C}$  record from a deep ocean substrate, where the lion’s share of carbon lies, shows such a shift [McInerney and Wing, 2011]. Second, and more directly, the inference hinges on the notion that the composition of organic matter did not change within the PETM (equation (1)) [Cui *et al.*, 2011]. In fact, the sedimentary organic matter C/N ratios at the studied location vary between 9 and 15. Moreover, the relative abundance of terrestrial and marine palynomorphs at a nearby section [Harding *et al.*, 2011] suggest that the deposition of marine material increased across the PETM at sites on Spitsbergen. Moreover, even if the proportion of

terrestrial and marine organic matter did not change at Spitsbergen during the PETM, vegetation may have changed significantly, so that more angiosperms contributed to the terrestrial fraction [Schouten *et al.*, 2007]. In addition, carbon isotope fractionation relative to the local source of carbon has to be assumed constant (equation (2)). For multiple reasons, the measured  $-4.2\text{‰}$  CIE in  $\delta^{13}\text{C}_{\text{TOC}}$  at Spitsbergen is probably greater than the magnitude of the CIE excursion for the exogenic carbon cycle, as has been inferred above for Hole 302-4A and other locations (Figure 5).

[49] The magnitude of truly global CIEs, such as those related to the PETM and ETM2 relates to the size of the carbon injection as recorded in sedimentary components [Dickens, 2001]. Some authors have suggested that the CIE across the hyperthermals must be very large, because the magnitude of warming is very large [Kurtz *et al.*, 2003; Higgins and Schrag, 2006; Pagani *et al.*, 2006a]. This is true, even if the source of carbon is very depleted in  $^{13}\text{C}$  source, such as methane, requires a large excursion [Dickens *et al.*, 1997]. The basic assumption underlying this logic, however, is that the injection of  $^{13}\text{C}$ -depleted carbon caused all of the warming, while high-resolution records suggest that the onset of warming preceded the CIE [e.g., Thomas *et al.*, 2002; Sluijs *et al.*, 2007b].

[50] Quantification of the magnitudes of CIEs across the PETM and other hyperthermals remains a major challenge at least in terms of the exogenic carbon cycle. Until the generalities of equations (1), (2), (3), and (4) can be constrained in multiple records, the CIEs remain insufficiently constrained. Certainly, however, we argue that smaller CIEs are easier to explain from a mass balance perspective. Moreover, many processes will amplify the magnitude of the CIE during a short-term warming event, certainly in nearshore regions and organic matter substrates.

## 6. Conclusions

[51] Records of  $\delta^{13}\text{C}$  on various carbon-bearing phases in sediment sections deposited during late Paleocene–early Eocene hyperthermals show a very large variation in the magnitude of their CIEs. The variation depends on location and analyzed substrate. Three factors might cause individual carbon isotope records across the same stratigraphic interval to differ in shape and magnitude from variations in the global exogenic carbon cycle: (1) changes in the relative abundance of components with different  $\delta^{13}\text{C}$  within a measured substrate, (2) changes in isotope fractionation through physiological response to ecological change, and (3) changes in the isotope composition of the carbon source that is fixed. All three factors, which we describe in three simple equations, likely influence many early Paleogene  $\delta^{13}\text{C}$  records, especially across the PETM and other hyperthermal events.

[52] We apply these concepts to records of a late Paleocene–early Eocene interval ( $\sim 58$ – $52$  Ma) from Lomonosov Ridge, Arctic Ocean. Linear regression analyses show correlations between  $\delta^{13}\text{C}$  of total organic carbon (TOC), and two proxies for the relative contribution of terrestrial organic components to TOC: BIT index and palynomorphs. The BIT index, a biomarker-based proxy, correlates to  $\delta^{13}\text{C}_{\text{TOC}}$  with  $R^2 = 0.91$ , while the abundance of terrestrial pollen and spores shows a weaker correlation with  $R^2 = 0.48$ . The larger scatter in the %

TP regression is likely due to variations in taphonomy. End-member terrestrial and marine organic matter  $\delta^{13}\text{C}$  values equal approximately  $-23\%$  and  $-27\%$ , respectively, which is consistent with published records.

[53] We use these correlations between BIT, %TP and  $\delta^{13}\text{C}_{\text{TOC}}$  to subtract the terrestrial component from the  $\delta^{13}\text{C}_{\text{TOC}}$  record and subsequently calculate the evolution of Arctic marine organic carbon  $\delta^{13}\text{C}$ . The results show that the magnitude of the CIE in  $\delta^{13}\text{C}_{\text{TOC}}$  across the Paleocene-Eocene thermal maximum (PETM) is exaggerated relative to the magnitude of the CIE in marine organic matter by  $\sim 3\%$  due to increased contributions of terrestrial organic carbon during the event. Collectively, most, if not all, carbon isotope records across the PETM and likely all major climate perturbations are biased through one or more of the above factors. In fact, this carbon cycle recording problem is universal for all carbon cycle – climate perturbations in Earth's history, including Paleozoic carbon isotope excursions, the Permian-Triassic transition, the Triassic-Jurassic boundary, Mesozoic anoxic events, and the Cretaceous-Paleogene boundary. Indeed, it is highly unlikely that any  $\delta^{13}\text{C}$  record shows the true shape and magnitude of the CIE for the global exogenic carbon cycle. This work introduces a way forward, based on three simple equations and empirically based exclusions of sedimentary components, to improve our quantification of global exogenic carbon cycle trends.

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