The Palaeocene–Eocene carbon isotope excursion: constraints from individual shell planktonic foraminifer records

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The Palaeocene–Eocene thermal maximum (PETM) is characterized by a global negative carbon isotope excursion (CIE) and widespread dissolution of seafloor carbonate sediments. The latter feature supports the hypothesis that the PETM and CIE were caused by the rapid release of a large mass (greater than 2000 Gt C) of ^{12}C-enriched carbon. The source of this carbon, however, remains a mystery. Possible sources include volcanically driven thermal combustion of organic-rich sediment, dissociation of seafloor methane hydrates and desiccation and oxidation of soil/sediment organics. A key constraint on the source(s) is the rate at which the carbon was released. Fast rates would be consistent with a catastrophic event, e.g. massive methane hydrate dissociation, whereas slower rates might implicate other processes. The PETM carbon flux is currently constrained by high-resolution marine and terrestrial records of the CIE. In pelagic bulk carbonate records, the onset of the CIE is often expressed as a single- or multiple-step excursion extending over 10^4 years. Individual planktonic shell records, in contrast, always show a single-step CIE, with either pre-excursion or excursion isotope values, but no transition values. Benthic foraminifera records, which are less complete owing to extinction and diminutive assemblages, show a delayed excursion. Here, we compile and evaluate the individual planktonic shell isotope data from several localities. We find that the most expanded records consistently show a bimodal isotope distribution pattern regardless of location, water depth or depositional facies. This suggests one of several possibilities: (i) the isotopic composition of the surface ocean/atmosphere declined in a geologic instant (<500 yr), (ii) that during the onset of the CIE, most shells of mixed-layer planktonic foraminifera were dissolved, or (iii) the abundances or shell production of these species temporarily declined, possibly due to initial pH changes.

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1. Introduction

The Palaeocene–Eocene thermal maximum (PETM) represents the single largest well-documented warming event in Earth's history. The rise in global temperature, more than 5°C, occurred in less than 10 kyr and was sustained for a few tens of thousands of years before gradually abating. With a few exceptions, mainly along Antarctica and in coastal regions, the warming of the sea surface appears to have been relatively uniform from the equator to the pole (e.g. Kennett & Stott 1991; Thomas *et al.* 2002; Zachos *et al.* 2003, 2006; Sluijs *et al.* 2006). This pattern together with the transient nature of the event is consistent with warming driven by greenhouse forcing. In model simulations absent an ice-albedo feedback, for example, greenhouse forcing will typically generate globally uniform warming (Shellito *et al.* 2003). The geochemical evidence for massive carbon release to the atmosphere/ocean during the PETM is also quite strong. The large magnitude of the CIE, its relative abruptness, along with global carbonate dissolution horizons can only be explained by the release of a large mass (much greater than 1000 Gt) of isotopically depleted carbon into the ocean and atmosphere (Dickens *et al.* 1995, 1997).

Despite the overwhelming evidence for massive carbon release during the PETM, a lack of consensus still exists over the source and trigger. Decomposition of seafloor methane hydrates was the first source to be implicated, in large part, owing to the magnitude and apparent abruptness of the CIE (Dickens *et al.* 1995, 1997). One hypothesis suggests long-term gradual warming or deep-ocean circulation changes (Bice & Marotzke 2002) eventually nudged ocean temperatures over a thermal stability threshold for seafloor hydrates, thereby initiating runaway decomposition. Numerical modelling showed that as little as 2000 Gt C from methane hydrates would be sufficient to produce a 3.0‰ negative excursion (Dickens *et al.* 1995, 1997; Dickens 2000). However, this mass of carbon, assuming oxidation to CO_2, might be insufficient to drive and sustain the warming, at least for a period longer than a few thousand years (Zachos *et al.* 2003; Higgins & Schrag 2006). Moreover, the scale of carbonate dissolution would suggest a much larger mass (Zachos *et al.* 2005). Another potential source involves the thermal decomposition of crustal organic matter in the vicinity of the North Atlantic Igneous Province (Svensen *et al.* 2004). This model proposes that intrusion of magma associated with the Iceland plume rapidly generated large quantities of methane and CO_2 that escaped to the ocean/atmosphere via a vast network of fluid/gas seeps between the Greenland and Norwegian margins. The mass of carbon generated by this activity would be limited by the scale of dike intrusion and carbon content of the crust (Higgins & Schrag 2006). Finally, other models invoke widespread oxidation of subaerially exposed marine organic matter in a desiccating epicontinental sea or the widespread oxidation of organic matter (lignites) in soils (Kurtz *et al.* 2003; Higgins & Schrag 2006). Although these sources are posited as the primary cause of the PETM, either could have operated purely in a positive feedback mode as well.

One of the key challenges in identifying the source and trigger is to constrain the rate and magnitude of the CIE. This task is complicated by the fact that all pelagic P–E boundary sections are truncated or condensed as a consequence of ocean acidification and carbonate dissolution. These sections are characterized by distinct clay layers or low carbonate dissolution horizons (Kennett & Stott 1991;

Thomas *et al.* 1999; Zachos *et al.* 2005). Even though most dissolution involved sediment deposited prior to the event (Zeebe & Zachos in press), it is clear that much of the deep sea was undersaturated throughout the onset of the CIE. As a consequence, the pelagic sediment record of the initial phase of the CIE is not likely to have been preserved, at least in the highly undersaturated portions of the ocean that probably included most of the ocean below the thermocline.

It is probable that carbonates deposited in relatively shallow areas of the ocean with high sedimentation rates (i.e. the shelves) may have escaped severe dissolution, thereby preserving the initial phase of the CIE. The Eocene surface ocean, much like the modern, would have been highly oversaturated with respect to $CaCO_3$, in large part owing to the export of organic carbon. Therefore, even though pH and carbonate ion content would have declined in the surface ocean with increased CO_2, those waters should have remained oversaturated. Deeper in the water column, higher saturation levels could only be maintained in regions where the carbonate flux was sufficiently high to suppress the local CCD. To test this, we examine new single-shell isotope data generated for a shelf sequence preserved in a core from Bass River, NJ. Previous work on this core identified the CIE and indicates that the P–E boundary contact is conformable (Cramer *et al.* 1999). The sediments, which are composed predominantly of clay with some carbonate, were deposited on the outer shelf at depths less than several hundred metres. As a consequence, bottom water carbonate ion concentration at this location would have been higher than in the deep ocean during the PETM. Moreover, owing to high sedimentation rates and high clay content, foraminifer preservation is excellent. Comparison of this record with pelagic records characterized by high and low carbonate flux should allow us to assess the impact of dissolution on the pelagic isotope records, in particular, the extent to which the CIE is truncated. If the CIE is indeed geologically rapid, this would strengthen the case for models invoking rapid release of carbon, as might occur with massive decomposition of methane hydrates.

(*a*) *CO_2 flux and ocean acidification*

Model simulations of the time-dependent impacts of current anthropogenic CO_2 emissions on ocean carbonate saturation state provide insight into what might have transpired during the PETM over short and long time-scales. In effect, because the large flux of carbon in these simulations transpires over a brief period (approx. 300 years) relative to the vertical ocean mixing time (approx. 1000 years), the surface ocean pH rapidly drops (Archer *et al.* 1997; Caldeira & Wicket 2003). Eventually, as the CO_2 flux subsides and the ocean mixes, the acidified waters are transferred down into the ocean interior where they are buffered through reactions with seafloor carbonate. For several thousand years, such reactions chemically erode seafloor carbonate until complete buffering is achieved (Archer *et al.* 1997). Carbonate accumulation gradually increases as CO_2 levels begin to decline and saturation levels rise.

This anthropogenic ocean acidification model represents an extreme case for the PETM, one that may have been realized only if the release of carbon occurred all at once or in pulses. If the carbon were released gradually, say over 5–10 kyr, the effects of acidification on the surface ocean would have been less severe.
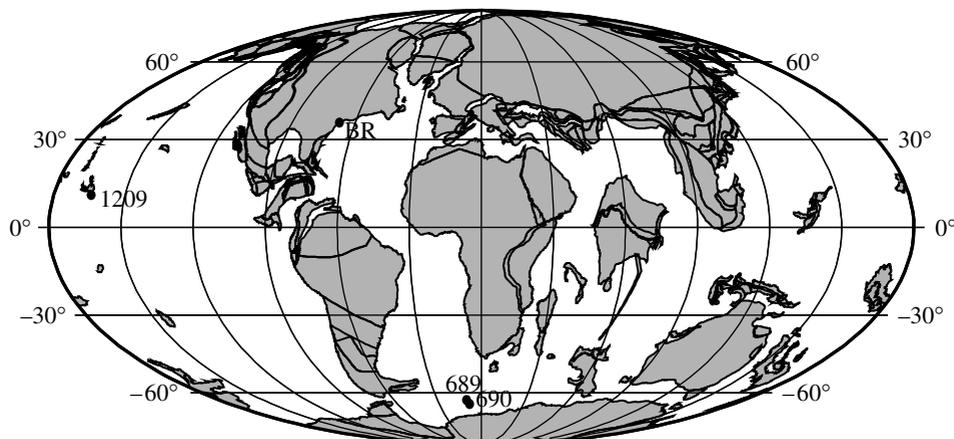
Figure 1. Palaeogeographic reconstruction (55 Ma; from the Ocean Drilling Stratigraphic Network, http://zeus.palaeoz.geomar.de) with locations of ODP Sites 689, 690 and 1209, and the core from Bass River, NJ.

Nevertheless, this model provides insight into how carbon uptake by and redistribution within the ocean might have progressed, as well as the potential impact on calcareous plankton production and preservation. In particular, the pH of the surface ocean should have declined, possibly inhibiting biogenic calcification. The extent of pH change would simply depend on the rate of carbon release, which was probably slower during the PETM. Regardless, the long-term impacts on deep-sea carbonate chemistry would be very similar with the scale of change depending primarily on the mass of carbon released. The main impact would be significant deep-sea carbonate undersaturation and chemical erosion, which would create clay-rich condensed layers over much of the deep sea (Zeebe & Zachos in press). Even in places where carbonate was not completely dissolved, very little of the sinking shell mass would survive dissolution until the carbonate saturation state of the deep sea recovered (figure 1).

(b) CO_2 flux and ocean carbon isotopes

The above anthropogenic emissions scenario also provides insight into how the distribution of carbon isotopes in the ocean might have evolved during the CIE. With the rapid flux scenario, the surface ocean $\delta^{13}C_{DIC}$ rapidly drops, again owing to relatively slow vertical mixing. With a sustained flux of isotopically depleted carbon, the $\delta^{13}C_{DIC}$ of the large deep-sea carbon reservoir eventually begins to drop. As an example, just in the last century, $\delta^{13}C_{DIC}$ of the surface ocean has decreased by 1.4‰ (figure 2), while the deep-sea $\delta^{13}C_{DIC}$ has remained constant (Böhm et al. 2002). Eventually, with continued anthropogenic carbon release and mixing, the deep-sea $\delta^{13}C_{DIC}$ will decline, though more gradually. With the PETM, the pattern and magnitude of change in ocean $\delta^{13}C_{DIC}$ would have similarly depended on the flux and isotopic composition of the carbon source as well as the rate of oceanic mixing. As such, information on the rate and magnitude of $\delta^{13}C$ change in each reservoir is essential for identifying the carbon source.
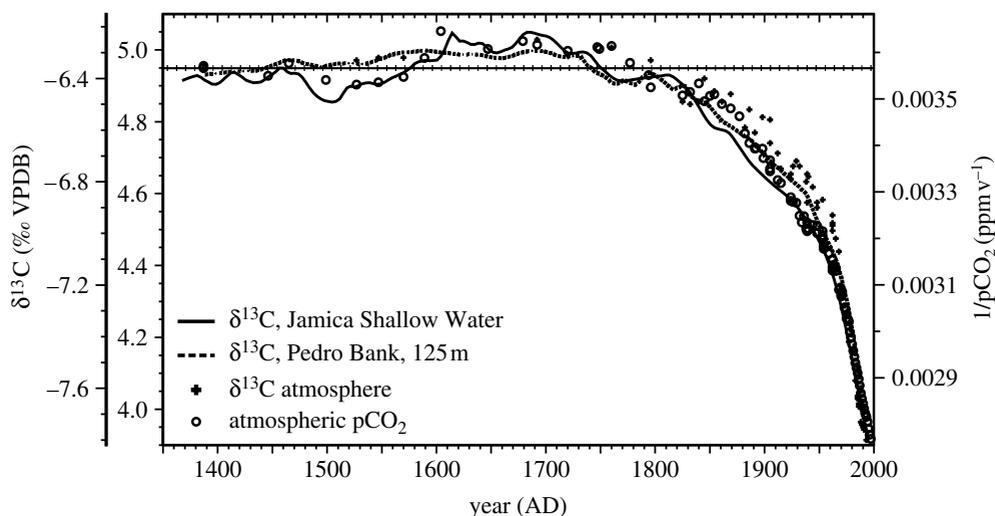
Figure 2. Record of atmospheric pCO_2 between AD 1350 and AD 2000 plotted along with $\delta^{13}C$ of atmospheric CO_2 (from analysis of ice cores) and mixed-layer $\delta^{13}C_{DIC}$ as reconstructed from two Atlantic coralline sponges (Böhm *et al.* 2002).

2. The marine carbon isotope excursion

The magnitude and timing of the marine carbon isotope excursion (CIE) across the Palaeocene–Eocene boundary has been established through the analysis of a variety of sedimentary components including bulk inorganic and organic carbon, organic biomarkers, coccoliths (i.e. fine fraction) and benthic and planktonic foraminifera (e.g. Kennett & Stott 1991; Bralower *et al.* 1995; Kaiho *et al.* 1996; Schmitz *et al.* 1996, 2001; Thomas & Shackleton 1996; Bralower *et al.* 1997; Kelly *et al.* 2005; Sluijs *et al.* 2006). Each of these offers advantages and disadvantages. Ideally, biomarkers or specific species of foraminifera are preferred because the fractionation of isotopes between the dissolved carbon pool and these products is likely to have remained relatively constant with time (within certain limits). High-resolution marine biomarker records, however, have been difficult to construct due to the low organic carbon content of pelagic sediments. Foraminifer stable isotope records, on the other hand, are common. Typically, for both the reasons of analytical and statistical precision, each data point is generated by analysis of multiple shells. A drawback, however, is that the range of variability among individual specimens in each sample interval is lost. This limitation becomes especially acute when investigating periods of rapid environmental change, where slow sedimentation rates combined with bioturbation tend to smooth transitions.

The potential artefacts created by sample smoothing became obvious with one early investigation of the PETM in Pacific ODP Site 865, where a carbon isotope time-series constructed from analyses of a mixed-layer foraminifer species of the genera *Morozovella* and *Acarinina* yielded a CIE smaller than recorded elsewhere (Kelly *et al.* 1996). Bioturbation was suspected and as a test, dozens of shells were collected from several of the boundary samples and analysed individually. The results demonstrated that each sample was in fact, composed of mixtures of pre-excursion and excursion specimens, but no specimens with transitional $\delta^{13}C$
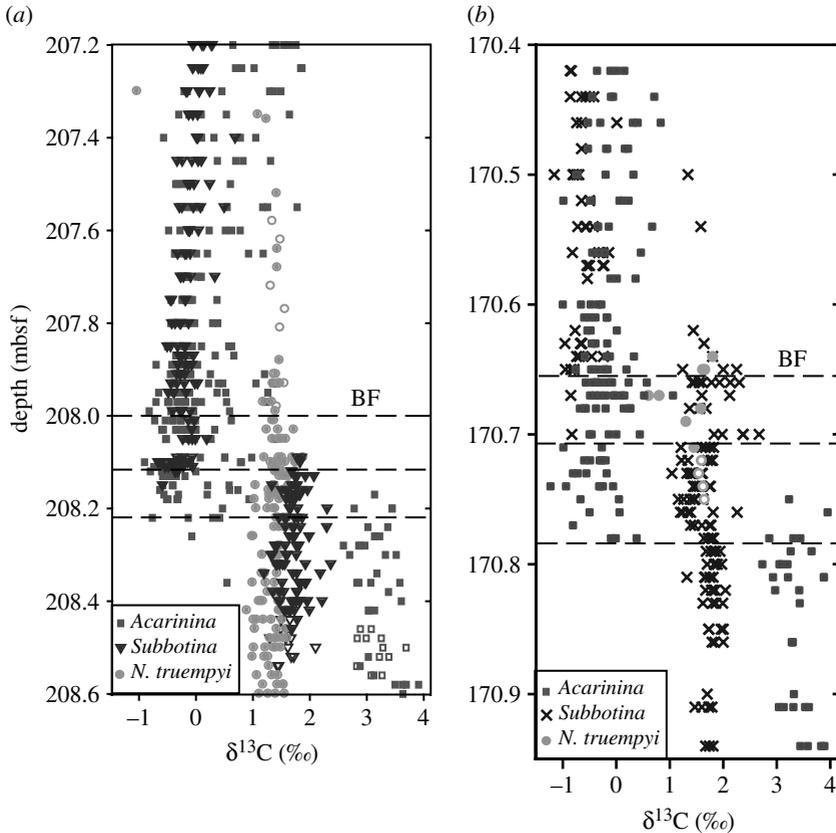
Figure 3. Single-shell foraminifer isotope data for ODP Sites (*a*) 689 (Nielsen *et al.* submitted) and (*b*) 690 (Thomas *et al.* 2002), both located on Maud Rise, South Atlantic. Multiple shell isotope data for *Nuttalides truempyi* are represented by open circles, single shells by filled circles. Sedimentation rates at these sites were in excess of 2.8 cm kyr^{-1}.

values. Even peak excursion samples further up-section contained reworked pre-excursion shells. In addition to resolving the full magnitude of the CIE at this site, this individual shell dataset suggested that the excursion might have been geologically instantaneous, at least in the ocean mixed layer, though potential artefacts were identified as well, including a hiatus. This bimodal pattern, however, was eventually found at several other sites, including ODP Site 690 (figure 3; Thomas *et al.* 2002). As with Site 865, the mixed-layer foraminifera CIE showed only pre-excursion and excursion values indicating that this phenomenon was a global occurrence. Similar patterns have been subsequently identified in the North Pacific, ODP Site 1209 (figure 4; Zachos *et al.* 2003), at shallower location on Maud Rise, ODP Site 689 (figure 3; Nielsen *et al.* submitted) and in a continental shelf section in the Atlantic (figure 5).

(*a*) Top-down propagation of the CIE

In the Maud Rise sites, appearance of the first excursion values in benthics and deeper dwelling planktonic foraminifer, species of *Subbotina*, stratigraphically lags the excursion values of the mixed layer planktonic foraminifera implying a
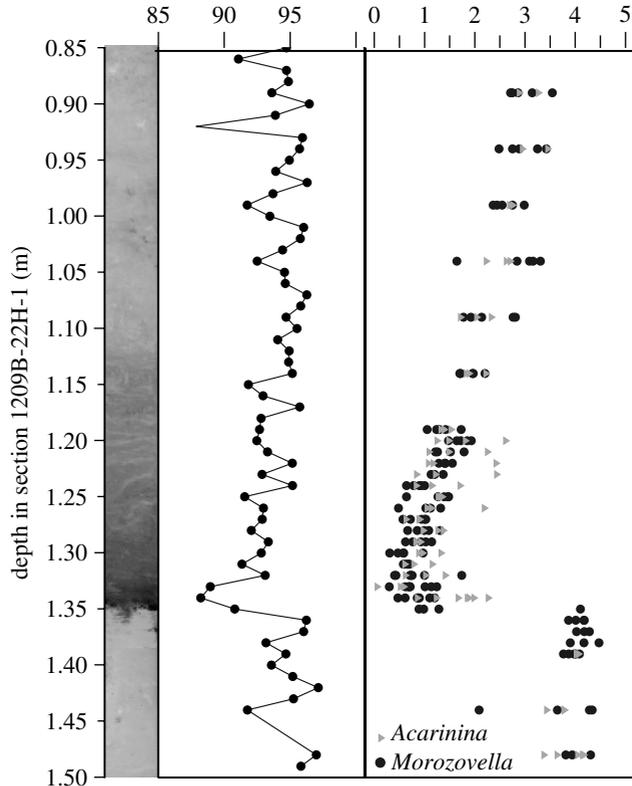
Figure 4. The $\delta^{13}C$ and $\delta^{18}O$ values of individual specimens of *Morozovella velascoensis* (circles) and *Acarinina soldadoensis* (triangles) plotted versus depth in core section for ODP Site 1209 (Zachos *et al.* 2003). Hole 1209B was drilled at a water depth of 2385 m (Bralower *et al.* 2002). The sampled 80 cm interval was recovered at a sub-bottom depth of 195.8–196.60 m. The sediment is calcareous nannofossil ooze. The sharp contrast lies just above the Palaeocene–Eocene boundary (approx. 1.35 m in this section). Also plotted are the weight per cent $CaCO_3$ concentrations.

top-down propagation of the $\delta^{13}C$ signal. While the stratigraphic offset could potentially be explained by a combination of preservation and reworking artefacts, this result has since been reproduced at a nearby shallower Site 689 (Nielsen *et al.* submitted). No such lag between planktics and benthics is observed at Bass River, nor should we expect this at such shallow depths where the added isotopically depleted carbon would be quickly transferred to the base of the water column. Biological pumping and release of respired carbon on the bottom, however, would still maintain the vertical $\delta^{13}C$ gradient.

Collectively, these records imply that the CIE was first recorded in the ocean mixed layer, which would have been in near isotopic equilibrium with the atmosphere. The signal then appears to propagate downward into the thermocline and deep sea. This pattern bears some similarity to the decrease in the $\delta^{13}C$ of carbon in the atmosphere and surface ocean over the last 150 years as recorded in ice cores and sclerosponges (figure 2; Böhm *et al.* 2002). The overall decrease of 1.1‰ in sclerosponges more or less parallels the rise in atmospheric pCO_2 indicating that (i) anthropogenic carbon (approx. −22‰)
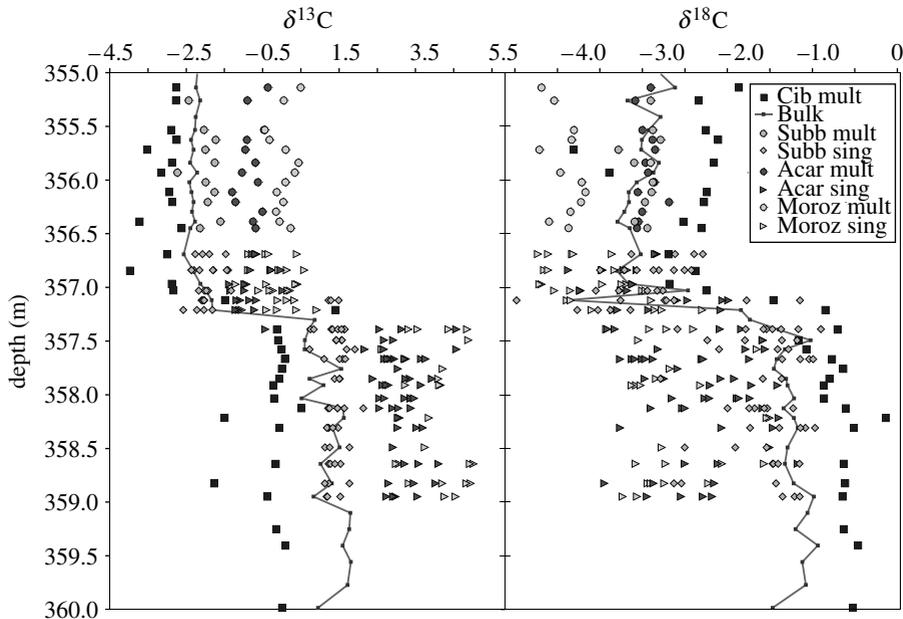
Figure 5. Single and multiple shell foraminifer isotope data for Bass River, NJ. Analyses were carried out on specimens of *Morozovella*, *Acarinina* and *Subbotina* from the greater than 300 μm size fraction (John *et al.* submitted). All of the benthic data are based on analysis of multiple shells of *Cibicidoides* spp.

is the primary source and (ii) it is rapidly being absorbed by the ocean-mixed layer. The magnitude of the decrease also demonstrates that this carbon is largely accumulating in the surface ocean/atmosphere. Because the rate of release is rapid relative to the vertical mixing time of the ocean, the invasion of anthropogenic CO_2 deeper into the ocean has been limited largely to regions of vertical advection such as the North Atlantic (Feely *et al.* 2004; Sabine *et al.* 2004). On such brief time-scales, the deep sea is not in equilibrium with the surface ocean/atmosphere and may remain so for at least one mixing cycle.

With the PETM, a similar situation could have arisen if the rate of carbon release were relatively rapid when compared with the vertical mixing time of the ocean. The abrupt step in mixed-layer foraminifera $\delta^{13}C$ values and top-down propagation of the CIE in the isotope records might be indicative of such phenomena. Still, several features of the single-shell record are difficult to reconcile with a top-down propagation scenario. The first is the apparent length of delay for the full CIE to be expressed in the deep-sea reservoir. The delay recorded at Site 690 is estimated to be of the order of 5–10 kyr (Thomas *et al.* 2002), or longer if sedimentation rates slowed (Farley & Eltgroth 2003). If the carbon were released in less than 1000 years, with an ocean mixing time of similar duration, the carbon along with its depleted isotopic signature should have been transferred to the deep sea within two to three mixing cycles. For the signal to lag by more than this, vertical mixing rates must have slowed significantly, a plausible scenario if the polar regions warmed rapidly, thereby increasing the

density stratification in regions of deep water formation. However, if vertical overturn did slow, the disparity in the surface to deep $\delta^{13}C$ gradient should also continue to grow during this period. Instead, it appears to immediately stabilize suggesting some quasi-equilibrium in the flux of light carbon.

Could the patterns in the individual shell records be artefacts of differential dissolution and reworking? For example, preferential dissolution of Late Palaeocene mixed-layer foraminifera would create an apparent stratigraphic offset with the more dissolution-resistant thermocline and benthic foraminifera extending further up section. However, the first excursion values of the mixed-layer values should then lag those of the more dissolution-resistant species. Instead, there is a lead lag relationship between the first mixed-layer foraminifer excursion values relative to those in the thermocline and deep sea. This lead lag relationship is of the order of tens of thousands of years and implies a top-down propagation of the CIE, from the mixed-layer to thermocline and deep sea.

The extra long lag in the benthic $\delta^{13}C$ CIE relative to planktic in deep-sea cores is probably an artefact of reworking. The primary species used to reconstruct most benthic $\delta^{13}C$ records spanning the P–E boundary is *Nuttalides truempyi*. Even though specimens can be found in the excursion layer, it appears these are reworked, and that *N. truempyi* temporarily disappeared in most pelagic locations coeval with the benthic extinction horizon. This assertion is based on the sudden decrease in the relative abundances of this species at the benthic extinction horizon (Thomas & Shackleton 1996; Thomas 1998, 2003). Apparently, the initial chemical/physical changes associated with the PETM that were responsible for the extinction, also forced *N. truempyi* to abandon large areas of the seafloor, which were replaced by 'excursion' taxa, such as *Bulimina* spp. that increase in abundance during the event (Thomas & Shackleton 1996; Thomas 1998). These excursion taxa which are much too small to be analysed individually, apparently could tolerate the harsh conditions that terminated or excluded other species. Still, it is possible that these taxa also do not record the full CIE. Even so, it would be hard to determine this using a single-specimen approach.

The lag in bulk carbonate may also be an artefact of reworking coupled with dissolution. Clearly, such an effect is evident in the Walvis Ridge transect, where there is a depth-dependent shift in the pattern of the bulk CIE (Zachos *et al.* 2005). In the clay or low carbonate layers, much of the carbonate present at the base of these layers would probably be Palaeocene in age as these layers are forming primarily by chemical erosion of existing sediment. As chemical erosion slows, more of the sinking carbonate is preserved which along with bioturbation creates a more gradual transition.

(*b*) *Magnitude of the marine CIE*

Terrestrial carbon isotope records across the P–E boundary generally show excursions of the order of 5–6‰. The larger magnitude of the CIE, as recorded by plant-derived organic matter or soil nodules, very likely reflects the effect of humidity and/or pCO_2 on fractionation during photosynthesis, an effect that might amplify the signal (Bowen *et al.* 2004). Regardless, there is some suspicion that the record of the marine CIE is attenuated, possibly owing to pH or carbonate ion effects or even a preservation artefact (Bowen *et al.* 2004; Pagani
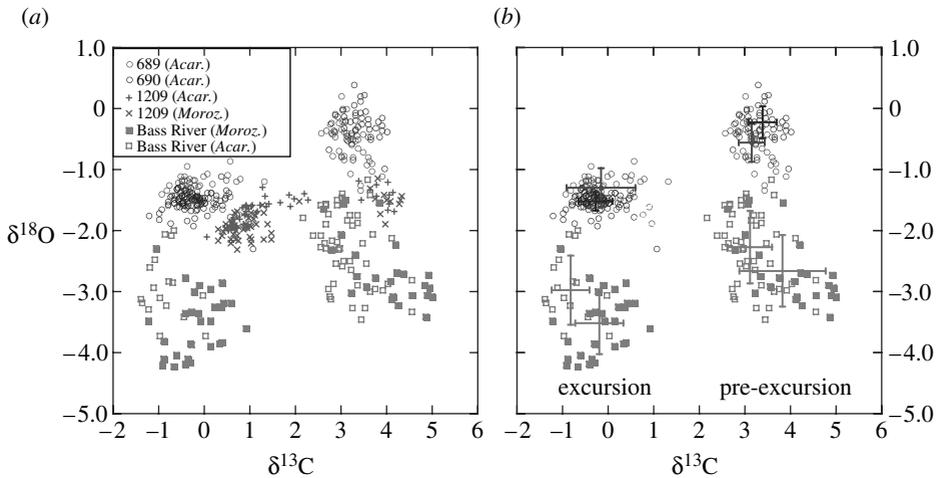
Figure 6. (*a*) Oxygen and carbon isotope cross-plot of single-shell mixed-layer foraminifer isotope data from ODP Sites 689, 690, 1209 and Bass River, NJ. Data included in this plot are from an interval of ± 0.2 m of the CIE at Sites 689 and 690, ± 0.1 m at Site 1209 and ± 0.5 m at Bass River. (*b*) Same as (*a*) but excluding the Site 1209 data. Also included are the mean values and standard deviation (cross bars) for each pre-excursion and excursion data cluster at each location. Mean pre-excursion and excursion *Acarinina* δ^{13}C values are 3.17 and $-0.14\permil$ at Site 689; 3.40 and $-0.26\permil$ at Site 690; and 3.12 and $-0.81\permil$ at Bass River. Mean pre-excursion and excursion *Morozovella* δ^{13}C values at Bass River are 3.84 and $-0.18\permil$.

et al. 2006). Are all the pelagic records of the CIE truncated owing to ocean acidification and widespread dissolution of carbonate? To test this, we cross-plotted the δ^{18}O and δ^{13}C values of mixed layer foraminifer shells from immediately above and below the boundary from Sites 690 (± 0.2 m) and 1209 (± 0.1 m) (Thomas *et al.* 2002; Zachos *et al.* 2003) along with new data from Sites 689 (Nielsen *et al.* submitted) and Bass River (John *et al.* submitted). The duration of the intervals selected represent less than 20 kyr. We included only data for species of *Acarinina* and *Morozovella*, taxa that are thought to have harboured photosymbionts (D'Hondt *et al.* 1994) and thus would have resided in the photic zone. The range of excursion and pre-excursion δ^{13}C values for Sites 689, 690 and Bass River are actually very similar and strongly bimodal (figure 6). The values for Site 1209 shells show less separation between the pre-excursion and excursion values, and are on an average also slightly heavier than the other sites (figure 6). Owing to the rapid exchange rate of CO_2 between the ocean/atmosphere, the δ^{13}C of surface water DIC should be globally uniform ($\pm 0.5\permil$). Larger deviations reflect the influences of local processes on carbon fluxes, such as intense vertical mixing (e.g. upwelling) or phytoplankton blooms, which can create temporary disequilibrium. For example, the initial reduction in the δ^{13}C gradient between *Acarinina* and thermocline dweller *Subbotina* during the CIE could be attributed to either increased vertical mixing/or reduced export production at the Maud Rise and Bass River sections (Kennett & Stott 1991; Thomas *et al.* 2002). Alternatively, the positively offset excursion values at Site 1209 may simply reflect a temporal gap due to the effects of dissolution in this low-accumulation rate setting. The entire excursion layer at Site 1209 is less than

0.5 m thick, much thinner than at Maud Rise (approx. 2 m) and Bass River (approx. 10 m; John *et al.* submitted). The fact that the pre-excursion and excursion values are nearly identical at Maud Rise and Bass River, both sections characterized by high-accumulation rates, but in very different depositional environments, suggests the sections were less impacted by dissolution, and thus more likely to record the full magnitude of the CIE in the surface ocean mixed-layer, approximately -3.5 to $-4.0‰$.

With the exception of a few data points near the base of the CIE at Site 1209 (figure 4), there are no transitional carbon isotope values among individual mixed-layer shell data generated to date, implying a rapid shift in surface ocean $\delta^{13}C$. Are there other factors that might have contributed to the lack of transitional carbon isotope values in mixed-layer foraminifera? It is possible that the abundances of these species decreased during the period of lowest pH or warmest temperature (Kelly *et al.* 1996, 1998; Kelly 2002), or that these and other planktonic foraminifera precipitated thinner shells which did not readily preserve. In either case, the implications are significant that pH changes might have impacted the biomineralization and ecology of planktonic foraminifera. Additional analyses of individual shells of both common and rare species, and from locations where dissolution was minimal should help to resolve this issue.

3. Summary

The marine record of the CIE has been constructed from analysis of a large variety of materials ranging from bulk inorganic and organic carbon to individual foraminifer shells. Analyses of individual mixed-layer planktonic shells from cores spanning the boundary generally yield pre-excursion or excursion carbon isotope values, but no transitional values suggesting that the $\delta^{13}C$ of the atmospheric and surface ocean carbon pools changed very rapidly on geologic time-scales (less than 500 years). Close agreement of the absolute pre-excursion and excursion foraminifera carbon isotope values between pelagic and coastal sections suggests that the magnitude of the CIE in the atmosphere and surface ocean was between 3.5 and 4.0‰, almost 1.0‰ greater than that recorded in deeper dwelling planktonic and benthic foraminifera. While the pattern inferred for the mixed-layer might be an artefact of preservation, the similarity in foraminifer records from diverse depositional facies strongly suggests otherwise. Consequently, any attempt to characterize the nature and origin of the carbon cycle perturbation must also reconcile the rapid and large change in the $\delta^{13}C$ of surface ocean DIC relative to the smaller anomaly recorded in the deep sea.

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