Bolide summer: The Paleocene/Eocene thermal maximum as a response to an extraterrestrial trigger

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Abstract

The standard paradigm that the Paleocene/Eocene thermal maximum (PETM) represents a threshold event intrinsic to Earth's climate and connected in some way with long-term warming has influenced interpretations of the geochemical, climate, and biological perturbations that occurred at this event. As recent high-resolution data have demonstrated that the onset of the event was geologically instantaneous, attempts to account for the event solely through endogenous mechanisms have become increasingly strained. The rapid onset of the event indicates that it was triggered by a catastrophic event which we suggest was most likely a bolide impact. We discuss features of the PETM that require explanation and argue that mechanisms that have previously been proposed either cannot explain all of these features or would require some sort of high-energy trigger. A bolide impact could provide such a trigger and, in the event of a comet impact, could contribute directly to the shape of the carbon isotope curve. We introduce a carbon cycle model that would explain the PETM by global warming following a bolide impact, leading to the oxidation of terrestrial organic carbon stores built up during the late Paleocene. Our intention is to encourage other researchers to seriously consider an impact trigger for the PETM, especially in the absence of plausible alternative mechanisms.
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1. Introduction

At the Paleocene/Eocene boundary, ~55 Ma, a catastrophic event produced dramatic changes in Earth's biogeochemical systems. Global temperatures abruptly warmed by 4–5 °C at the same time when a perturbation to the biogeochemical carbon cycle led to a >4‰ decrease in atmospheric and surface ocean $\delta^{13}C$ values

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and soon thereafter a ~2.5‰ $\delta^{13}C$ decrease in the deep ocean (e.g., Kennett and Stott, 1991). Major changes in community structure are recorded in marine microfossils (planktonic and benthic foraminifers, calcareous nannoplankton, dinoflagellates, ostracodes), including an extinction of 30–50% of species of bathyal–abyssal benthic foraminifers (e.g., Thomas, 1998). Terrestrial faunas were also affected, with the first appearance of most modern mammalian orders occurring at the P/E boundary (e.g., Maas et al., 1995).

In seeking the causes of this catastrophic event, most researchers have focused on the large decrease in $\delta^{13}C$ values, which seemed too large and too rapid to be easily explained within the context of standard carbon cycle models. This led to the proposal that the large decrease reflected the input of substantial quantities of isotopically light methane from thermal dissociation of seafloor clathrate deposits (Dickens et al., 1995; Matsumoto, 1995). As discussed below, the documented rapidity of the onset of the event and lower estimates of the size of the methane hydrate reservoir indicate that this cannot be the major source for the carbon isotope excursion (CIE). Kurtz et al. (2003) showed that the late Paleocene was a time of increasing terrestrial organic carbon-rich deposition and suggested that the $\delta^{13}C$ may have resulted from the burning of large peat deposits. With several coauthors, we have recently presented evidence that an extraterrestrial impact occurred at the onset of the PETM (Kent et al., 2003a), which would provide a trigger of sufficiently large energy to account for the rapidity of the onset of the event.

In this contribution, we explore the mechanisms by which an impact could trigger a "bolide summer:" the prolonged interval of warmth during the PETM. Our discussion focuses mainly on evidence for changes in the carbon cycle during the PETM, which we believe has been obscured in the literature by the emphasis on methane hydrate. As background, however, it is useful to summarize the published evidence for an impact at the P/E boundary and for a major perturbation to biological systems, although only benthic foraminifers suffered a mass extinction during the PETM.

1.1. Evidence for a P/E impact

In the first comprehensive study to consider the possibility that the PETM was caused by an impact (Kent et al., 2003a), we proposed that (1) a published report of an iridium (Ir) anomaly coincident with the initial decrease in $\delta^{13}C$ values and (2) discovery of abundant magnetic nanoparticles (a condensation product from the impact plume) in the interval of minimal $\delta^{13}C$ values at sites on the North American North Atlantic shelf could be taken as evidence for a bolide impact at the onset of the PETM. We suggested that the initial, rapid decrease in $\delta^{13}C$ values could have resulted directly from a cometary impact, as cometary carbon is greatly enriched in ^{12}C (e.g., Arpigny et al., 2003; Messenger, 2000). The $\delta^{13}C$ record cannot be taken as unique to an impact, since terrestrial ^{12}C-enriched carbon could be the source, but the apparent extreme rapidity of the initial $\delta^{13}C$ decrease is difficult to explain without a very high-energy trigger.

Increased levels of Ir have been reported associated with the P/E boundary in at least two locations. A small but reproducible Ir anomaly (~140 ppt Ir, reproduced in samples collected in three different years) occurs precisely (centimeter scale) at the onset of the CIE at Zumaya, Spain (Schmitz et al., 1997). The small magnitude of this Ir anomaly lends itself to several possible explanations, although consideration of the stratigraphic, sedimentological, and geochemical context led Schmitz et al. (1997) to conclude that it was most likely due to either volcanism (for which no other evidence was presented) or an impact. A subsequent study resulted in peak Ir concentration of 423 ppt at the same level in Zumaya, although also demonstrating that the Ir is concentrated in the "yellowish fraction" of the sample (Schmitz et al., 2004). A much larger Ir anomaly (maximum of 2.3 ppb) occurs near the P/E boundary in the Goriska Brda section in Slovenia (Dolenec et al., 2000), although the precise relationship to the CIE has not been established.

A novel potential proxy of impact ejecta is iron-rich nanophase material, which was detected at several K/T boundary sites and interpreted as a condensate from an impact plume (Wdowiak et al., 2001; Verma et al., 2001). Mössbauer spectroscopy, which is especially sensitive to the presence of the finest grained iron-rich component, was employed in these studies. The discovery of an unusual abundance of magnetite nanoparticles restricted to sediments that coincide with the CIE at one drill site (Lanci et al., 2002) was confirmed at two other drill sites on the

New Jersey coastal plain and, by analogy with the K/T boundary occurrences, interpreted as an impact plume condensate (Kent et al., 2003a; data are included in the Background Data Set for this paper[1]). In this study, magnetic hysteresis was used to detect the nanoparticles, where the ratio of saturation-remanent magnetization to saturation magnetization (M_{sr}/M_s) is an effective measure of the overall magnetic grain size distribution. The magnetic properties of magnetite are highly grain size dependent: theoretically, values of M_{sr}/M_s that approach 0.5 are characteristic of grains over a very narrow size range known as single domain, from about 30 nm to only about 100 nm, and decrease precipitously to less than 0.1 at smaller and, more pertinently, larger grain sizes (Dunlop and Özdemir, 1997; Newell and Merrill, 2000; Lanci and Kent, 2003). What is so remarkable about the magnetic properties of the CIE sediments on the New Jersey coastal plain is the prevalence of high values close to the theoretical limit of M_{sr}/M_s (for example, a median M_{sr}/M_s of 0.42 for 17 samples over nearly 8 m of CIE sediments in the Clayton core) which are unusual when compared with published values from a wide variety of environments (Kent et al., 2003a,b).

The CIE clastic sediments with anomalously high M_{sr}/M_s values are enriched in kaolinite, a product of continental weathering. The conundrum is how such a sediment could be produced and transported at the exclusion of normal neritic sedimentary components. We maintain that the abundant magnetic nanoparticles in the CIE interval on the New Jersey coastal plain are best explained as a condensation product of an impact plume, whose unconsolidated ejecta-dust blanket was rapidly weathered into a kaolinite-rich product that was then eroded and redeposited on the adjoining marine shelf, becoming more diluted and mixed with other sediment with distance from the continent.

The possible presence or absence of other evidence for an extraterrestrial impact (e.g., osmium isotopes, helium isotopes, shocked quartz, large crater) is discussed in our earlier papers (Kent et al., 2003a,b).

1.2. Biological response

The possibility of an impact trigger for the PETM was dismissed in the first study to recognize the event due to the "lack of major extinctions in oceanic plankton and in shallow-water benthic communities" (Kennett and Stott, 1991), an expectation clearly influenced by the K/T example. However, it has been demonstrated since then that major perturbations did occur to oceanic plankton communities, in shelf environments, and in terrestrial environments during the PETM, in addition to the well-known benthic foraminiferal extinction.

Planktonic foraminifers and calcareous nannoplankton assemblages were severely affected by the PETM. The changes were widespread, abrupt, and indicate up to a nearly complete replacement of the pre-PETM communities (Kelly et al., 1996; Kelly, 2002; Bralower, 2002). At Site 690, where the timing is best constrained, these assemblage changes took place within <10 k.y. following the initial decrease in surface-ocean $\delta^{13}C$ values. Complementing these changes, a suite of "excursion taxa" evolved closely associated with the onset of the CIE in low- to mid-latitude locations (Kelly et al., 1996; Aubry et al., 2000; Aubry and Sanfilippo, 1999; Cramer et al., 1999; Kahn and Aubry, 2004). The changes in community structure are largely transient: the excursion taxa are present only within the interval of low isotopic values, and assemblages return to compositions more similar to pre-PETM conditions during the interval of isotopic recovery. Interestingly, a "top–down" progression of events, the perturbation initially affecting the surface environment and only later the deeper ocean, has been inferred on the basis of planktonic community changes (Kelly, 2002; Bralower, 2002) in addition to geochemical changes (Thomas et al., 2002) which is exactly what we would expect from an impact event.

The perturbation to the deep-ocean environment at the P/E boundary led to a major extinction event among benthic foraminifers (35–50% of species; see Thomas, 1998). Deep-ocean ostracodes also show a perturbation shifting to an assemblage of smaller size and thinner walls (consistent with benthic foraminiferal changes), although there is no associated extinction (Steineck and Thomas, 1996). The dominant factors that have been considered as causing the extinction are decreased oxygenation and increased corrosiveness of deep and intermediate waters, and changes in surface water productivity affecting deep-ocean nutrient availability (Thomas, 1998).

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[1] http://www.elsevier.com/locate/palaeo.

The Paleocene/Eocene boundary marks the transition from an "archaic" mammalian assemblage to one dominated by representatives of major modern mammalian groups, such as primates, artiodactyls, and perissodactyls. Although a more detailed analysis may reveal the presence of an extinction "event" in this interval, current analyses suggest that the Paleocene fauna disappeared gradually through the late Paleocene, but that Eocene taxa appeared abruptly at the PETM. Gunnell (1998) shows that the earliest Eocene fauna were substantially different from the Paleocene fauna at the ordinal taxonomic level. The number of modern orders represented in the latest Paleocene is ~12% of the total assemblage, while immediately following the PETM, it had increased to ~48%. The identification of the CIE in the Bighorn Basin and intensive sampling of this interval has revealed an impressively abrupt change in the mammalian assemblage associated with the onset of the event. In conjunction with major taxonomic changes in the assemblage, Gingerich (2003) documented a distinctive decrease in the size of the fauna; such "dwarfing" is consistent with a major climate perturbation. This analysis shows that the largest pulse in the late Paleocene–early Eocene transition in mammalian fauna, which can be regarded as equally or more important to mammalian evolution as the extinction of the dinosaurs, occurred precisely synchronous with the PETM (Gingerich, 2003; Clyde and Gingerich, 1998).

2. Global warming and the carbon isotope excursion

Transient decreases in stable carbon and oxygen isotopic values, now supplemented by Mg/Ca ratios, have become central to understanding the PETM. These global perturbations have been documented in numerous geologic sections representing deep-ocean, shallow-marine, and terrestrial environments (Fig. 1). Marine carbonate $\delta^{18}O$ records, which reflect changes in water temperature and salinity, indicate that temperatures increased throughout the water column. Benthic foraminiferal $\delta^{18}O$ values decreased by 1.0–1.8‰; a portion of this decrease may be attributable to melting of small ice sheets (0.2–0.3‰, e.g., Browning et al., 1996), possibly resulting in a ~20-m rise in sea

level (Speijer and Morsi, 2002), but most of the decrease must be attributed to a deepwater temperature increase of 4–7 °C. Planktonic foraminiferal $\delta^{18}O$ values show a larger decrease at high latitudes (~2‰ at Site 690; Kennett and Stott, 1991; Thomas et al., 2002) than at low latitudes (0.94‰ at Site 527, Thomas et al. (1999); 0.5–0.8‰ at Site 1209, Zachos et al. (2003); <0.4‰ at Site 865; Bralower et al., 1995). A different temperature proxy, the Mg/Ca ratio in foraminiferal tests, indicates that the small $\delta^{18}O$ decrease at low latitudes reflects the counteracting effect of an increase in salinity and a 4–5 °C temperature increase (Zachos et al., 2003; Tripati and Elderfield, 2004). It is likely that the large $\delta^{18}O$ decrease at high latitudes and in shallow waters reflects a decrease in salinity together with a temperature increase (e.g., Cramer et al., 1999). The good correspondence between the deep-ocean $\delta^{18}O$-based estimate and the surface ocean Mg/Ca-based estimate of the temperature increase indicates that global temperatures increased by 4–5 °C. This implies a 2–8× increase in atmospheric pCO_2 (using the relationship 1.5–4.5 °C temperature increase per pCO_2 doubling; e.g., Houghton et al., 2001; Crowley and Hegerl, 2003) during an interval lasting several tens of thousands of years. Such a rapid increase in pCO_2, maintained over several ocean mixing times, must partially reflect a transfer of carbon from the deep ocean to the surface ocean/atmosphere reservoir (producing this increase simply by adding carbon would require the addition of 4500–31,500 Gt C, since the ocean will take up 6.5 times as much carbon as the atmosphere; Siegenthaler and Sarmiento, 1993).

The carbon isotope excursion (CIE) provides evidence for both a large input of carbon to the ocean/atmosphere reservoir and a transfer of carbon from the deep ocean to the atmosphere/surface ocean reservoir. In the following discussion, we use as a reference the record from Site 690, where the CIE was initially recognized and is still best constrained (Fig. 2; Kennett and Stott, 1991; Bains et al., 1999; Thomas et al., 2002), but our observations are confirmed by data from other locations. We focus on three characteristics of the event that must be explained by a viable model for the PETM:

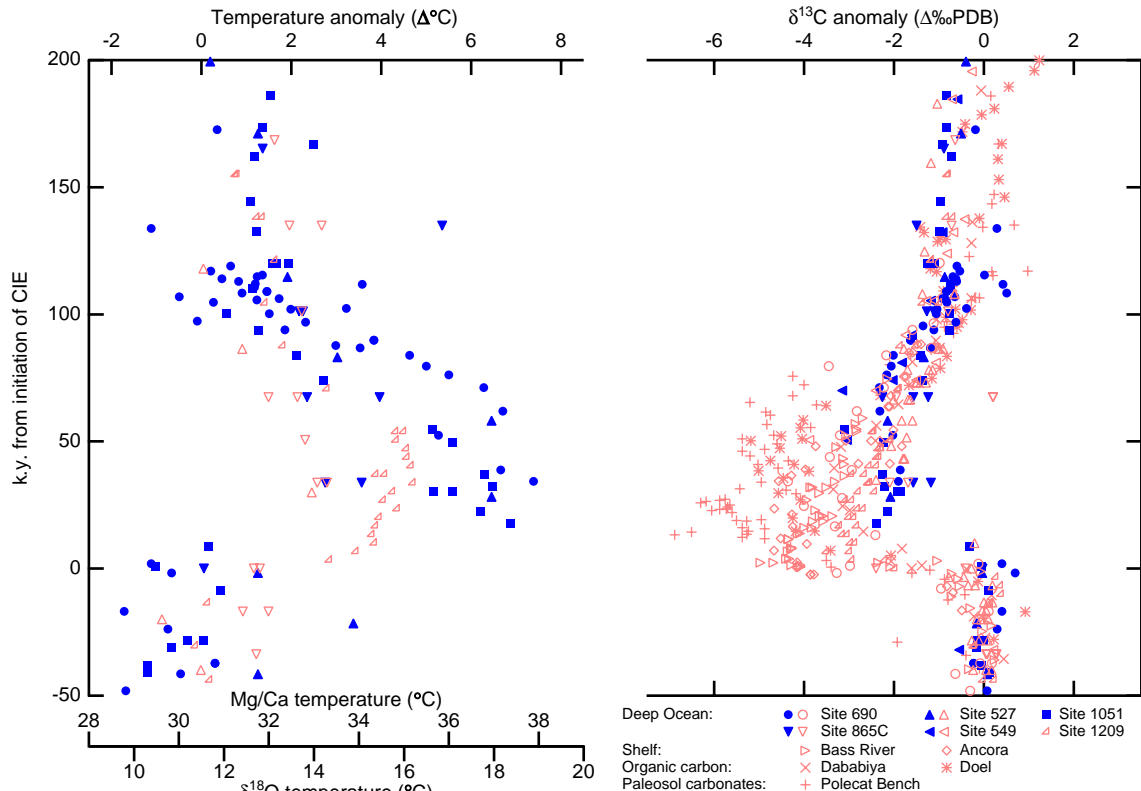(1) The initial shift in carbon isotopic values was geologically instantaneous.

Fig. 1. Compilation of carbon isotope records (right) and temperature proxy records (left) through the PETM. Blue (dark), solid markers are values for intermediate/deep ocean benthic foraminifers, red (light) markers are values for planktonic foraminifers, shelf benthic foraminifers, organic carbon, or paleosol carbonates (e.g., proxies for atmosphere/surface changes). Note that the shift in intermediate/deep ocean $\delta^{13}C$ values is less than that in grey values, indicating that the atmosphere/surface ocean to deep ocean $\delta^{13}C$ gradient decreased during the first ~50 k.y. of the PETM. Data plotted are from Polecat Bench, Wyoming, USA (Bowen et al., 2001), Dababiya, Egypt (Dupuis et al., 2003), Doel Borehole, Belgium (Steurbaut et al., 2003), and DSDP/ODP Sites 690 (Kennett and Stott, 1990, 1991; Stott et al., 1990; Thomas and Shackleton, 1996), 527 (Thomas and Shackleton, 1996; Thomas et al., 1999; Tripati and Elderfield, 2004), 1051 (Katz et al., 1999), 865C (Bralower et al., 1995), 549, Bass River (Cramer et al., 1999), and Ancora (unpublished data of B.S. Cramer, see online Background Data Set). Benthic foraminiferal isotope data were corrected to *Cibicidoides* according to equations given in Katz et al. (2003). In order to show the difference in the magnitude of the $\delta^{13}C$ decrease, each record was shifted so that pre-CIE values are plotted at ~0‰. Benthic foraminiferal values were all adjusted by −1.5‰. Planktonic foraminiferal, organic carbon, and paleosol carbonate $\delta^{13}C$ values are not expected to have a consistent offset relative to atmosphere/ surface ocean $\delta^{13}C$ values, so these records were individually adjusted (planktonic foraminiferal values were adjusted by −2.1 to −4.1‰, organic carbon values were adjusted by 24‰, and paleosol carbonate values were adjusted by 9‰). Paleotemperature estimates were calculated according to the equations in Erez and Luz (1983) for $\delta^{18}O$ (assuming seawater $\delta^{18}O = -1.2$‰; Shackleton and Kennett, 1975) and Tripati and Elderfield (2004) for Mg/Ca (assuming seawater Mg/Ca = 3.19 mol/mol). Age model for Site 690 is after Farley and Eltgroth (2003); age models for the other records were constructed by aligning the initial decrease in $\delta^{13}C$ values and the increase in $\delta^{13}C$ values between ~60 and ~110 k.y. post-initiation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(2) Intermediate/deep-ocean benthic foraminiferal $\delta^{13}C$ values indicate a 2–3‰ decrease while the atmosphere/surface-ocean $\delta^{13}C$ decrease was 3–5‰ (Fig. 1).

(3) At ~40 k.y. following the initial bulk sediment $\delta^{13}C$ shift, surface-dwelling planktonic foraminiferal $\delta^{13}C$ values increased by ~2‰, while

benthic foraminiferal, deeper dwelling planktonic foraminiferal, and bulk carbonate $\delta^{13}C$ values remained low until ~90 k.y. following the initial isotopic shift (Fig. 2).

These documented features are best discussed in the context of a global carbon cycle box model, in
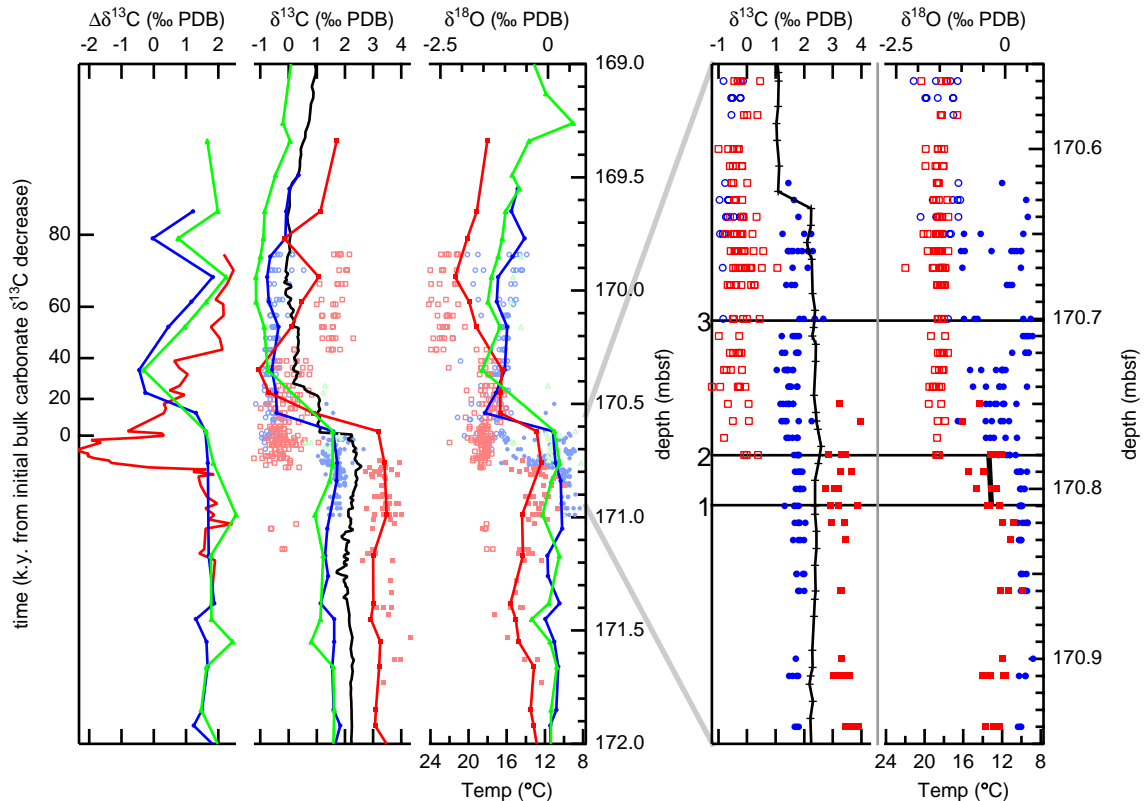
Fig. 2. Carbon and oxygen isotope values through the PETM interval at ODP Site 690. Records are shown for isotopic analyses of bulk carbonate (black line; Bains et al., 1999), analyses of multi-specimen foraminiferal samples (symbols connected by lines; Kennett and Stott, 1991), and analyses of single foraminiferal tests (unconnected symbols; Thomas et al., 2002). Red squares indicate analyses of surface-dwelling planktonic foraminifers (*Acarinina*), blue circles indicate deep-dwelling foraminifers (*Subbotina*), and green triangles indicate benthic foraminifers (*Nuttalides truempyi*). For the single-specimen foraminiferal analyses, open symbols are used for analyses with $\delta^{13}C$ values <2.3‰ for *Acarinina* and <0.6‰ for *Subbotina* (i.e., CIE samples) while filled symbols are used for other analyses (i.e., pre-CIE samples). The left panel also shows the calculated difference between $\delta^{13}C$ values for surface-dwelling planktonic foraminifers and $\delta^{13}C$ values for thermocline-dwelling planktonic foraminifers (red line for the median value of single-specimen analyses, blue circles for multi-specimen analyses) or benthic foraminifers (green triangles). The far left axis gives a relative timescale modified after Farley and Eltgroth (2003). Numbered horizontal lines in the right-hand panel are levels identified by Thomas et al. (2002) as (1) the initiation of warming in surface waters, (2) the initial $\delta^{13}C$ decrease in surface waters, and (3) the initial $\delta^{13}C$ decrease in deeper waters. We instead believe that level 2 marks the initial perturbation to both $\delta^{13}C$ and $\delta^{18}O$ values, with normal variability below that level. It is not clear why the initial shift in isotopic values for *Acarinina* does not occur at the same level in the Thomas et al. (2002) record as in the record of Kennett and Stott (1991); the former indicates a lag between the initial surface ocean and intermediate ocean changes while the latter indicates synchronous changes. Calculated temperatures are given for $\delta^{18}O$ analyses using the paleotemperature equation of Erez and Luz (1983) and assuming an ice-free ocean $\delta^{18}O$ value of $-1.2‰$ (Shackleton and Kennett, 1975). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

which estimates of the amount of carbon in various discrete reservoirs combined with estimated fluxes between those reservoirs are used to evaluate mechanisms of perturbation to the carbon cycle (Table 1; see Broecker and Peng, 1982). Carbon is constantly exchanged among the ocean, atmosphere,

and terrestrial biomass reservoirs, which we refer to collectively as the exchangeable reservoirs. Carbon that has been sequestered through sedimentary processes (e.g., in fossil fuels, peat, and methane hydrates) and of extraterrestrial origin from comets can potentially be rapidly added to the exchangeable

Table 1
Exchangeable carbon reservoirs and external resources

Carbon reservoir	Recent (pre-industrial)	Latest Paleocene	Normal exchange rate with atm/ocean (Gt/year)[a]	$\delta^{13}C$ (PDB)
Atmosphere oceans	600[b]	820[c]	100[b]	−6 to −4[d]
Surface inorganic	1000[b]	1830[e]	100[b]	2–4[d]
Deep inorganic	38,000[b]	36,000[e]	30[f]	1–2[d]
Organic	700[b]	850[e]	30[f]	−17[g]
Terrestrial biosphere				
Land biota	600[b]	1700[h]	100[b]	−25[g]
Soil and detritus	1500[b]	1200[h]	50[b]	−25[g]
Total exchangeable	42,400	42,400		
Coal	3700[i]			−25[j]
Oil	700[i]		0.1–0.4[k]	−18 to −34[j]
Gas	500[i]		0.02–0.07[k]	−40 to −70[j]
Peat	500[l]	up to 15,000[m]	0.06[m]	−25[g]
Gas hydrates	500–2500[l]	200–1100[l]	0–0.01[n]	−40 to −70[j]
Comets	up to 2000[o]	up to 2000[o]	Sporadic	−45[p]; −110[q]

[a] Estimates are for the present carbon cycle, but should be of similar magnitude in the latest Paleocene.

[b] Siegenthaler and Sarmiento (1993).

[c] See Royer et al. (2001).

[d] Assuming a fractionation of $\delta^{13}C$ values between the atmospheric and surface ocean of ~8 and that deep-ocean $\delta^{13}C$ values are 1–2 less than those in the surface ocean due to oxidation in the deep ocean of organic carbon produced in the surface ocean ("export productivity"; see, e.g., Broecker and Peng, 1982).

[e] Based on equilibrium calculations using latest Paleocene ocean temperature estimates, 385 ppmv atmospheric $p\mathrm{CO_2}$, and assuming that the total exchangeable carbon was the same as today.

[f] Assuming a ~1000 year mixing time for the ocean (e.g., Broecker and Peng, 1982).

[g] Photosynthetic fractionation is ~−20, with a difference between marine and terrestrial values due to the fractionation between atmosphere and surface ocean $\mathrm{CO_2}$ (e.g., Broecker and Peng, 1982).

[h] Beerling (2000).

[i] Houghton et al. (2001).

[j] Faure (1986).

[k] Hornafius et al. (1999).

[l] Milkov (2004).

[m] Kurtz et al. (2003).

[n] Extrapolation from Milkov and Sassen (2003).

[o] Based on a maximum 20 km diameter with density 1500 kg/m^3 and 25% C.

[p] Mean value of IDPs thought to be derived from comets (Messenger, 2000).

[q] Median value of ground-based determinations for a variety of comets given in Arpigny et al. (2003) and Wyckoff et al. (2000).

reservoirs (Table 1). In addition, carbon is constantly added to the exchangeable reservoirs from the mantle and weathering at a rate that is balanced by removal of carbon through sedimentation. Changes in the relative sizes of the exchangeable reservoirs result in variations in the $\delta^{13}C$ values that will have different magnitudes and directions in different reservoirs. The addition of carbon to the exchangeable reservoirs and altering the net isotopic value of carbon removed from those reservoirs (i.e., by changing the relative rates of organic carbon and carbonate sedimentation) result in $\delta^{13}C$ variations that are equivalent in magnitude in each of the exchangeable reservoirs.

2.1. Deep-ocean shift

Most authors have focused on the 2–3‰ decrease in the deep-ocean $\delta^{13}C$ value, which indicates a major perturbation to the exchangeable carbon cycle. It would take oxidation of all of the estimated late Paleocene biomass (equivalent to 3600 Gt of C) to cause a comparable decrease. Since oxidation of all biomass is clearly unrealistic, the $\delta^{13}C$ decrease indi-

cates the addition of a significant amount of carbon from other sources and variations in relative rates of removal, through sedimentation, of organic carbon vs. carbonate carbon.

Methane hydrate has been proposed and is widely accepted as the source of the carbon required to explain the CIE (Dickens et al., 1995; Matsumoto, 1995). Clathrate, a solid composed of water and various gases, but predominantly methane (CH_4), naturally occurs in marine sediment within a region known as the gas hydrate stability zone (GHSZ). Because of its dependence on temperature and pressure, the GHSZ occupies the upper several hundred meters of sediment where water depth (pressure) is great enough and sediment temperature (increasing with depth in sediment due to the geothermal gradient) is sufficiently cool. Using estimates of bottom-water temperature (derived from $\delta^{18}O$ analyses on benthic foraminifers) and an assumed geothermal gradient, the configuration and volume of the GHSZ can be approximated for any time in the past (e.g., Dickens, 2001). This exercise leads to the recognition that the 4–8 °C increase in bottom-water temperature that occurred during the PETM would have significantly reduced the region of stability and would have resulted in areas where the GHSZ completely disappeared, potentially allowing methane from previously stable hydrate to escape into the water column. Recognizing that the $\delta^{13}C$ value for carbon in methane hydrates is approximately −60‰, the thermal dissociation hypothesis posits that the CIE resulted from ~1700 Gt of carbon from methane that was released when the documented bottom-water temperature increase led to a smaller GHSZ (Dickens et al., 1995).

When this hypothesis was first formulated, it was believed that an "enormous amount of carbon" (7500–15000 Gt) was stored in the form of methane hydrates (Dickens et al., 1995). Under the dubious assumption that a similar quantity of hydrate was uniformly distributed throughout the late Paleocene GHSZ, the 14–19% of gas hydrate that would have been in this region and the amount of methane hydrate-derived carbon required to account for the magnitude of the CIE seemed to match well (Dickens et al., 1995). This apparent concordance has taken on the status of a tautology among many researchers studying the PETM: methane hydrate is assumed to be the only source of ^{12}C-enriched carbon able to

account for the magnitude of the CIE (e.g., Zachos et al., 2001; Dickens, 2003), and the logical converse, that the magnitude and shape of the CIE are entirely due to methane hydrate release, is the basis for some interpretation (e.g., Thomas et al., 2002; Bains et al., 1999). The idea that no process other than dissociation of hydrate had any effect on carbon isotope variations during the CIE would require that there were no isotopic effects from the inevitable physical and biological responses to the climate perturbation, which we regard as untenable. The hydrate dissociation hypothesis also begs the question of what caused the extreme warming: any process that would cause a rise in atmospheric $p$$CO_2$ sufficient to account for the PETM warming would have also resulted in alteration of $\delta^{13}C$ values, but the thermal dissociation hypothesis predicts that virtually all of the documented warming would have had to precede the $\delta^{13}C$ decrease in order to melt hydrate (e.g., Katz et al., 2001).

Thermal dissociation may result in release of methane directly to the water column only at relatively shallow water depths where the total GHSZ may be eliminated (Milkov and Sassen, 2003). At greater water depths, the GHSZ becomes thinner but is still present. Pore water within the GHSZ, and especially its upper part near the seafloor, is often undersaturated with gas (Xu and Ruppel, 1999; Milkov et al., 2003), so in regions where the GHSZ is not eliminated, the hydrate-derived gas will migrate upwards into a "new" GHSZ and recrystallize as gas hydrate. Even in regions where the GHSZ is eliminated as a result of warming, gas derived from hydrate is likely to be rapidly oxidized by bacteria and archaea within the sediment and the resulting increase in pore water CO_2 will lead to methane-derived carbon being precipitated as carbonate rather than escaping into the ocean. Oxidation of methane released from gas hydrates within the sediment column appears to be very efficient, and the resulting CO_2 is readily incorporated in authigenic carbonates which could potentially prevent any of the dissociated methane from reaching the exchangeable carbon reservoirs (Milkov and Sassen, 2003). Since only a portion of hydrate-derived gas is likely to vent from sediments into the water column and atmosphere, and to impact climate change through the global carbon cycle, the hydrate dissociation hypothesis requires the assumption of a very

large methane hydrate reservoir (Milkov and Sassen, 2003).

The crucial flaw in the hydrate dissociation hypothesis is that the global volume of gas hydrate appears to be an order of magnitude smaller than previously believed. Results from two recent Ocean Drilling Program legs have constrained sediment methane concentrations in passive (Blake Ridge) and active (Hydrate Ridge) margin regions thought to represent areas especially rich in methane. Milkov et al. (2003) extrapolated from the direct measurements in these two areas to arrive at a new estimate of only 1600–2700 Gt of carbon stored in the global methane hydrate reservoir. This is supported by an analysis of all published estimates of the quantity of hydrate, indicating that the amount of carbon is likely to be in a similar range (500–2500 Gt; Milkov, 2004). Due to much higher bottom-water temperatures in the Paleocene, the GHSZ was only 40–50% of its present volume (Dickens, 2001). Assuming that the distribution of hydrate within this zone was similar to today points to a total late Paleocene hydrate reservoir of only 200–1100 Gt of carbon, of which ~19% (40–200 Gt of carbon) would have been dissociated in shallow areas where the GHSZ would have entirely disappeared (Milkov et al., 2003; Milkov, 2004), and an even smaller fraction would be expected to enter the exchangeable carbon reservoirs. This implies a rate of methane release of 0.01–0.07 Gt C/year (assuming release over 3000 years, e.g., Katz et al., 2001), which is roughly equivalent to the estimated natural rate of gas seepage from petroleum systems (Table 1; e.g., Milkov and Sassen, 2003) and an order of magnitude less than the estimated rate of methane release from all natural sources at the present day (~0.45 Gt C/year, Houghton et al., 2001). In order to maintain the tautology that only dissociation of methane hydrate can account for the CIE, it has been suggested that this implies either a much higher average sediment hydrate content during the Paleocene or the presence of large amounts of free methane gas below the hydrate stability zone. Modeling results suggest that the average hydrate present within the GHSZ is linearly dependent on the proportion of organic carbon in total sedimentation (Davie and Buffett, 2001); in order to achieve an average hydrate abundance sufficient to account for the CIE through thermal dissociation (~14% of pore space filled;

Dickens, 2001) it seems that organic carbon would have had to make up on average ~10% by weight of total sedimentation in the GHSZ on a global basis, which is unreasonably high. Moreover, the global quantity of free gas underlying the hydrate zone appears to be limited, due to mechanical properties of sediment, to ≪1150 Gt carbon for the modern ocean (Hornbach et al., 2004), probably smaller during the Paleocene, and only a portion of this would have been in regions where the overlying GHSZ would have disappeared during the PETM. We conclude that the total contribution from gas hydrates to the decrease in $\delta^{13}C$ values during the PETM is ≪0.3‰, which we note is less than the uncertainty in the actual magnitude of the total $\delta^{13}C$ decrease.

A more likely scenario involves terrestrial carbon stores such as peat. Modern peat deposits include ~500 Gt of carbon with an isotopic composition of approximately −25‰, but the volume of this reservoir may have been more than an order of magnitude larger during the late Paleocene (Table 1; Kurtz et al., 2003). This reservoir represents a sequestration from the rapidly exchangeable carbon cycle, but it is available for oxidation and rapid introduction into the ocean/atmosphere inorganic reservoir as a result of climate change or fire. Kurtz et al. (2003) concluded that terrestrial sequestration of large amounts of organic carbon, likely in the form of peat deposits, was a primary cause of the long-term late Paleocene increase in global $\delta^{13}C$ (e.g., Shackleton, 1986; Zachos et al., 2001) and suggested that large fires occurring as a result of gradual climate warming and drying during the late Paleocene could account for some or all of the CIE. It would require the oxidation of ~4000 Gt of C derived from peat (~25% of the calculated increase in this reservoir during the late Paleocene) to account for a 2.5‰ decrease at the PETM (Kurtz et al., 2003).

A final source of ^{12}C-enriched carbon is extraterrestrial: as comets are 20–25% carbon by weight and have a $\delta^{13}C$ value of −45‰ or lower (Delsemme, 1988; Jessberger and Kissel, 1991; Jewitt et al., 1997; Messenger, 2000; Wyckoff et al., 2000; Arpigny et al., 2003), the impact of a reasonably large-size comet should result in a decrease in the $\delta^{13}C$ value of the rapidly exchangeable carbon cycle (Kent et al., 2003a; Bowring et al., 1998; Deming, 1999; Wilde and Quinby-Hunt, 1997). Accounting for a 2.5‰

decrease in deep-water δ^{13}C values in this way would require an extremely, but not impossibly, large comet: assuming cometary density of 1500 kg/m^3, a 20–22-km-diameter comet would deliver the requisite ~2200 Gt of carbon. This seems unlikely since cometary carbon would be added instantaneously to the atmosphere, so that the shift in atmospheric δ^{13}C values would be expected to be approximately $-20‰$, considerably larger than observed. A ~15-km-diameter comet would bring with it ~900 Gt of carbon, leading to a ~1‰ decrease in deep-ocean δ^{13}C values, while more reasonably sized comets of 10 km diameter (~200 Gt carbon) and 5 km diameter (30 Gt carbon) would result in decreases of only $-0.2‰$ and $-0.03‰$ in deep-ocean values, but would still lead to $-4.5‰$ and $-0.7‰$ decreases, respectively, in atmosphere/surface ocean values until mixed into the deep ocean. It is quite possible that cometary δ^{13}C values are actually much lower than the nominal value of $-45‰$ we adopted from measurements on interplanetary dust particles, in which case the isotopic effects might be substantially greater (the median of cometary determinations given in Arpigny et al., 2003, and Wyckoff et al., 2000, is $-110‰$, but individual determinations have a large error).

Although it has not been generally acknowledged, it is important to note that some portion of the deep-ocean δ^{13}C decrease may reflect an alteration in the relative rates of organic carbon and carbonate sedimentation at the onset of the event. The large difference in isotopic value between carbonate and organic carbon means that variations in the relative burial rates of these components can have a fairly rapid effect on the δ^{13}C value in the exchangeable reservoirs. Cramer et al. (2003) documented numerous rapid (<50 k.y.) δ^{13}C decreases that occurred regularly at eccentricity maxima in the late Paleocene–early Eocene and demonstrated that these events could be explained by variations in the relative proportions of carbonate and organic carbon sedimentation. It therefore must be considered plausible that a similar portion of the CIE (up to 1‰) may have also resulted from variations in the burial rates of carbonate and organic carbon. If so, then the amount of carbon added to the exchangeable reservoirs necessary to account for the magnitude of the CIE would be reduced by up to 40%.

2.2. Surface ocean/atmosphere shift

Benthic foraminiferal isotopic measurements from various locations in the deep ocean indicate that intermediate/deep-ocean δ^{13}C values decreased by 2–3‰ during the PETM (Katz et al., 2001; Thomas and Shackleton, 1996; Kennett and Stott, 1991; Bralower et al., 1995) while values reflecting the atmosphere/surface ocean reservoir show a larger decrease (Fig. 1): 3–4.5‰ for surface-dwelling planktonic foraminifers (Kennett and Stott, 1991; Stott, 1992; Stott et al., 1996; Kelly et al., 1996; Thomas et al., 2002; Zachos et al., 2003), 4–5‰ for shallow-water planktonic and benthic foraminifers (Cramer et al., 1999; Cramer and Wright, unpublished data given here), 3.5–5‰ for organic carbon (Steurbaut et al., 2003; Dupuis et al., 2003; Knox et al., 2003), and 6–8‰ for terrestrial paleosol carbonates and mammalian tooth enamel (Bowen et al., 2001; Koch et al., 1992, 1995, 2003). The discrepancy between the magnitude of the shift in these reservoirs indicates that the carbon isotopic gradient between the surface ocean/atmosphere and deep-ocean reservoirs decreased by 1–2‰ during the PETM. The reduction in this gradient is well constrained by foraminiferal isotope records from Site 690 (Fig. 2; Kennett and Stott, 1991), where the carbon isotope value for shallow-dwelling planktonic foraminifers (*Acarinina*) is ~2‰ greater than that for benthic foraminifers prior to the CIE, but is reduced to values similar to (even lower than) benthic and deep-dwelling planktonic foraminiferal values for ~40 k.y. beginning at the onset of the event. Carbon and oxygen isotopic analyses on planktonic foraminifers inferred to have inhabited the thermocline (*Subbotina*) are close to those of benthic foraminifers, consistent with inferences that the southern ocean was a source of deepwater at this time (Pak and Miller, 1992; Thomas et al., 2003).

The gradient between the δ^{13}C values of inorganic carbon in the surface ocean and deep-ocean reservoirs exists as a result of organic carbon produced in the surface water sinking and being oxidized in the deep ocean ("export productivity"). This process is also responsible for an enrichment in inorganic carbon in the deep ocean and a depletion of surface-ocean inorganic carbon and atmospheric pCO$_2$ relative to equilibrium values. The magnitude of the gradient is determined by the relative rates of

export productivity (the sinking organic matter) and ventilation of the deep ocean. Although input of ^{12}C-enriched carbon directly to the atmosphere/surface ocean may have contributed to the initial change in the surface to deep-water $\delta^{13}C$ gradient (e.g., Thomas et al., 2002), this cannot be the cause of a prolonged interval of reduced gradients: because the residence time of carbon in the surface ocean/atmosphere is $\ll 100$ years, maintenance of a reduced atmosphere/surface ocean $\delta^{13}C$ value for ~40 k.y. would require gradually adding ~400 times the amount of ^{12}C-enriched carbon required for an instantaneous shift, which would then be expected to result in a $\delta^{13}C$ decrease throughout the exchangeable reservoirs >10 times the magnitude of the reduction in the surface- to deep-ocean gradient (i.e., a 10–20‰ decrease in the ocean, atmosphere, and biomass). The reduction in the $\delta^{13}C$ gradient instead reflects a net transfer of carbon from the deep ocean to the atmosphere/surface ocean, as a result of reduced export productivity and/or increased ventilation of the deep ocean. A reduction in export productivity is the most likely mechanism (e.g. Kennett and Stott, 1991; Zachos et al., 1993; Thomas and Shackleton, 1996) as has been invoked for a similar reduction in this gradient at the Cretaceous/Tertiary boundary (D'Hondt et al., 1998; Hsü and McKenzie, 1985; Zachos et al., 1989; Adams et al., 2004). Inferences from $\delta^{13}C$ values are relevant to changes in global net export productivity and do not preclude an increase in export productivity at individual sites (e.g., Stoll and Bains, 2003; Thomas et al., 2000) or an increased food supply at the seafloor (Thomas, 2003). Reduced surface productivity does appear to be consistent with calcareous nannoplankton (Bralower, 2002) and planktonic foraminiferal (Kelly et al., 1996) community changes. The ~2‰ increase in planktonic foraminiferal $\delta^{13}C$ values ~40 k.y. after the onset of the CIE at Site 690 (Fig. 2), which is supported by similar increases in other atmosphere/surface-ocean proxy records (Fig. 1), is therefore significant in that it reestablished the same surface to deep-ocean $\delta^{13}C$ gradient that existed prior to the CIE. This implies that the oceanic carbon cycle (productivity and circulation patterns) recovered to pre-PETM conditions by ~40 k.y. after the initial perturbation.

2.3. Temperature and the initial $\delta^{13}C$ perturbation

We regard the initiation of the PETM as being a geologically instantaneous event. This is indicated in high-resolution isotopic records from bulk carbonate from several locations, which show a large shift (1–2‰) between samples taken at centimeter resolution or less (Fig. 3). At all of these sites, sedimentation rates are higher than 1 cm/k.y., so that changes that take place in <1 cm of sediment must have occurred on timescales of hundreds of years. It is also indicated by four studies involving isotopic analyses on single specimen planktonic foraminifers, which show a bimodal distribution of carbon isotopic values separated by 3–4‰ and no intermediate values (level 2 in Figs. 2 and 3; Stott, 1992; Kelly et al., 1996; Thomas et al., 2002; Zachos et al., 2003). Because each foraminiferal test represents less than a single year of growth, if the 3–4‰ shift in $\delta^{13}C$ occurred over an appreciable amount of time, it would be expected that intermediate values would have been measured and these are not observed. The sharp lithologic contact present at many deep-sea sites is also indicative of an extremely rapid onset of the event (Fig. 3); the reduction in surface ocean/atmosphere $\delta^{13}C$ values may have occurred prior to the lithologic change (e.g., at Site 1209, Fig. 3) but such an offset is consistent with a propagation of changes from the surface to the deep sea. Available data suggest that the onset of the event occurred in <100 years, and the available data do not exclude the hypothesis that the initial perturbation occurred in <1 year.

It has recently been claimed that isotopic analyses of single foraminiferal tests show a decrease in $\delta^{18}O$ values beginning prior to the shift in $\delta^{13}C$ values (Thomas et al., 2002), which would indicate that warming occurred prior to the carbon cycle perturbation and might therefore have triggered this perturbation. We believe that these data support a very different conclusion. A linear regression through the $\delta^{18}O$ data in the interval that Thomas et al. (2002) claim shows a warming (between levels 1 and 2, Fig. 2) yields an insignificant slope (0.019 ± 0.056‰/cm, 1σ error), while the mean of all $\delta^{18}O$ values corresponding to pre-CIE $\delta^{13}C$ values higher in the section than level 1 (including the two points higher in the section than level 2) is not significantly different from the mean for all points lower in the section
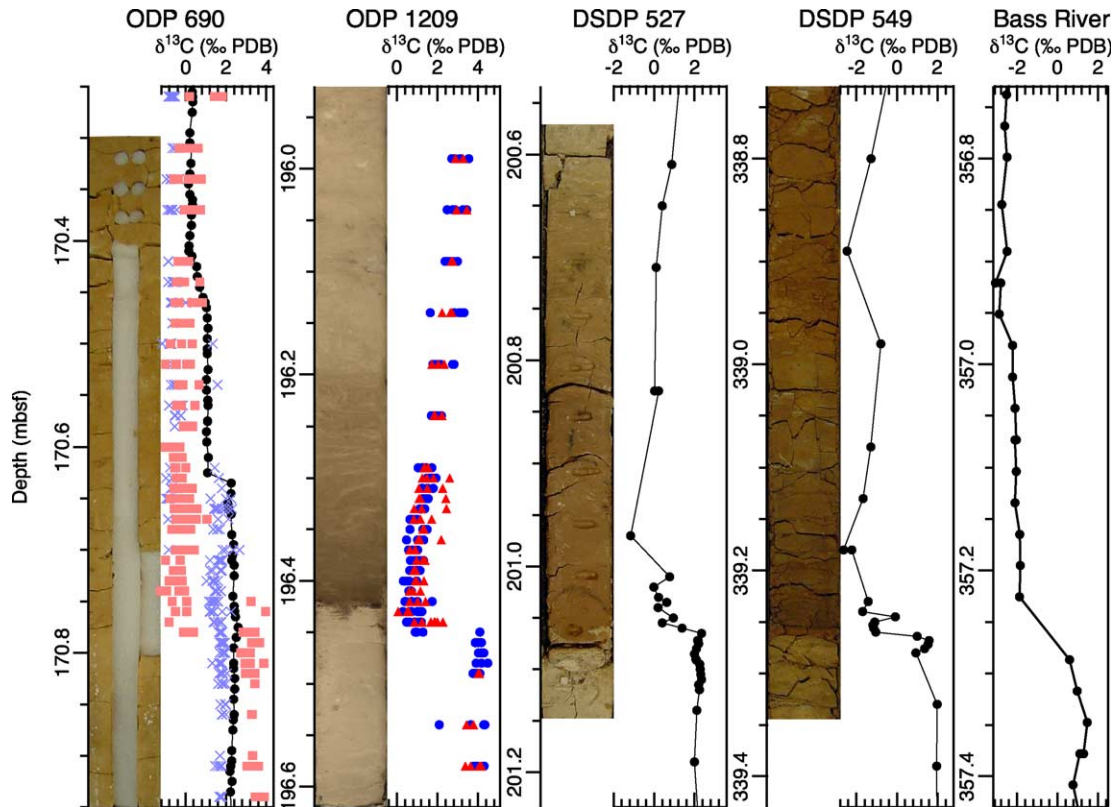
Fig. 3. Carbon isotope records showing abrupt carbon isotope decreases at Sites 690 (Thomas et al., 2002; Bains et al., 1999), 1209 (Zachos et al., 2003), 549 (see Background Data Set), 527 (see Background Data Set), and Bass River (Kent et al., 2003a; see Background Data Set). Core photographs show sharp lithologic contacts at Sites 549, 527, and 1209 nearly coincident with the carbon isotope shifts (Site 1209 photograph courtesy of ODP; other photographs taken for this study). Site 690 is unusual in showing only subtle lithologic changes at the onset of the PETM.

$(-0.45 \pm 0.29‰$ vs. $-0.35 \pm 0.36‰$, 1σ error). The data therefore indicate that any warming was negligible (in statistical phrasing, the data do not support rejection of the null hypothesis that there was no warming trend prior to the initial change in $\delta^{13}C$ values). Moreover, we note that the lowest pre-CIE $\delta^{18}O$ value for an individual planktonic foraminifer is attained during the $\delta^{18}O$ minimum at ~171.5 mbsf, which is not associated with any decrease in $\delta^{13}C$ values. This value is at the nadir of a $>1‰$ decrease in $\delta^{18}O$ values that begins at 172.14 mbsf (Kennett and Stott, 1991), so if the very minor warming possibly evident at ~170.8 mbsf was sufficient to trigger the CIE, it would be expected that a much larger $\delta^{13}C$ decrease should have occurred at ~171.5 mbsf. Cramer et al. (2003) showed convincing evidence that deep-ocean temperatures were highly variable in re-

sponse to precessional climate forcing during the latest Paleocene–earliest Eocene, with a temperature response at eccentricity maxima of up to 4 °C, but that $\delta^{13}C$ decreases associated with these temperature increases were much smaller than the CIE. It is therefore unreasonable to attach undue significance to the disputable evidence of warming immediately prior to the CIE. Similar reasoning undermines the claim that warming preceded the $\delta^{13}C$ perturbation at Sites 865 and 527 (Tripati and Elderfield, 2004). We view the single-specimen planktonic foraminiferal isotopic analyses at Site 690 as strongly supportive of the hypothesis that the carbon cycle perturbation and warming at the PETM were synchronous and occurred geologically instantaneously (although it is not clear why the initial shift in surface-dwelling planktonic foraminiferal isotope values does not occur at the

same level in the records of Thomas et al., 2002, and Kennett and Stott, 1991). In consideration of plausible mechanisms for rapid warming, it is most likely that the carbon cycle perturbation reflected in the $\delta^{13}C$ decrease triggered warming as a result of elevated atmospheric pCO_2.

Assuming that the initial perturbation affected a pool of 2000–4000 Gt of carbon (surface ocean, atmosphere, and some portion of biomass), the decrease of ~4‰ could be explained by the addition of 320–640 Gt of organic carbon ($-25‰$), 130–270 Gt of methane hydrate-derived carbon ($-60‰$), or 170–360 Gt of cometary carbon ($-45‰=$~10-km-diameter comet). Given the magnitude of available sources, these numbers are all plausible. However, the release of methane, oxidation of organic carbon, and collapse of oceanic productivity have the disadvantage of requiring a triggering mechanism, while cometary impact is a viable trigger for all of these as well as being a source of carbon on its own.

Proposed triggers for the release of hydrate are (1) melting in response to rapid changes in ocean circulation resulting from the gradual (59–51 Ma) warming trend (e.g., Zachos et al., 2001, and see Zachos et al., 1993), perhaps aided by volcanism associated with the North Atlantic igneous province (Thomas and Shackleton, 1996) and Caribbean explosive volcanism (Bralower et al., 1997), somehow causing a rapid warming of bottom water; (2) a greenhouse warming feedback mechanism relying on minor warming to release an initial pulse of methane to the atmosphere, resulting in further warming (Thomas et al., 2002); and (3) catastrophic slope failure along the North and South American Atlantic continental margin, presumably oversteepened by several million years of erosion (Katz et al., 2001).

Thermal dissociation (which includes the first two triggers listed above) is not a viable mechanism for releasing ~200 Gt C to the atmosphere. As discussed above, this quantity is equivalent to the total quantity of hydrate-derived carbon that could potentially have been released during equilibration of the sediment geothermal gradient to the peak PETM deep/intermediate ocean temperatures. This equilibration would require ~3000 years (Katz et al., 2001), but instead, it appears that the increase in deep/intermediate ocean temperatures (at depths where methane hydrate would have existed) lagged

the initial carbon cycle perturbation by several thousand years (Thomas et al., 2002). Moreover, thermal dissociation would result in release of methane to the water column above the depth of hydrate stability and an empirical study has shown that in such a case, most of the methane will be dissolved and oxidized in the deep ocean (Rehder et al., 2002), buffering its effect on surface ocean/atmosphere $\delta^{13}C$ values. Catastrophic slope failure (the third proposed trigger) is a more viable mechanism for rapid addition of carbon from methane hydrates to the atmosphere, since in this case, the methane would be released into the water column below the depth of hydrate stability (e.g., Rehder et al., 2002) and would escape sequestration in authigenic carbonates precipitated within the sediment (Milkov and Sassen, 2003). The 200 Gt of carbon required to account for the full atmosphere/surface-ocean shift is large, however, given that only ~35 Gt C is present as methane hydrate or gas in the 26,000-km^2 area of the Blake Ridge, a region thought to be relatively hydrate rich. Slope failure would have had to occur over an extended area; although Katz et al. (2001) presented evidence that this may in fact have happened, slope failure over such an extended region within a very short (<1 k.y.) period would require a high-energy trigger.

The amount of organic carbon required to explain the atmosphere/surface-ocean shift (~500 Gt) is equivalent to 10–20% of the estimated marine and terrestrial organic carbon reservoir (Table 1), but only 2–4% of the estimated late Paleocene buildup in longer term terrestrial organic deposits such as peat (Kurtz et al., 2003). There is evidence indicating that extensive fires occurred during the PETM, possibly coincident with the onset of the CIE (Collinson et al., 2003; Kaiho et al., 2003), which might in part reflect burning of large peat deposits (Kurtz et al., 2003). Again, however, the instantaneous nature of the initial atmosphere/surface ocean $\delta^{13}C$ shift would require a trigger for fires that would have had to cover a significant fraction of the global continental area.

Both the hydrate dissociation and peat burning hypotheses have been presented under the assumption that the several million-years-long warming trend from the late Paleocene to early Eocene was gradual and monotonic. Indeed, most authors have considered that the PETM resulted when this gradual warming

crossed some "critical threshold" that resulted in a rapid change in Earth's climate state, or as a result of a volcanic perturbation to the otherwise gradually changing climate (e.g., Zachos et al., 1993; Thomas and Shackleton, 1996; Bralower et al., 1997). However, Cramer et al. (2003) demonstrated that Earth's climate and carbon cycle were highly variable throughout the late Paleocene–early Eocene, when numerous episodes similar to the PETM, but of much smaller magnitude, occurred at maxima in Earth's orbital eccentricity. Because episodes of significant insolation-driven climate change did not lead to carbon isotope shifts of the magnitude of the CIE, and insolation-driven climate variations were relatively small at the initiation of the PETM, Cramer et al. (2003) concluded that the closely coupled CIE and PETM must have been triggered by an event external to the normal climate system.

Given the lack of any connection between the timing of the CIE and standard climate forcing mechanisms, the fact that an irresolvably rapid, large initial decrease in δ^{13}C values is observed synchronous with an irresolvably rapid, large temperature increase points to an external (to the climate system) trigger for the event. The rate of change exceeded the rate at which parts of Earth's climate that have principally been implicated in causing the event are capable of changing: the rate of ocean circulation limits significant changes in deep-water temperature and the oceanic carbon cycle to timescales of ~1000 years, while sediment thermal diffusivities limit the time it would take to appreciably warm sediment at depths where significant hydrate occurs to ~2000 years (Katz et al., 2001), and we believe that an extraterrestrial impact is the only reasonable external trigger. The rapidity and magnitude of the initial climate change at the PETM renders triggering mechanisms involving ocean circulation changes or melting of methane hydrate untenable.

3. Comet impact scenario for the PETM

We believe that the large amount of energy involved in a bolide impact is the most plausible explanation for the geologically instantaneous onset of the PETM, but a mechanism must be identified that could plausibly extend the climate perturbation to the carbon cycle for the duration of the PETM. The perturbation to the carbon cycle is indicated both by δ^{13}C variations and by globally warmer temperatures, which can only reasonably be explained by an increase in atmospheric pCO$_2$ levels.

We have undertaken a modeling exercise to determine the feasibility of accounting for the PETM as a "bolide summer" resulting from feedbacks following an impact. The model is highly simplified: we have made the assumption that the atmosphere and surface ocean are fully equilibrated on ~100-year timescales, and that the deep ocean is equilibrated with these reservoirs on ~1000-year timescales, and the model conditions are calculated only at a few select times post-impact (Table 2, Fig. 4). The model is forced by the addition of quantities of ^{12}C-enriched carbon in order to match the δ^{13}C trends observed in geologic records. The addition of a large quantity of carbon will initially cause a rise in atmospheric pCO$_2$ and ocean $\sum$CO$_2$, the latter resulting in a rise in [HCO$_3^-$] and decrease in [CO$_3^{2-}$] in order to maintain charge balance in the oceans. The decrease in [CO$_3^{2-}$] during the PETM is reflected in decreased carbonate preservation, resulting in a sharp lithologic contact at many deep sea sites (see Fig. 3). On longer timescales, the decreased carbonate preservation would lead to a buildup of positively charged ions (e.g., Ca^{2+}, Mg^{2+}) in the ocean, eventually leading to removal of the excess $\sum$CO$_2$ through deposition of excess carbonate (e.g., Broecker and Peng, 1987), which we model by removing quantities of carbon as carbonate (having a surface ocean δ^{13}C value) equivalent to the amount added (Table 2). We calculated variations in δ^{13}C values, atmospheric pCO$_2$, and ocean [CO$_3^{2-}$] (Table 2, Fig. 4) in response to the model forcing. We also calculated the range of temperature increase implied by the calculated increase in atmospheric pCO$_2$ (shaded region in Fig. 4), although for simplicity a 5 °C temperature increase was imposed in the model. The scenario we present is highly speculative, and we acknowledge that other forcing mechanisms could have been chosen that would be equally consistent with available data, but it is useful to assess the forcing required to account for the PETM in the absence of substantial methane hydrate.

We assume that the event that triggered the PETM was the impact of a ~9-km-diameter comet, delivering ~150 Gt of carbon δ^{13}C = −45‰) directly to the

Table 2
Modeled variation in the carbon cycle during PETM[a]

Time from impact	pCO_2 (ppmv)[b]	$[TCO_2]$ (mol/m^3)[b]		$[CO_3^{2-}]$ (mol/m^3)[b]	$\delta^{13}C$ (‰ PDB)[b]			T anomaly[c]	
	Atm[b]	Surface	Deep	Deep	Atm	Surface	Deep	Minimum	Maximum
Pre-PETM	386	2.18	2.45	0.078	−4.5	3.5	1.5	−0.0	−0.0
Impact (<10 years)	456	2.18	2.45	0.078	−10.8	3.5	1.5	0.4	1.1
100 years	653	2.22	2.45	0.078	−9.3	−1.3	1.5	1.1	3.4
2000 years	1266	2.31	2.48	0.060	−6.9	1.1	0.3	2.6	7.7
20,000 years	1157	2.30	2.47	0.065	−7.7	0.3	−0.5	2.4	7.1
50,000 years	386	2.18	2.45	0.078	−7.1	0.9	−0.9	0.0	0.0
120,000 years	386	2.18	2.45	0.078	−4.8	3.2	1.3	0.0	0.0

Time from impact	T (°C)[d]		Organic input[d] (Gt C)	Excess CaCO$_3$[d] (Gt C)	Sources of forcing
	Surface	Deep			
Pre-PETM	20	12	0	0	
Impact (<10 years)	20	12	0	0	input of cometary C (150 Gt, −45‰)
100 years	25	12	450	0	atmosphere/surface ocean mixing; organic C input
2000 years	25	17	1800	0	deep-ocean mixing; organic C input; decrease in biopump
20,000 years	25	17	1100	1500	organic C input, CaCO$_3$ compensation
50,000 years	20	12	0	2000	recovery of biopump, CaCO$_3$ compensation
120,000 years	20	12	0	0	$\delta^{13}C$ recovery, ocean carbon replacement

[a] Formulas and parameters used in the calculations were taken from Toggweiler (1999).
[b] Calculated model response.
[c] Estimated response to atmospheric pCO_2 variations. Minimum estimate assumes a temperature response of 1.5 °C/ pCO_2 doubling, maximum estimate assumes 4.5 °C/ pCO_2 doubling.
[d] Imposed forcing.

atmosphere. This would have instantaneously raised atmospheric pCO_2 by ~70 ppmv and lowered atmospheric $\delta^{13}C$ by ~7‰ before mixing with the surface ocean. Although we chose to use a large comet in our model, a similar perturbation to atmospheric pCO_2 could be obtained with a smaller bolide impact triggering release of terrestrial carbon stores. Effects resulting from a high-energy impact that might release carbon to the atmosphere include (1) superheating of the atmosphere from the shock wave preceding the bolide as well as dispersion of melted material excavated at the site of impact and from the bolide itself, which have been implicated in widespread fires at the K/T boundary (but see Belcher et al., 2003) and could account for fires that have been more firmly documented coincident with the CIE (Collinson et al., 2003; Kaiho et al., 2003); (2) a large tsunami in the event of an oceanic impact, which has been implicated at the K/T boundary in slope failures along the North American Atlantic continental margin and widespread turbidite deposits (Norris and Firth, 2002; Olsson et al., 2002) and could account for slope failure at the P/E boundary documented along the North American

Atlantic continental margin (Katz et al., 2001), potentially releasing methane and/or hydrocarbon reserves (although we note that there was no whole-ocean $\delta^{13}C$ decrease at the K/T boundary); (3) vaporization of the impactor and target rock (e.g., O'Keefe and Ahrens, 1989); and (4) in the event of an oceanic impact, the initial warming would have been enhanced by rapid venting of much of the excess deep-ocean CO_2 to the atmosphere and enhanced atmospheric H_2O. In fact, our choice of a large comet minimizes the initial perturbation to the carbon cycle: reducing the size of the comet, or assuming a non-carbon-rich bolide, would force us to add more carbon from a less ^{12}C-enriched source in order to account for the initial decrease in $\delta^{13}C$ values.

In order to produce a ~5‰ decrease in surface ocean/atmosphere $\delta^{13}C$ values, we added an additional ~450 Gt of organic carbon ($\delta^{13}C=-25‰$) to the atmosphere and surface ocean within ~100 years following the impact. This additional carbon could have come from burning (either impact-induced or as a result of impact-induced climate warming) of terrestrial biomass and organic-rich deposits, re-
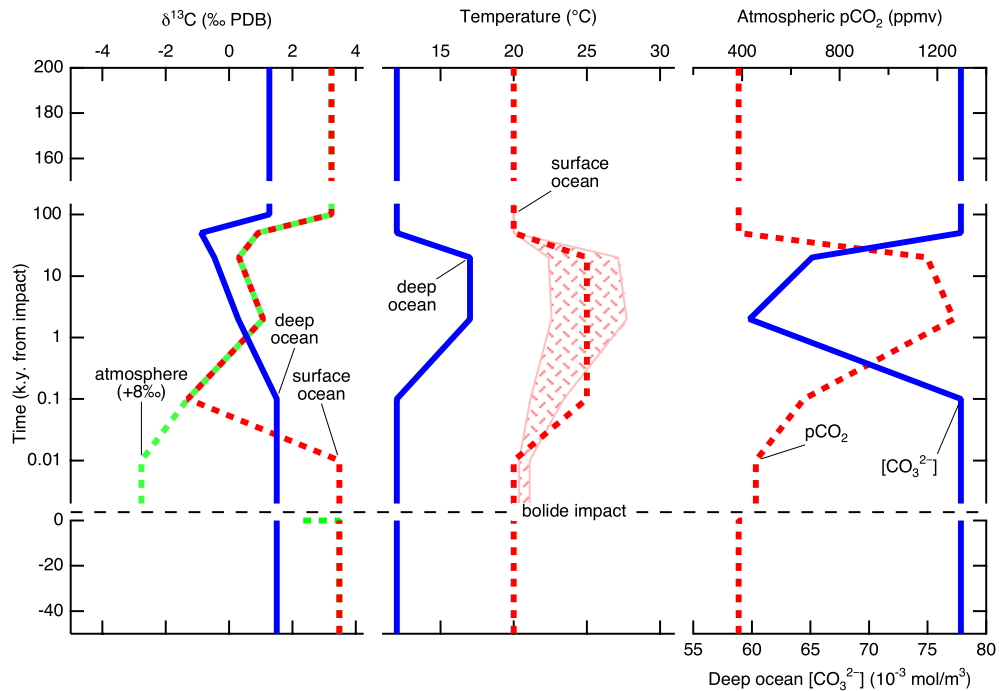
Fig. 4. Schematic diagram of climate and carbon cycle effects during the PETM, according to the model in Table 2. In the temperature plot, lines show the imposed model forcing, while the shaded region indicates the expected response from the pCO_2 variations resulting from the model, based on an assumption of 1.5–4.5 °C temperature increase per pCO_2 doubling. Note that the timescale for the central portion of the plot is expanded and plotted on a logarithmic scale.

duced productivity/reduction in the biological pump (thereby retaining CO_2 in the surface ocean/atmosphere that would otherwise have been transported to the deep ocean as organic carbon or sequestered in terrestrial biomass), and/or release of methane or hydrocarbon reserves as a result of slumping along continental margins. Although sources such as methane hydrate are substantially more enriched in ^{12}C than organic carbon, it is likely that carbon from sources less ^{12}C enriched (deep-ocean $\sum CO_2$, carbonate sediments) would have been released. We regard the amount of carbon added in our model as a conservative estimate of the amount that must have been added to account for the surface-ocean/ atmospheric $\delta^{13}C$ decrease. Most realistic changes in the assumptions (e.g., using a smaller or non-carbon-rich bolide) would require a larger input of carbon to account for the $\delta^{13}C$ decrease, and it is likely that a substantial amount of isotopically "neutral" carbon would have been released at the time of impact. In the scenario, we present atmo-

spheric pCO_2 increases by an additional ~195 ppmv (to ~265 ppmv above pre-impact conditions) both as a direct result of added carbon and indirectly due to reduced solubility of CO_2 in warmer surface ocean waters (~15 ppmv). The increase in atmospheric pCO_2 in this scenario would not appear to be sufficient to account for a ~5 °C increase in surface temperatures (as indicated by the $\delta^{18}O$ data from Site 690), suggesting that the net $\delta^{13}C$ value of the carbon added was more positive than the organic carbon source we assume.

Benthic foraminiferal isotope records have been unable to capture the shape of the decrease in deep/ intermediate ocean $\delta^{13}C$ values. At Site 690, two different inferences can be made on the basis of isotopic analyses of *Subbotina*, a deep-dwelling planktonic foraminifer, and bulk carbonate, which is primarily made up of deep-dwelling calcareous nannofossils. *Subbotina* $\delta^{13}C$ values at 690 are similar to those of benthic foraminifers prior to the event, but diverge from the benthic records during

the recovery from the event; these indicate an abrupt decrease in δ^{13}C values by 2‰ with only a minor subsequent decrease (Fig. 2). The bulk carbonate δ^{13}C values are consistently offset from those of benthic foraminifers by ~1‰ throughout the event and show a series of decreases, with an initial abrupt ~1.2‰ decrease followed by a further ~1.2‰ over ~60 k.y., most of which occurred at ~20 k.y. following the initiation of the event. We assume that the shape of the bulk carbonate record mimics that of deep-ocean δ^{13}C during the interval of this decrease, as it does in the portion of the record where benthic foraminiferal δ^{13}C values are available. In our speculative model, we therefore add 1800 Gt of carbon with an organic carbon δ^{13}C signature to the ocean/atmosphere within 2000 years following the bolide impact, during which time the initial perturbation to the surface ocean/atmosphere would have been mixed into the deep ocean. In addition, we assume that reduced export productivity relative to pre-PETM conditions (a 60% reduction in our model) resulted in a ~1.2‰ reduction in the surface- to deep-ocean δ^{13}C gradient. The reduction in the biological pump (54 ppmv) and reduced solubility of CO_2 in the warmer deep ocean (65 ppmv) contribute to a rise in atmospheric pCO_2, but more significantly, these processes result in the bulk of the added carbon pooling in the atmosphere, in total raising pCO_2 by an additional ~615 ppmv to ~1270 ppmv. This level (~$3.3 \times$ pre-PETM pCO_2) is sufficient to account for a 3–9 °C increase in global surface temperatures (Houghton et al., 2001; Crowley and Hegerl, 2003).

We call on an additional 1100 Gt of carbon from an organic source over the subsequent 20 k.y. and removal of 1500 Gt of carbon through carbonate sedimentation. The combined effect is to further decrease deep-ocean δ^{13}C values to 2‰ less than pre-PETM values, with a slight decline in atmospheric pCO_2 since more carbon is removed than is added. Although no ^{12}C-enriched carbon is added between 20 and 50 k.y. following the impact, deep-ocean δ^{13}C values continue to decrease as a result of excess carbonate sedimentation, removing 2000 Gt of carbon to bring the atmosphere/ocean carbon reservoir back to its pre-impact size. Removal of carbon combined with recovery of the biological pump results in a rapid decrease in atmospheric pCO_2 levels to nearly

pre-PETM levels, which should have resulted in a temperature decrease. Surface ocean δ^{13}C values increase as a result of the recovery of the biological pump while deep-ocean δ^{13}C values continue to decline due to excess carbonate sedimentation, which we assume has a surface ocean δ^{13}C value and is therefore less ^{12}C-enriched than the mean ocean. Recovery of δ^{13}C values to pre-PETM conditions occurs by ~120 k.y. as a result of the constant cycling of carbon through the ocean.

Our scenario makes the following predictions: (1) a total input of 3500 Gt C, which in combination with a reduction in the biological pump would have driven a fourfold increase in atmospheric pCO_2; (2) the temperature increase must have occurred primarily as a result of the perturbation to the carbon cycle, but because the bulk of additional carbon would have been input to the atmosphere (through oxidation of organic carbon stores), it is not expected that the lag could be observed in the geologic record, except possibly in highly expanded sections; (3) carbonate compensation offsetting the addition of carbon would have led to a relatively stable warm climate through several tens of thousands of years prior to recovery of the biological pump; (4) perturbations to the deep-water environment, including the benthic foraminiferal extinction, should have occurred in the first few thousand years following impact, in conjunction with lithologic changes related to carbonate dissolution. It is worth noting that the larger amount of carbon added in our scenario predicts a greater decrease in ocean sediment carbonate content than that predicted by the hydrate dissociation hypothesis.

In this model, the important role of the reduction in the biological pump is highlighted: although the ocean carbonate system would be expected to compensate for the addition of excess carbon on 10 k.y. timescales (Broecker and Peng, 1987), atmospheric pCO_2 would have remained high until recovery of organic carbon export to the deep ocean. There is good evidence that a reduction in the biological pump occurred – the reduction in the surface-to-deep ocean δ^{13}C gradient – but the mechanism for this reduction is unclear. In seeking to explain a similar reduction following the K/T impact event, Hsü and McKenzie (1985) called on a "Strangelove ocean" with very

reduced productivity, but D'Hondt et al. (1998) pointed out that such a productivity crash would only be expected during a very brief initial period of high atmospheric dust and reduced sunlight. Instead, D'Hondt et al. (1998) proposed that there was an increase in the proportion of organic production reconverted to inorganic form in the surface waters. In our model, we used a ~60% reduction in the biological pump; as pointed out by D'Hondt et al. (1998), this could be effected by an increase in the efficiency of surface-ocean organic carbon degradation from 90% to 97%, an effect that might be difficult to discern in proxy data.

Finally, we recognize that our model requires the input of a large amount of organic carbon and therefore relies heavily on the hypothesis of Kurtz et al. (2003) that terrestrial deposits of peat were much larger in the late Paleocene than today and could have been rapidly released during the PETM by wildfires occurring during a much warmer climate. In some sense, this hypothesis is similar to the invocation of a much larger hydrate reservoir during the late Paleocene, but Kurtz et al. (2003) have presented good arguments for excess terrestrial sequestration of 15,000 Gt of carbon during the late Paleocene, supported by their analysis of carbon and sulfur isotope data as well as known late Paleocene coal reserves, whereas warmer bottom-water temperatures require a smaller gas hydrate stability zone and no evidence has been presented that would indicate a larger methane hydrate reservoir than today. If Cramer et al. (2003) are correct in ascribing orbitally forced decreases in $\delta^{13}C$ values of up to 1‰ to variations in the relative deposition rates of carbonate vs. organic carbon, and if the same response was triggered at the PETM, then the amount of added carbon might have been half as much as we propose. However, this would imply a smaller increase in atmospheric pCO_2 levels and require that the global temperature sensitivity to pCO_2 levels was at the high end of the quoted range, rather than in the middle (Fig. 4).

4. Summary

While extraterrestrial impact has received serious consideration as the trigger for "instantaneous" en-

vironmental perturbations at other geologic boundaries, the possibility of an impact trigger for the PETM has received very little attention. Instead, most authors have focused on the magnitude of the $\delta^{13}C$ decrease and the hypothesis that this resulted from dissociation of methane hydrates. However, analyses now show that the methane hydrate reservoir was unlikely to have been large enough to account for the carbon isotopic perturbation, and that physical limitations to the rate at which thermal dissociation of hydrate could occur make it an implausible mechanism to account for the extremely rapid initial decrease in $\delta^{13}C$ values, especially given the evidence for stable pre-CIE temperatures at intermediate water depths where hydrate would have existed. Furthermore, methane hydrate as a sole source for the CIE cannot explain the extreme variations in climate and ecological perturbations that occurred: the very low $\delta^{13}C$ value of methane hydrate minimizes the amount of carbon needed to account for the CIE, while the thermal dissociation mechanism requires that the documented warming preceded and was independent of the perturbation to the carbon cycle. It is more reasonable to assume that the 4–5 °C temperature increase resulted from the perturbation to the carbon cycle that is reflected in the decrease in $\delta^{13}C$ values.

The instantaneous onset of the PETM, the top–down progression of environmental changes in the oceans, and the extreme perturbations to the surface environment are all consistent with a bolide impact. There is already tantalizing independent evidence that an impact occurred at the time of the PETM and the "bolide summer" hypothesis makes specific predictions that should motivate further investigations: we expect (1) normal climate variability prior to an abrupt onset of the event; (2) tracers of an impact corresponding to the abrupt initial climate perturbation; (3) a much larger decrease in carbonate preservation than that predicted by the hydrate dissociation hypothesis; (4) evidence for widespread terrestrial fires as a source of carbon; (5) a global net reduction in export productivity. To our knowledge, none of these predictions has been disproven, while some of them are supported by available data. Researchers involved in studies of the P/E boundary should consider whether their data

are consistent with the idea of an impact trigger for the event.[2]

Although there are no mass extinctions among planktonic organisms at the PETM, in contrast to the K/T boundary, we take the perspective that this more likely resulted from a difference in severity and character of perturbations to the surface environment rather than a difference in the ultimate cause of the changes. The perturbation in the surface-ocean environment at the K/T boundary was severe enough that pre-existing species were unable to maintain any ecological niche during the aftermath; as a result, the post-perturbation community was made up of the few survivors and newly evolved species. At the P/E boundary, pre-existing species were able to maintain viable populations in refugia, although at many sites they were temporarily absent or greatly reduced in abundance. The transient nature of these changes should be interesting from an evolutionary perspective: the P/E boundary may represent an event nearly serious enough to cause a global mass extinction, but the severity of the kill mechanisms fell somewhat short, allowing pre-existing communities to become reestablished and diversify following the climatic perturbation. In contrast, the major changes in ocean carbonate chemistry and export productivity evidently did lead to the mass extinction among benthic foraminifers at the P/E boundary.

In conclusion, we invoke a (cometary) bolide impact to explain the established extremely rapid

surface environment warming and carbon cycle perturbation at the onset of the PETM. We believe that this initial warming would have led to widespread burning of terrestrial peat deposits, as hypothesized by Kurtz et al. (2003), producing an extended period of high atmospheric pCO_2 and the warm climate of the PETM. The already extremely detailed documentation of the PETM may provide an excellent opportunity to examine the environmental and biological perturbation and recovery following a bolide impact.

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[2] During final revision of this manuscript, an alternative hypothesis was published that may be able to explain the initial, rapid decrease in $\delta^{13}C$ values at the onset of the CIE as the result of emplacement of basaltic sills in the northeast Atlantic (Svensen et al., 2004). Heating of organic-rich sediment surrounding the sills would result in the generation of large amounts of thermogenic methane (note that this is not hydrate-sourced methane); if sill emplacement and subsequent methane production was extremely rapid, then enough methane could potentially have been vented to the atmosphere to explain the initial atmosphere/surface ocean $\delta^{13}C$ decrease. While this hypothesis merits further investigation, we note that it does not obviously provide an explanation for the Ir and MNP anomalies and that the large amount of energy released virtually instantaneously in a bolide impact seems more consistent with the perturbation to surface marine biota documented synchronous with the extremely rapid initial decrease in $\delta^{13}C$ values. In any case, we believe that a carbon cycling scenario similar to the one we outline would still be necessary to explain the full event.

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