

## Uncorking the bottle: What triggered the Paleocene/Eocene thermal maximum methane release?

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**Abstract.** The Paleocene/Eocene thermal maximum (PETM) was a time of rapid global warming in both marine and continental realms that has been attributed to a massive methane (CH<sub>4</sub>) release from marine gas hydrate reservoirs. Previously proposed mechanisms for this methane release rely on a change in deepwater source region(s) to increase water temperatures rapidly enough to trigger the massive thermal dissociation of gas hydrate reservoirs beneath the seafloor. To establish constraints on thermal dissociation, we model heat flow through the sediment column and show the effect of the temperature change on the gas hydrate stability zone through time. In addition, we provide seismic evidence tied to borehole data for methane release along portions of the U.S. continental slope; the release sites are proximal to a buried Mesozoic reef front. Our model results, release site locations, published isotopic records, and ocean circulation models neither confirm nor refute thermal dissociation as the trigger for the PETM methane release. In the absence of definitive evidence to confirm thermal dissociation, we investigate an alternative hypothesis in which continental slope failure resulted in a catastrophic methane release. Seismic and isotopic evidence indicates that Antarctic source deepwater circulation and seafloor erosion caused slope retreat along the western margins of the North Atlantic in the late Paleocene. Continued erosion or seismic activity along the oversteepened continental margin may have allowed methane to escape from gas reservoirs trapped between the frozen hydrate-bearing sediments and the underlying buried Mesozoic reef front, precipitating the Paleocene/Eocene boundary methane release. An important implication of this scenario is that the methane release caused (rather than resulted from) the transient temperature increase of the PETM. Neither thermal dissociation nor mechanical disruption of sediments can be identified unequivocally as the triggering mechanism for methane release with existing data. Further documentation with high-resolution benthic foraminiferal isotopic records and with seismic profiles tied to borehole data is needed to clarify whether erosion, thermal dissociation, or a combination of these two was the triggering mechanism for the PETM methane release.

### 1. Introduction

A catastrophic, transient event at the Paleocene/Eocene (P/E) boundary (~55 Ma) led to rapid global warming, severe perturbation of the Earth's exogenic carbon cycle, and dramatic changes in marine and terrestrial ecosystems. During the Paleocene/Eocene thermal maximum (PETM; formerly known as the latest Paleocene thermal maximum, or LPTM), deep-ocean and high-latitude surface water temperatures rose by ~4°–6°C [e.g., Kennett and Stott, 1991; Zachos et al., 1993; Thomas and Shackleton, 1996; Katz et al., 1999] in <5000 years [Katz et al., 1999; Norris and Röhl, 1999; Röhl et al., 2000], archaic mammals died out while modern mammalian ancestors appeared in the geologic record [Hooker, 1996; Clyde and Gingerich, 1998], and many deep-sea species became extinct or disappeared temporarily [e.g., Tjasma and Lohmann, 1983; Steineck and Thomas, 1996].

The PETM coincided with a dramatic decrease of ~2–4‰ in δ<sup>13</sup>C values worldwide, called the “carbon isotope excursion” (CIE) [e.g., Kennett and Stott, 1991; Koch et al., 1992; Bralower et al., 1995; Katz et al., 1999]. The CIE occurred in <5 kyr and lasted ~150–220 kyr [Katz et al., 1999; Norris and Röhl, 1999; Röhl et

al., 2000]; it was followed by an exponential return to preexcursion δ<sup>13</sup>C values as excess <sup>12</sup>C was eventually transferred out of the ocean-atmosphere carbon reservoir, which is consistent with estimates of the modern residence time of carbon [Dickens, 2000]. Methane derived from frozen gas hydrate and underlying free and dissolved gas reservoirs (mean δ<sup>13</sup>C = ~–60‰ [see Kvenvolden, 1995]) is a plausible source for the large, rapid carbon isotopic change recorded at the P/E boundary [Dickens et al., 1995; Kaiho et al., 1996]. The rapid escape of 1500–2200 gigatons (Gt) of isotopically light CH<sub>4</sub> from multiple marine gas hydrate reservoirs stored within continental slope sediments and the subsequent transfer of CH<sub>4</sub> to the ocean-atmosphere system [Dickens et al., 1995, 1997a; Kaiho et al., 1996; Dickens, 2000, 2001] has become known as the “methane hydrate dissociation hypothesis.” An alternative source that may account for some or all of the CIE is a <sup>12</sup>C-enriched bolide [Wilde and Quinby-Hunt, 1997].

In this paper, we establish constraints on the proposed PETM thermal dissociation by modeling heat flow through the sediment column and determining the effect of the temperature change on the gas hydrate stability zone (GHSZ) through time. We also provide seismic evidence tied to borehole data for methane release along portions of the U.S. continental slope. Because our modeling results and the paleobathymetric distribution of the methane release sites do not conclusively confirm thermal dissociation as the causal mechanism for the PETM methane release, we consider erosion of continental slope sediments as an alternative trigger for methane release.

### 2. Thermal Dissociation Hypothesis

The PETM and CIE were short-term climatic perturbations superimposed on a long-term global warming trend that began in

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the late Paleocene at  $\sim 56.5$  Ma and continued for  $\sim 5$  Myr, culminating in the early Eocene at  $\sim 51.5$  Ma [Shackleton *et al.*, 1984; Miller *et al.*, 1987; Zachos *et al.*, 2001]. A gradual warming of the deep sea during this long-term warming trend would have caused a slow change in the temperature-pressure stability field of frozen gas hydrate, resulting in a gradual transfer of methane from gas hydrate reservoirs to the oceans. This gradual transfer could not have produced the rapid isotopic changes observed at the CIE, contrary to previous studies that have proposed incorrectly that long-term warming passed a critical temperature threshold for methane hydrate stability [e.g., Norris, 2001]. Instead, a rapid water temperature increase is required to trigger widespread thermal dissociation, presumably through a change in deepwater source region [Dickens *et al.*, 1995].

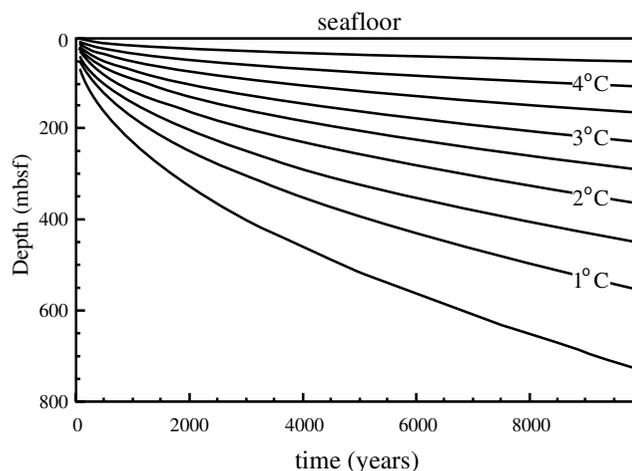
As proposed [Dickens *et al.*, 1995, 1997a; Kaiho *et al.*, 1996], the methane hydrate dissociation hypothesis maintains that long-term global warming during the late Paleocene [Shackleton *et al.*, 1984; Miller *et al.*, 1987; Zachos *et al.*, 2001] pushed the ocean-atmosphere system past a critical threshold [Zachos *et al.*, 1993; Thomas, 1998], causing warm surface waters to sink and intermediate to deep ocean temperatures to rise. This warming would have propagated into the sediments, melting once solid  $\text{CH}_4$  hydrates and releasing free gas bubbles into the sediments [Dickens *et al.*, 1995, 1997a; Kaiho *et al.*, 1996]. Thermal dissociation would have created an increase in sediment pore pressure and destabilized the sediment column, resulting in slope failure and the release of massive quantities of  $\text{CH}_4$  into the ocean. Methane release would have occurred on continental slopes between 900 and 2000 m water depth because all gas hydrate at these depths would have been prone to dissociation in the Paleocene with a  $4^\circ$ – $6^\circ\text{C}$  rise in bottom water temperature [Dickens *et al.*, 1995]. The gaseous  $\text{CH}_4$  would have reacted with dissolved  $\text{O}_2$  (likely via bacterial activity [Paull *et al.*, 1995; Buffett and Zatsepin, 2000]) to produce  $^{12}\text{C}$ -enriched  $\text{CO}_2$ , adding carbon to all global exogenic carbon reservoirs and significantly shoaling the depth of carbonate dissolution in the ocean [e.g., Dickens *et al.*, 1995, 1997a; Thomas, 1998; Katz *et al.*, 1999; Dickens, 2000]. Higher bottom water temperature, lower dissolved  $\text{O}_2$ , changes in surface water productivity, and/or more corrosive deep waters precipitated the extinction of many deep-sea species [e.g., Thomas, 1998].

## 2.1. Constraints on Thermal Dissociation: Heat Flow Model

Here we develop a simple model using heat flow parameters to assess temperature anomaly propagation through sediments and the expected duration and timing of the observed PETM isotopic changes. Within the context of published isotopic records, this model places narrow constraints on the boundary conditions under which sufficient amounts of methane could have been released via thermal dissociation alone at the PETM.

The deepwater temperature warming at the onset of the PETM is  $\sim 4^\circ$ – $6^\circ\text{C}$ , based on  $\delta^{18}\text{O}$  records [Kennett and Stott, 1991; Pak and Miller, 1992; Bralower *et al.*, 1995; Thomas and Shackleton, 1996; Katz *et al.*, 1999]. If thermal dissociation triggered the PETM methane release, then heat resulting from this deepwater warming must have propagated through the sediments of the GHSZ and melted the concentration of frozen hydrate that can form a seal at the base of the GHSZ [e.g., Kvenvolden, 1993], allowing methane to escape from both the melted gas hydrates and the free gas reservoir below [Dickens *et al.*, 1997b]. Heating at the base of the GHSZ must have been sufficient to release the  $\sim 1500$ – $2200$  Gt of C necessary to explain the CIE [Dickens, 2000].

To address this proposed heat flow scenario, we model the propagation of a temperature increase from the sediment-water interface through the underlying sediments (Figure 1). This model assumes one-dimensional heat flow through the sediments, an initial sediment surface temperature  $T_{is}$ , an increase in water



**Figure 1.** An instantaneous  $5^\circ\text{C}$  water temperature increase will propagate through the underlying sediments as a function of time. See text for input parameters.

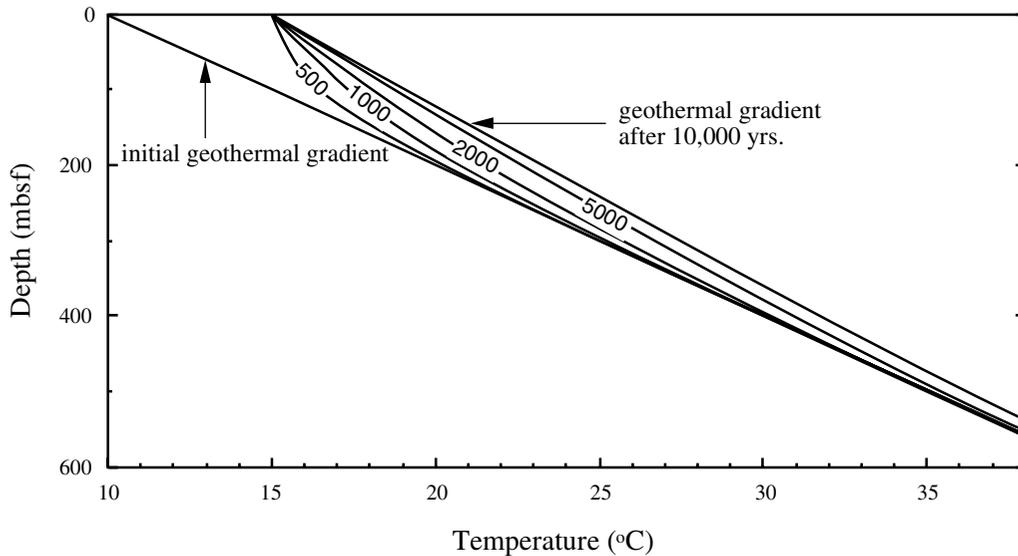
temperature at the sediment surface  $\Delta T_{is}$ , a geothermal gradient  $\beta$ , and a thermal diffusivity  $\kappa$  (adapted from Carslaw and Jaeger [1959, equation (13), p. 61] and Turcotte and Schubert [1982, problem 4–34]). An analysis of this model gives the change in temperature  $dT_z$  as a function of time  $t$  and depth  $z$ :

$$dT_z/\Delta T_{is} = \text{erfc} [z/(2(\kappa t)^{1/2})], \quad (1)$$

where erfc is the complementary error function (erfc = 1 – error function; values are from standard tables, e.g., Carslaw and Jaeger [1959, p. 485] and Turcotte and Schubert [1982, p. 161]),  $T_z = T_{is} + \beta z + dT_z$ ,  $\kappa = 3 \times 10^{-7} \text{ m}^2/\text{s}$  ( $=9.46 \text{ m}^2/\text{yr}$  [Hyndman *et al.*, 1979; Dickens *et al.*, 1995]), and  $\Delta T_{is} = 5^\circ\text{C}$  (approximate observed deepwater warming at the PETM).

We simplify our heat flow model with several assumptions that result in a maximum rate of temperature anomaly propagation (thereby favoring thermal dissociation); a more realistic analysis would lengthen the time required for the temperature increases predicted by this model. We use an instantaneous  $5^\circ\text{C}$  water temperature increase; in reality, the temperature increase resulting from a change to a warm, low-latitude deepwater source could take as long as the mixing time of the oceans (1000–2000 years). Furthermore, the phase change required to melt the frozen gas hydrate within the sediments would slow the propagation of the temperature anomaly because of the latent heat consumed when methane hydrate dissociates to methane and water ( $4.5 \times 10^8 \text{ J/m}^3$  [Sloan, 1990]). Additional factors complicate attempts to model this phase change, such as the variable surface area of hydrate particles, formation of an isolating ice film on the hydrate surface, hydrate density within sediments, and sublimation [e.g., Kim *et al.*, 1987; Ershov and Yakushev, 1992; Hatzikiriakos and Englezos, 1993; Taylor, 1999]. Furthermore, the presence of gas hydrate in the sediments will lower overall thermal conductivity within the sediment column [e.g., Sloan, 1998]. All of these factors increase the times predicted by (1) and Figures 1 and 2.

Our heat flow model shows that by  $\sim 2000$  years after the  $5^\circ\text{C}$  deepwater warming, sediment temperatures would be  $\sim 3^\circ\text{C}$  higher at 100 m below seafloor (mbsf) and  $\sim 1.5^\circ\text{C}$  higher at 200 mbsf (Figure 1), with the geothermal gradient reequilibrating in  $>10,000$  years (Figure 2). If methane were released through thermal dissociation in the late Paleocene, then the minimum estimate of 2000–4000 years required for the change in deepwater source region, ocean mixing, temperature anomaly propagation, and thermal dissociation (disregarding the phase change) should be detectable in geological temperature proxies. Deep-sea isotopic records should



**Figure 2.** An instantaneous 5°C water temperature increase will cause the geothermal gradient to readjust over >10,000 years as the temperature anomaly propagates through the sediment. See text for input parameters.

show a rapid  $\delta^{18}\text{O}$  decrease (indicating rapid warming) that precedes a rapid  $\delta^{13}\text{C}$  decrease (indicating  $\text{CH}_4$  release).

## 2.2. Constraints on Thermal Dissociation: Paleobathymetry

The water depth range over which thermal dissociation could have occurred in the latest Paleocene is a function of the magnitude of the water temperature increase. We model the change in temperature and gas hydrate stability field in the latest Paleocene using the benthic foraminiferal  $\delta^{18}\text{O}$  records from the Blake Nose Site 1051 [Katz *et al.*, 1999] and the gas hydrate distribution predicted by the temperature-hydrate stability relationship [Dickens and Quinby-Hunt, 1994] (Figure 3). On the basis of this modeled response of the GHSZ, we model the  $\delta^{13}\text{C}$  response to the predicted methane release (Figure 3).

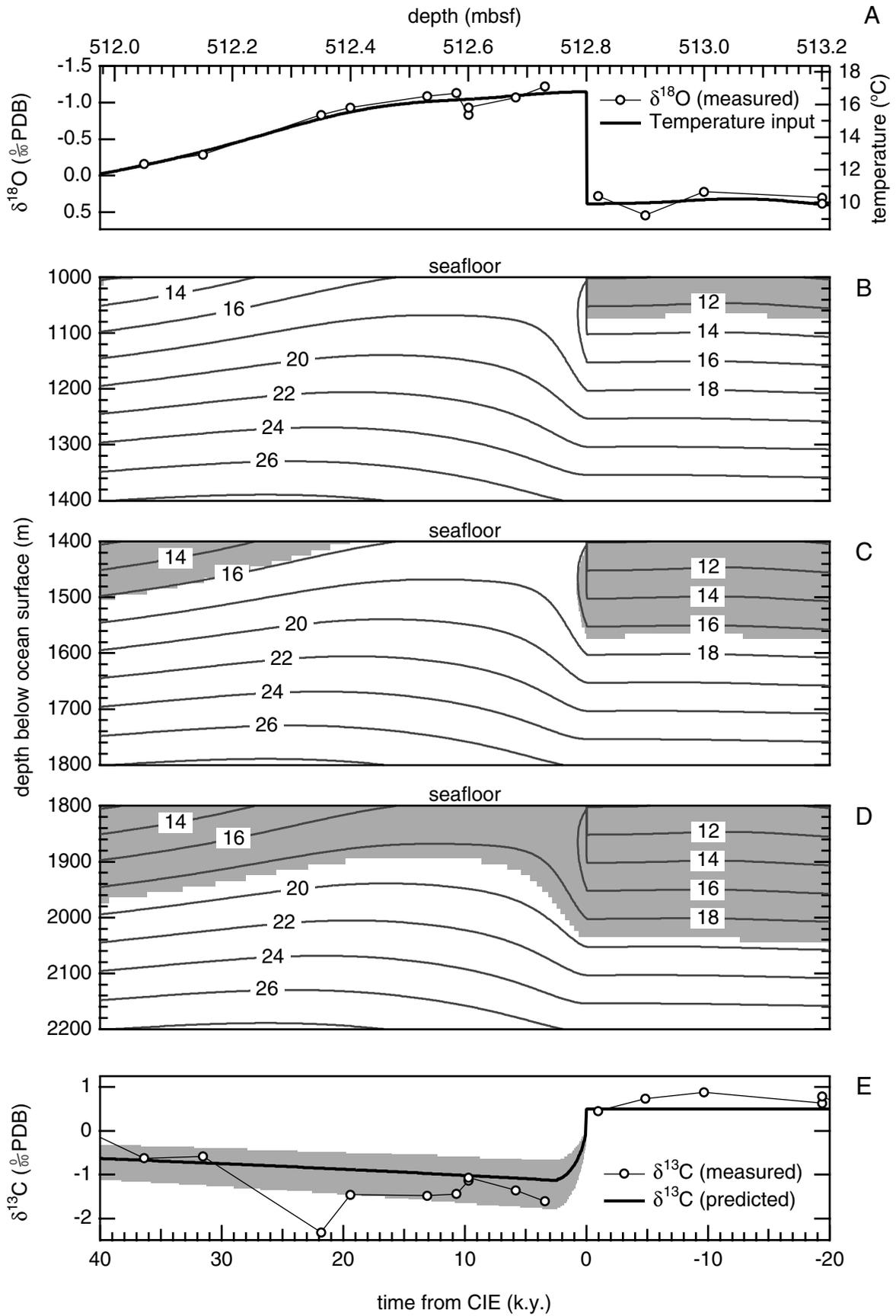
In this model, bottom water temperature is calculated from the Site 1051 isotopic record using the paleotemperature equation of Erez and Luz [1983]:  $T = 16.998 - 4.52 (\delta^{18}\text{O}_{\text{calcite}} - \delta^{18}\text{O}_{\text{water}}) + 0.028 (\delta^{18}\text{O}_{\text{calcite}} - \delta^{18}\text{O}_{\text{water}})^2$ , using  $\delta^{18}\text{O}_{\text{water}} = -1.2\text{‰}$  [Shackleton and Kennett, 1975]. *Oridorsalis* spp. apparently do not biologically fractionate oxygen isotopes [Shackleton *et al.*, 1984], so no correction factor was applied for  $\delta^{18}\text{O}_{\text{calcite}}$ . We assume that the water temperature increase at Site 1051 was instantaneous in order to provide an end-member scenario that favors the viability of thermal dissociation. The stratigraphic level of the instantaneous water temperature increase was placed at the base of the dissolution layer (512.80 mbsf; Figure 3). Sediment temperature is calculated from (1) in time steps of 50 years and depth increments of 10 m. A constant sedimentation rate of 20.625 m/Myr. is based on the cycle counts from Katz *et al.* [1999]. Initial geothermal gradient is  $0.04^\circ/\text{m}$ ;  $\kappa = 9.46 \text{ m}^2/\text{yr}$  ( $= 3 \times 10^{-7} \text{ m}^2/\text{s}$  [Hyndman *et al.*, 1979]). The modeled GHSZ (Figure 3) does not take into account the potential effects of dissolved ion concentrations [Katz *et al.*, 1959], trace gases [Hovland *et al.*, 1995], capillary action [e.g., Clennell *et al.*, 1999; Henry *et al.*, 1999], or pore fluid salinity [Dickens and Quinby-Hunt, 1994], none of which are known for the Paleocene. The modeled  $\delta^{13}\text{C}$  response to the predicted methane release is calculated in time steps of 50 years, water depth increments of 10 m, and sediment depth increments of 10 m for 50% sediment porosity with 7% of the pore space filled with frozen gas hydrate. Methane gas is assumed to remain trapped beneath the GHSZ until the base of the GHSZ shoals to the seafloor (i.e., frozen gas hydrate is no longer stable). Predicted changes in the mean ocean-atmos-

phere carbon isotopic value were calculated using an initial 40,000 Gt ocean-atmospheric carbon reservoir with  $\delta^{13}\text{C} = 0.5\text{‰}$  and a carbon residence time of 100,000 years.

The model results based on the isotopic response at Site 1051 and temperature-pressure gas hydrate stability curves [e.g., Sloan, 1998] show that all gas hydrate would have melted above 1570 m after 2350 years. This is a minimum time estimate because no time was allowed for methane diffusion through the sediments, shortening the predicted time for methane release. Our results provide narrower time constraints than Dickens *et al.* [1995], who found that a change in the pressure-temperature hydrate stability field caused by a 4°C water temperature increase over 10,000 years in the latest Paleocene would have melted all gas hydrate in marine sediments where the seafloor was between ~920 and 1460 m. At greater water depths the base of gas hydrate stability would have shoaled, but the base of the frozen gas hydrate-sediment layer would not have been breached and the underlying free and dissolved gas reservoirs would have remained trapped (Figure 3) [Dickens *et al.*, 1995; this study]. This underlying gas reservoir is an important component in any scenario that involves gas hydrate dissociation and past climate change [Dickens *et al.*, 1997b]. Any hydrate melted at the base of the GHSZ will either be added to the trapped gas reservoir or refrozen in overlying sediments as gases diffuse upward. Hence melting all frozen gas hydrate within the GHSZ is essential to releasing the substantial amounts of methane necessary to account for the CIE.

## 3. PETM Methane Release Sites

A critical sequence of events supporting the hydrate dissociation hypothesis has been documented at Ocean Drilling Program (ODP) Site 1051 (present water depth 1980 m) on the Blake Nose [Katz *et al.*, 1999], a reef-based salient protruding from the eastern rim of the Blake Plateau off the southeastern United States (Figure 4). The onset of the CIE immediately overlies the benthic foraminiferal extinction event (BFEE) at Site 1051, where ~55% of the benthic foraminiferal taxa disappear [Katz *et al.*, 1999]. This is correlatable with similar isotopic changes and benthic foraminiferal extinctions in other deep-sea PETM sections from around the world [e.g., Pak and Miller, 1992; Kaiho *et al.*, 1996; Thomas and Shackleton, 1996]. The majority (60%) of the disappearances at Site 1051 occur within an intraformational mud clast layer, where faunal



diversity plummets from  $\sim 25$ – $30$  to  $\sim 5$ – $10$  taxa/sample above the BFEE. Deposition of this clast layer has been attributed to slumping that was caused by methane release upslope from Site 1051. A surviving benthic fauna dominated by buliminids indicates a decrease in dissolved  $O_2$ , consistent with  $CH_4$  oxidation. At the same time, partly dissolved foraminiferal tests at Site 1051 indicate increased dissolved  $CO_2$  and decreased  $CaCO_3$  levels, as predicted for the by-products of  $CH_4$  oxidation [Katz *et al.*, 1999].

Seismic evidence updip from Site 1051 also is consistent with a massive methane release: a seismic profile shows an extensive interval of chaotic, hummocky reflections that is marked by bidirectional downlap (Figure 5). Hummock-like structures can form where gas-rich sediments immediately below the base of gas hydrate stability have converted into an easily mobilized, gassy mud, causing density-driven inversions with overlying sediments [e.g., McIver, 1982; Prior *et al.*, 1989; Vogt, 1997; Dillon *et al.*, 1998; Davies *et al.*, 1999]. A hummocky seismic pattern can occur where hummocks have collapsed and  $CH_4$  has escaped from marine sediments [Davies *et al.*, 1999]. The hummocky, chaotic seismic unit on the Blake Nose is  $\sim 125$ – $150$  m thick with fairly abrupt lateral terminations against well-defined seismic reflections (Figure 5). Deformation was most likely in situ; the chaotic unit does not pinch out laterally or drape over surrounding reflections, nor do surrounding reflections drape over the chaotic unit (Figure 5), as should occur in a redeposited unit such as a debris flow. Rather, it is a gas release site [Katz *et al.*, 1999].

A prominent seismic reflection can be traced from the chaotic seismic interval down slope to Site 1051, where this reflection correlates with the level of the onset of the CIE and the mud clast layer, linking methane release to sediment displacement [Katz *et al.*, 1999]. Proximal to Site 1051, this seismic reflection is caused by the impedance contrast between the displaced sediments and the overlying dissolution interval resulting from methane oxidation [Katz *et al.*, 1999]. This seismic reflection correlates to a disconformity at Site 1052 that spans much of the late Paleocene to early middle Eocene [Norris *et al.*, 1998], indicating that it is an erosional surface proximal to the release site.

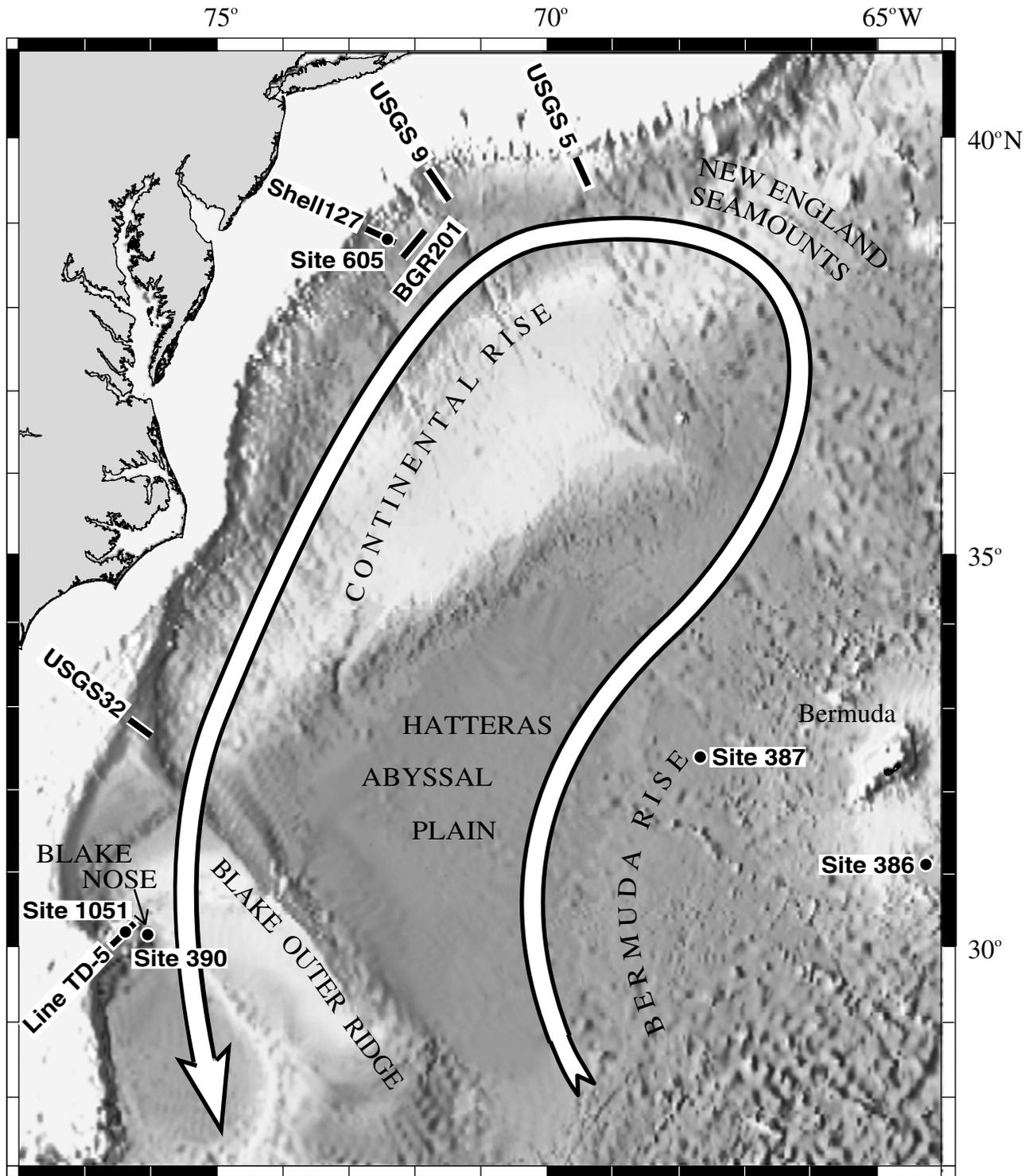
Evidence from the Blake Nose links methane release features to the onset of the PETM and CIE; however, the mass of  $CH_4$  released from this region alone is insufficient to account for the magnitude of the global perturbations at the PETM [Katz *et al.*, 1999]. Present-day methane volume in marine sediments provides the only available guideline to estimate the areal extent of the PETM methane release. Direct measurements on cores from the nearby Blake Ridge show that today, the GHSZ and the underlying free and dissolved gas reservoir contain  $\sim 35$  Gt of C (47 Gt of  $CH_4$ ) and cover 26,000 km<sup>2</sup> [Dickens *et al.*, 1997b]. Mass balance equations require the addition of  $\sim 1500$ – $2200$  Gt of C from  $CH_4$  to explain the CIE [Dickens, 2000, 2001]. Assuming similar volume and distribution, this indicates that methane from an area at least 54 times the size of the Blake Ridge was released during the PETM ( $\sim 1,400,000$  km<sup>2</sup>, or  $\sim 5\%$  of the size of the United States). This rough estimate shows that methane must have escaped from an area much larger than the Blake Nose alone.

New seismic evidence tied to borehole data indicates that additional methane may have been released in the latest Paleocene from the New Jersey continental slope. We use down-hole geophysical logs at Deep Sea Drilling Project (DSDP) Site 605 (present depth 2194 m [van Hinte *et al.*, 1987]) (Figure 4) to correlate a seismic reflector (Figure 5) to the level within the core where an unconformity separates uppermost Paleocene dark green bioturbated clays from lowermost Eocene banded marls (563.85 mbsf [van Hinte *et al.*, 1987; Lang and Wise, 1987]). This unconformity encompasses the time interval of the PETM, which is consistent with correlating this unconformity to the timing of the methane release. The underlying Cretaceous-Paleogene (K-P) reflector is truncated by the Paleocene-Eocene (P-E) reflector  $\sim 9$  km upslope from Site 605 (Figure 5). Traced farther upslope, this disconformable surface is expressed as a strong reflection overlying an  $\sim 160$  m thick unit of irregular, chaotic reflections with bidirectional downlap. As on the Blake Nose, this chaotic unit does not pinch out laterally or drape over surrounding reflections, nor do surrounding reflections drape over the chaotic unit, indicating that deformation was most likely in situ. On the basis of the similar acoustic expressions of the Blake Nose chaotic seismic interval and the correlation of the reflector to the hiatus in the core record at Site 605, we propose that the New Jersey slope was an additional PETM methane release site.

Similar chaotic seismic intervals with bidirectional downlap overlie Mesozoic reefs in several other eastern U.S. continental slope seismic profiles: (1) USGS Line 9, shotpoints  $\sim 1740$ – $1800$ ,  $\sim 2.3$ – $2.6$  two-way travel time [Mountain and Tucholke, 1985, Figure 8–13] and (2) USGS Line 5, shotpoints  $\sim 1800$ – $1850$ ,  $\sim 50$  mbsf [Grow *et al.*, 1979, Figure 9]. We propose that these chaotic zones are PETM methane release sites. They are bracketed by seismic reflector A<sup>u</sup> (latest Eocene-earliest Oligocene) and reflector A\* (mid-Maestrichtian), with no nearby borehole data available to firmly correlate to the PETM event. Nonetheless, the stratal relationships and two-way travel times provided by these reflectors are consistent with similar methane release features on the Blake Nose and the New Jersey slope.

Seismic evidence [Grow *et al.*, 1979; Jansa, 1981] shows that the PETM methane release sites are proximal to a Mesozoic reef front along the eastern U.S. continental margin (Figure 5). Gases can accumulate and become trapped below a top seal (such as a sediment and gas hydrate layer) that is bowed upward or where the updip portion of gas-bearing strata terminate against a gas hydrate seal, creating a gas overpressure zone that may facilitate methane release [e.g., Dillon *et al.*, 1980, 1998; Prior *et al.*, 1989; Sloan *et al.*, 1999]. The geometry of the Mesozoic reef front and adjacent sediments may have been an important factor in the PETM methane release: interstitial methane may have migrated up strata that dipped seaward from the Mesozoic reef front and became trapped below the overlying gas hydrate top seals. The thickness of the chaotic layers at the release sites is  $\sim 125$ – $160$  m (Figure 3), consistent with the depth to the base of the GHSZ predicted for late Paleocene-early Eocene deepwater temperatures that were  $>10^\circ C$  warmer than today (based on the temperature-pressure stability field of gas hydrates [e.g., Sloan, 1998]).

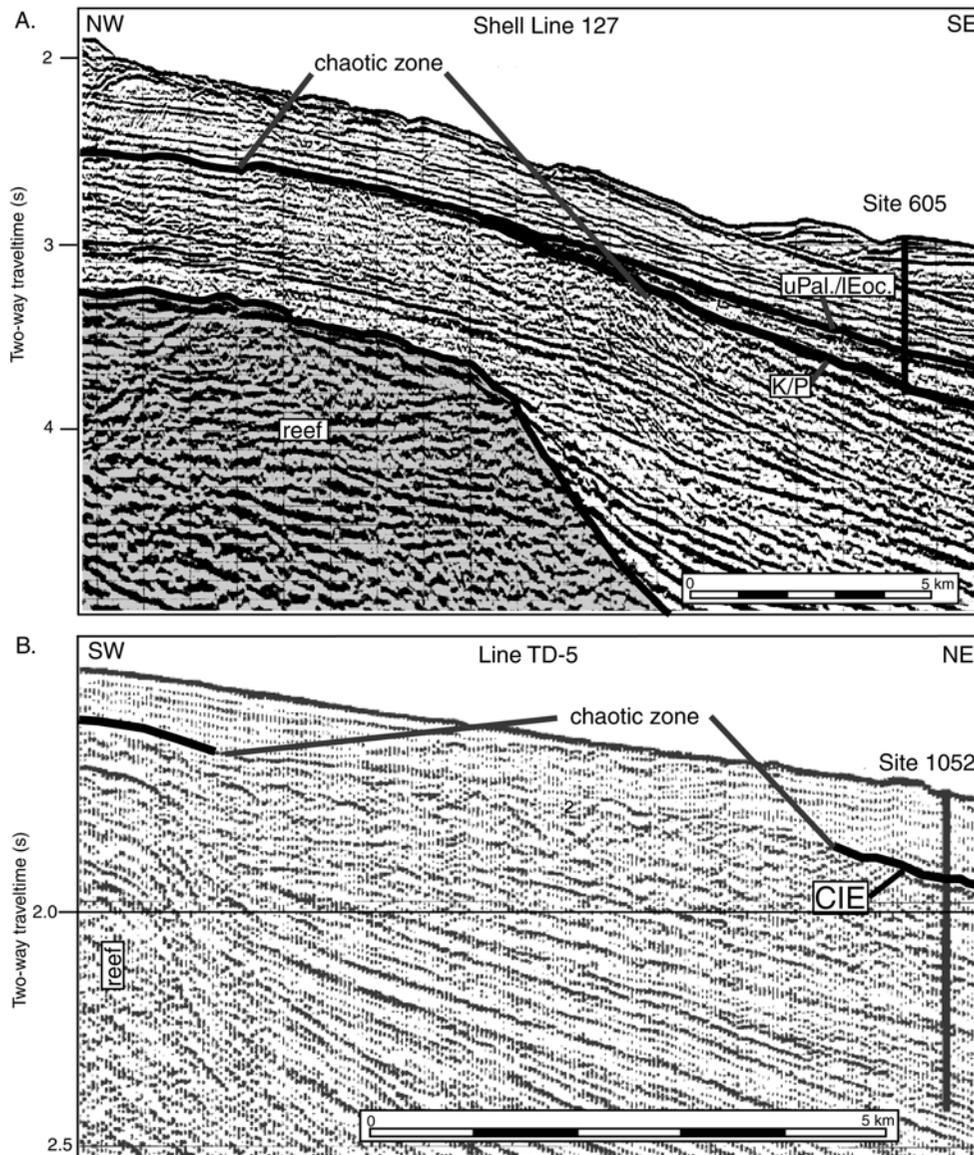
**Figure 3.** (opposite) Response of the gas hydrate stability zone (GHSZ) (shaded areas in Figures 3b–3d) to a water temperature increase at the Blake Nose (Site 1051). An instantaneous water temperature increase provides an end-member scenario that favors the feasibility of thermal dissociation. Sediment temperatures are calculated from (1) in time steps of 50 years and depth increments of 10 m. Age on the horizontal axis represents the time elapsed from an instantaneous temperature change. (a) The benthic foraminiferal isotopic record from Site 1051, which was used to calculate bottom water temperatures (bold line) (see text). (b) The 1000 m water depth. (c) The 1400 m water depth. (d) The 1800 m water depth. In Figures 3b–3d the isotherms curve backward during the initial stages of the temperature anomaly propagation because a temperature inversion in the sediments is created as the surface sediments warm more rapidly than the underlying sediments. (e) Modeled response (thick line) and Site 1051 record (circles) of the  $\delta^{13}C$  signal to the change in GHSZ and methane release (calculated in time steps of 50 years, water depth increments of 10 m, and sediment depth increments of 10 m and based on 50% sediment porosity [Gornitz and Fung, 1994] with 7% of the pore space filled with frozen gas hydrate; shaded area indicates an envelope ranging from 5 to 10% hydrate-filled pore space [e.g., Dickens *et al.*, 1997b]).



**Figure 4.** Location map showing seismic profiles and DSDP/ODP sites (the portion of each seismic profile discussed in text is indicated rather than the entire length of each profile). Large arrow indicates late Paleocene deepwater flow path in the western North Atlantic basin [after *Mountain and Miller, 1992*]. The Blake Outer Ridge is a post-Eocene depositional feature and therefore did not impede Paleocene deepwater flow.

Paleodepth estimates place the Blake Nose and New Jersey slope release sites at 1000–1500 m water depth based on reassessments of benthic foraminiferal data from Sites 605 [Hulsbos, 1987; Saint-Marc, 1987; van Hinte et al., 1987], 1051 [Norris et al., 1998; Katz et al., 1999; Katz, 2001], and 1052 [Norris et al., 1998; M. E. Katz,

unpublished data, 1998] (Appendix A). There are no benthic foraminiferal data to constrain the paleobathymetry of the possible release sites on USGS Lines 5 (New England margin) and 9 (Long Island margin) because no boreholes are available from these areas. Nonetheless, their two-way travel times and proximity to the



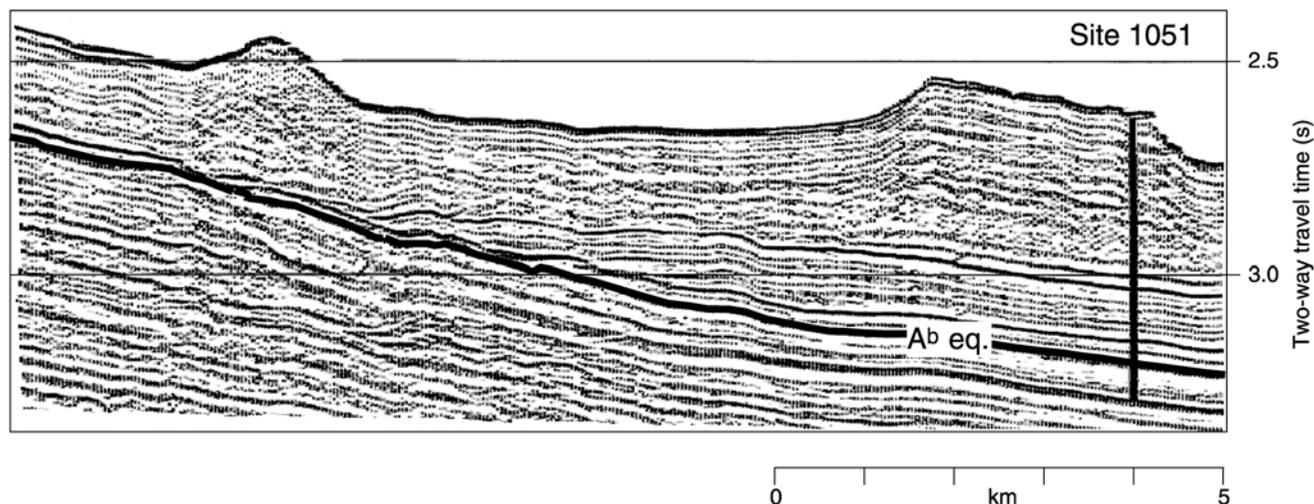
**Figure 5.** (a) New Jersey continental margin (Shell Line 127) and (b) Blake Nose (Line TD-5; adapted from Norris *et al.* [1998]) seismic profiles showing the zone of chaotic seismic reflections that was caused by the methane escape that triggered the PETM. See Figure 4 for locations. See Katz *et al.* [1999] or Norris *et al.* [1998] for correlation of Line TD-5 to ODP Site 1051. The strong seismic reflection that overlies the chaotic interval on the New Jersey margin marks the sharp acoustic and lithologic contrast between lower Eocene chert-bearing sediments [Ewing *et al.*, 1969; Tucholke, 1979] and the underlying uppermost Cretaceous sediments that were disturbed by the PETM methane release. Lowermost Eocene sediments are missing from the region of the Blake Nose PETM methane release site (ODP Site 1052 [Norris *et al.*, 1998]); hence there is no corresponding bright seismic reflection at this location.

Mesozoic reef front indicates that they were likely at similar paleodepths (Appendix A).

#### 4. Model Constraints Versus the Geologic Record

If thermal dissociation were the primary mechanism for the PETM methane release, then (1) deep-sea isotopic records should show a rapid  $\delta^{18}\text{O}$  decrease (indicating rapid warming) that precedes a rapid  $\delta^{13}\text{C}$  decrease (indicating  $\text{CH}_4$  release) by at least 2000–4000 years, (2) there should be evidence for a change in deepwater source region that caused the rapid water temperature increase, and (3) the paleobathymetry of the methane release sites must be consistent with the depths predicted for thermal dissociation.

Published isotopic records do not show any time lag between deep-sea warming and methane release [Kennett and Stott, 1991; Bralower *et al.*, 1995; Thomas and Shackleton, 1996; Pak and Miller, 1992; Katz *et al.*, 1999], although low sedimentation rates ( $\sim 2$  cm/kyr), dissolution, and possible bioturbation may make it difficult to extract a high-resolution deep-sea record that could show the time lag necessary to verify thermal dissociation. Nonetheless, there is little direct evidence for the change from high-latitude to low-latitude deepwater source(s) that is necessary to cause the rapid water temperature increase predicted by the thermal dissociation hypothesis. Pak and Miller [1992] suggested that a warm saline deepwater (WSDW) component might have existed in the late Paleocene to early Eocene on the basis of benthic



**Figure 6.** A section of Blake Nose seismic Line TD-5 (adapted from *Norris et al.* [1998]) showing reflector  $A^b$  equivalent and overlying current-controlled sedimentation. See *Katz et al.* [1999] or *Norris et al.* [1998] for correlation to Site 1051.

foraminiferal  $\delta^{18}\text{O}$  values that show warmer deepwater temperatures in the Pacific and North Atlantic than in the Antarctic near the Paleocene/Eocene boundary. However, these comparisons suffer from substantial correlation uncertainties [Aubry, 1998]. It has been proposed that Tethyan waters may have become dense enough to form WSDW [Kennett and Stott, 1990, 1991; Katz and Miller, 1991; Pak and Miller, 1992; Zachos et al., 1993, 1994; Thomas and Shackleton, 1996; Bralower et al., 1997], but available carbon isotopic data do not support such a hypothesized WSDW [e.g., Pak and Miller, 1992; Schmitz et al., 1996], and climate models show that prolonged WSDW production is unlikely [e.g., Sloan and Thomas, 1998]. Therefore neither isotopic comparisons nor modeling efforts substantiate the change in water mass source region that is required to trigger thermal dissociation.

The paleobathymetric distribution of the release sites must be consistent with the causal mechanism for methane release. All four potential PETM release sites lie within the water depth range predicted for complete gas hydrate thermal dissociation given the late Paleocene deepwater temperatures [Dickens et al., 1995; this study]. However, the release sites are limited to a narrow region proximal to the Mesozoic reef front rather than extending across the broader depth range predicted for thermal dissociation. Therefore thermal dissociation as the trigger for PETM methane release cannot be unequivocally confirmed using the distribution of the PETM release sites.

Methane can also escape via the mechanical disruption of sediments [e.g., Gornitz and Fung, 1994]. Regardless of the initial triggering mechanism (thermal or mechanical), methane can only escape from hydrate deposits through sediment failure [Paull et al., 1996; Dillon et al., 1998], complicating the search for the causal mechanism for methane release. In thermal dissociation, frozen hydrate dissociates to water and free gas, which destabilizes the sediment column, leading to slope failure and gas release into the overlying waters. In contrast, mechanical disruption of sediments can breach the base of a frozen gas hydrate and sediment layer to open a conduit to a free gas reservoir trapped below, with the potential to release larger quantities of methane than predicted from thermal dissociation alone [Gornitz and Fung, 1994].

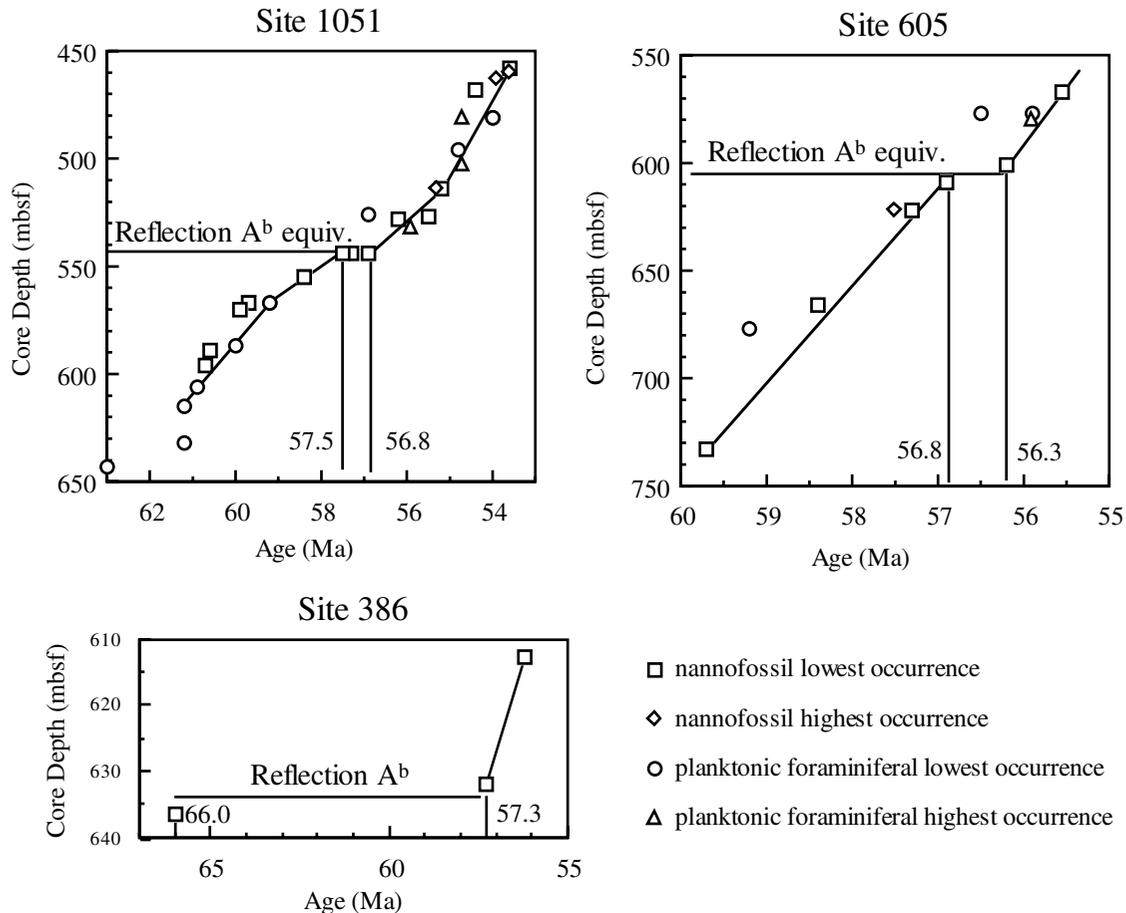
## 5. An Alternative Hypothesis

In the absence of firm evidence to verify thermal dissociation, we investigate an alternative hypothesis in which methane release

(via erosion) preceded the rapid temperature increase. In this scenario, erosion along the oversteepened U.S. continental margin may have allowed methane to escape from gas reservoirs trapped between the frozen hydrate-bearing sediments and the underlying buried Mesozoic reef front. An important implication of this scenario is that the methane release was the cause (rather than the result) of the rapid temperature increase. Methane that escapes the seafloor will be oxidized in the oceans; excess methane will escape to the atmosphere [e.g., Ehhalt, 1974; Ward et al., 1987; Cicerone and Oremland, 1988]. Increased concentrations of atmospheric  $\text{CH}_4$  [Peters and Sloan, 2000] and/or its oxidant,  $\text{CO}_2$  [Kennett and Stott, 1991], could have been the cause (rather than the result) of warming during the PETM.

Seismic profiles show that widespread deepwater erosion occurred in the western North Atlantic in the late Paleocene, providing a potential mechanical trigger for methane release. On the western Bermuda Rise, an angular unconformity marked by seismic reflector  $A^b$  resulted from swiftly flowing bottom currents [Mountain and Miller, 1992]. Seismic ties to piston cores and boreholes (e.g., DSDP Site 386) show that peak erosion occurred on the western Bermuda Rise prior to circa 57.3 Ma (Mountain and Miller [1992], revised to the timescale of Berggren et al. [1995]) (Figure 7). Late Paleocene erosion associated with reflector  $A^b$  can be distinguished clearly from a more widespread and severe erosional event associated with reflector  $A^u$  (latest Eocene-earliest Oligocene) [Tucholke and Mountain, 1979; Mountain and Tucholke, 1985] that was caused by a pulse of northern component water flowing from the northern North Atlantic [Miller and Tucholke, 1983].

Hiatuses documented in drill cores from the U.S. margin indicate that  $A^b$  erosion was most likely basin-wide; seismic data presented below strengthen this argument. A coeval hiatus has been identified at DSDP Site 390, 700 m downslope from Site 1051 on the Blake Nose [Gradstein et al., 1978; Schmidt, 1978]. A prominent seismic reflection associated with an unconformity at Site 1051 on the Blake Nose (~544 mbsf [Norris et al., 1998]) (Figure 6) is dated at 56.8–57.5 Ma (Figure 7). This is referred to as “reflector  $A^b$  equivalent” because although it is potentially coeval with reflector  $A^b$ , it cannot be traced seismically to the Bermuda Rise with existing data. A similar seismic reflection on the New Jersey continental rise is associated with an unconformity at Site 605, where biostratigraphic correlations reveal a hiatus from 56.3 to 56.8 Ma at ~605.0 mbsf (Figure 7). We also refer to this as “reflector  $A^b$  equivalent.”



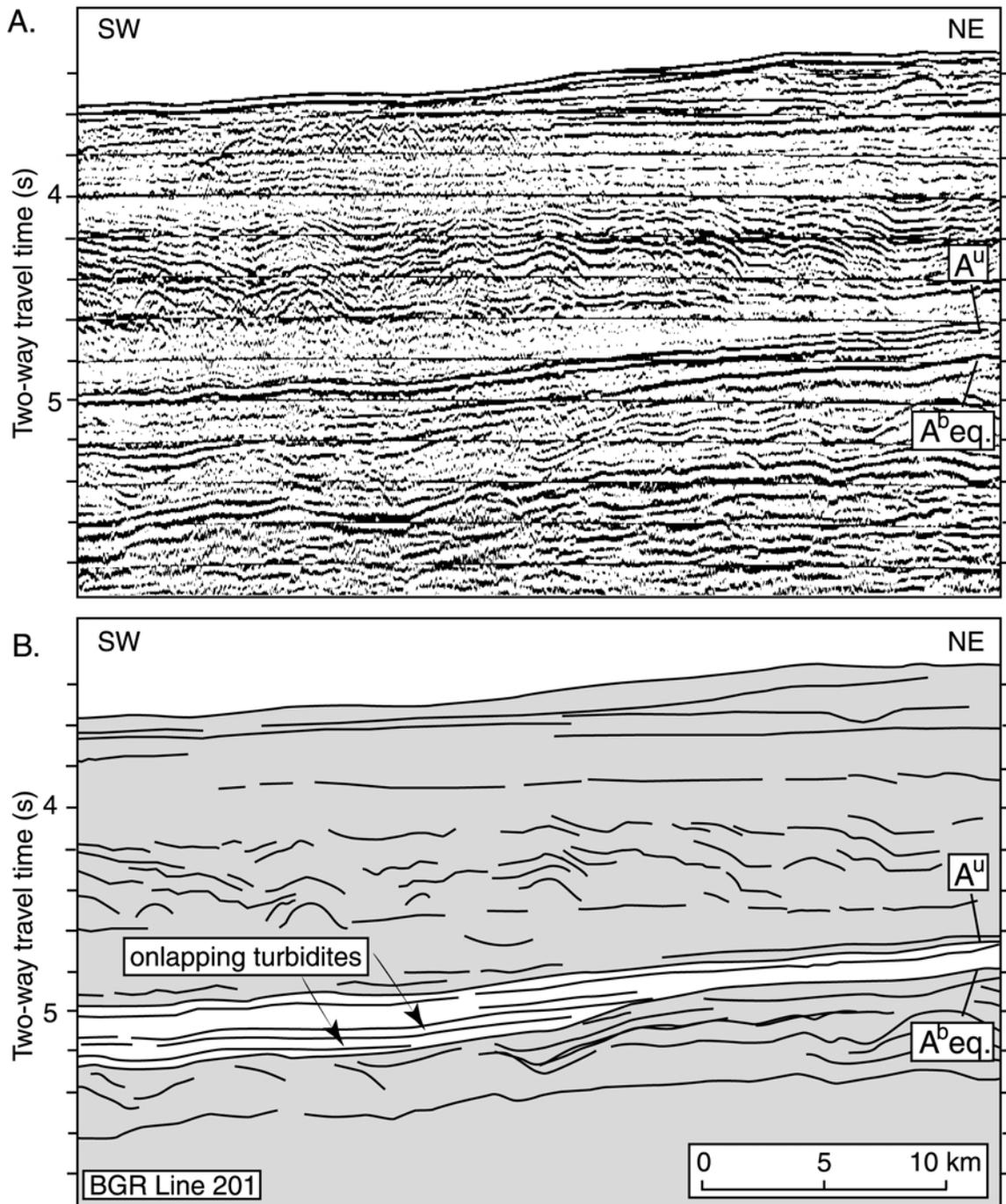
**Figure 7.** Age-depth plots used to assign ages to reflector A<sup>b</sup> (Site 386) and reflector A<sup>b</sup> equivalent (Sites 605 and 1051). Site 386 data are after *Mountain and Miller* [1992]; Site 1051 data are after *Norris et al.* [1998]; Site 605 data are after *van Hinte et al.* [1987], *Lang and Wise* [1987], and *Saint-Marc* [1987].

On the basis of the distribution of reflector A<sup>b</sup>, its associated hiatuses, and *Pak and Miller's* [1992] interbasinal carbon isotopic comparisons, *Mountain and Miller* [1992] concluded that A<sup>b</sup> erosion was caused by Southern Ocean bottom water that flowed into the western Atlantic in the late Paleocene. Geostrophic considerations dictate that this southern component water (SCW) must have flowed north along the South American continental margin, swung east as it crossed the equator, and flowed north along the western flank of the mid-Atlantic Ridge (this ridge crust was ~50 Myr old in the Paleocene, and therefore it was relatively shallow). *Mountain and Miller* [1992] proposed that SCW circulated cyclonically around the western North Atlantic basin and swept southward along the U.S. continental rise (Figure 4). On the Blake Nose, reflector A<sup>b</sup> equivalent erosion and overlying current-controlled sedimentation provide evidence that late Paleocene deepwater flow affected the U.S. continental slope (Figure 6).

This SCW eroded the base of the eastern U.S. continental slope during the late Paleocene, resulting in slope instability. Extensive sediment failure [*Tucholke and Mountain*, 1986; *Mountain*, 1987] (Figures 8 and 9) resulted in the landward retreat of the U.S. continental slope by ~15 km in the early Tertiary [*Schlee*, 1981]. Evidence from the New Jersey and North Carolina margins confirms that late Paleocene deepwater flow undercut the continental margin and caused slope failure (Figures 8 and 9). Downslope from Site 605 on the New Jersey continental rise, an along-strike seismic profile shows that reflector A<sup>b</sup> equivalent truncates underlying sediments and is immediately overlain by turbidites that onlap the adjacent topographic high (Figure 8).

Seaward of Cape Fear, North Carolina, the landward edge of predominantly slumped sediments are bracketed by reflectors A<sup>u</sup> and A<sup>b</sup> equivalent (Figure 9; see caption for discussion of diapir tectonism). Similar reflector geometries are observed elsewhere along the margin, and we believe that all are the result of Paleocene undercutting and slope failure. This resulted in the seaward advance of Paleogene turbidites containing slope sediments, as documented at DSDP Sites 386 and 387 on the western Bermuda Rise (Figure 4) [*Tucholke et al.*, 1979; *Tucholke and Mountain*, 1979], where turbidites onlap reflector A<sup>b</sup> [*Mountain and Miller*, 1992].

Pervasive late Paleocene erosion at widely separated locations (Bermuda Rise, New Jersey slope, North Carolina slope, and Blake Nose) is consistent with a basin-wide cause: a pulse of SCW. Seismic evidence indicates that this vigorous deepwater current undercut the base of the U.S. continental slope, which was already steep because it was underlain by extensive Mesozoic carbonate platforms and reefs [see *Grow and Sheridan*, 1988]. Current-controlled sedimentation on the Blake Nose shows that erosion that began in the late Paleocene continued through the time of the CIE and into the early Eocene, although this feature is not adjacent to the methane release site (Figure 6). Erosion at the base of the slope very likely caused margin oversteepening, widespread slope failure, and the landward retreat of the slope in the latest Paleocene. We propose that continental slope failure may have breached the base of the GHSZ proximal to the reef front, thereby accessing the free and dissolved methane gas reservoirs below, releasing methane and precipitating the PETM. Slope failure may have resulted from ongoing SCW erosion or from seismic activity.

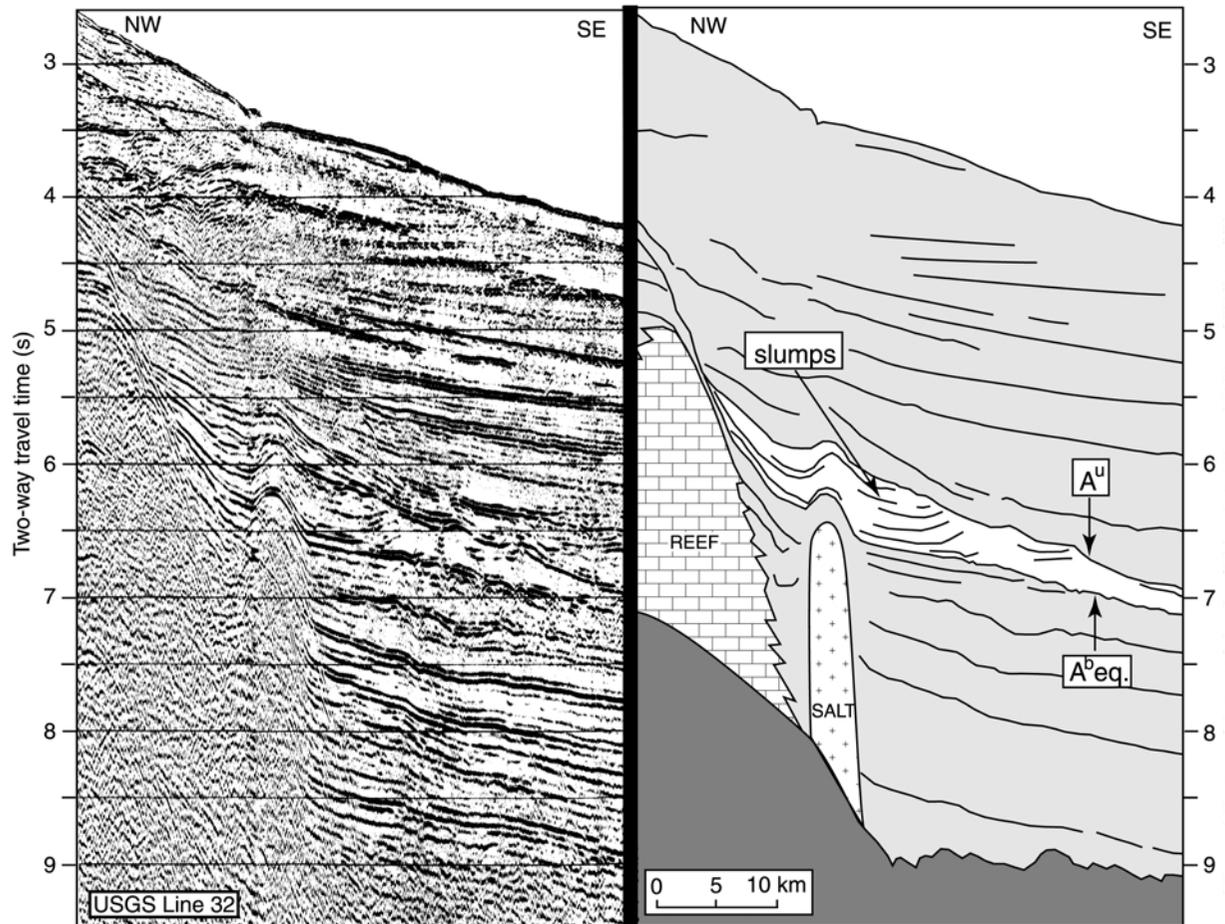


**Figure 8.** New Jersey continental margin seismic profile (BGR Line 201) showing turbidites that onlap reflector  $A^b$  equivalent. See Figure 4 for location. (a) Uninterpreted seismic profile. (b) Interpreted seismic profile.

Widespread deepwater erosion and margin failure may extend to other continental margins. A counterpart to reflector  $A^b$  has been tentatively identified in the western South Atlantic [Mountain and Miller, 1992]. Seismic and lithologic evidence for the northward flow of SCW through the South Atlantic at this time (outlined above) has been noted in the sub-Antarctic sector of the South Atlantic [Ciesielski *et al.*, 1988] and the Brazil Basin and Rio Grande Gap [Gamboa *et al.*, 1983]. We suggest that as in the western North Atlantic, base-of-slope erosion along the South American margin could have oversteepened the margin and precipitated methane release also. Detailed analysis of seismic profiles

and sediment cores from the western South Atlantic is needed to assess this possibility. Even though the deep basins of the Atlantic were smaller in the Paleocene than they are today, the volume of the margin (where most gas hydrate reservoirs occur today) was not drastically different.

Methane may have escaped from margins throughout the Atlantic, yet it is difficult to explain massive slope failure over a large area within a brief time period. Limited evidence for multiple methane releases [Bains *et al.*, 1999] may indicate that methane release occurred over  $\sim 20,000$  years. If this is the case, then methane may have escaped through both mechanical disruption



**Figure 9.** North Carolina continental margin seismic profile (USGS Line 32) showing slump deposition associated with late Paleocene deepwater erosion. See Figure 4 for location. (a) Uninterpreted seismic profile. (b) Interpreted seismic profile. A salt diapir affected stratal geometries immediately seaward of the Mesozoic reef front, complicating the interpretation of this profile. Because (1) the slumped unit is more deformed than the underlying and overlying units and (2) irregular seismic reflectors in this unit are observed >10 km seaward of the diapir, we believe that this unit resulted from large-scale slumping from the adjacent slope, independent of salt tectonism.

and thermal dissociation. Greenhouse warming (including deep and bottom water warming) caused by an initial mechanical methane release may have triggered subsequent thermal dissociation, resulting in additional methane release. As we have shown, the ~20,000 year duration for successive methane releases suggested by *Bains et al.* [1999] provides sufficient time for propagation of a thermal anomaly and destabilization of the GHSZ.

## 6. Summary and Conclusions

The major conclusions of this paper are the following.

1. Our heat flow model provides an end-member, minimum estimate of the time required for thermal dissociation of methane hydrates at the Paleocene/Eocene boundary; this predicts that a rapid  $\delta^{18}\text{O}$  decrease (indicating rapid warming) should precede the rapid  $\delta^{13}\text{C}$  decrease (indicating  $\text{CH}_4$  release) by at least 2000–4000 years.
2. We use the Site 1051  $\delta^{18}\text{O}$  record to model the effect of the temperature change on the GHSZ through time, showing that >2350 years is necessary to melt all gas hydrate at locations shallower than 1570 m.
3. A PETM release site was identified on the Blake Nose [*Katz et al.*, 1999]; here we identify three additional release sites on the northeastern U.S. continental margin. All release sites are limited

to a narrow region proximal to a Mesozoic reef front, in contrast to the broader depth range predicted for methane release via thermal dissociation.

4. Our model results, release site locations, published isotopic records, and ocean circulation models neither confirm nor refute thermal dissociation as the trigger for the PETM methane release.

5. In light of inconclusive evidence confirming the PETM thermal dissociation hypothesis, we consider mechanical disruption of sediments as an alternate causal triggering mechanism for the methane release. (1) Seafloor erosion caused by SCW circulation led to oversteepening and retreat of the continental slope along the western margins of the Atlantic in the late Paleocene. (2) Continental slope failure may have breached the base of the GHSZ proximal to a reef front, thereby accessing the free and dissolved methane gas reservoirs below, releasing methane, and precipitating the PETM. Slope failure may have resulted from ongoing SCW erosion or from seismic activity.

6. If mechanical disruption were the primary trigger, then methane release may have been the cause (rather than the result) of the rapid temperature increase. The resulting greenhouse warming may have triggered subsequent thermal dissociation.

Neither thermal dissociation nor erosion and margin failure are fully supported by existing records as the triggering mechanism for

methane release at the PETM. Additional high-resolution benthic foraminiferal isotopic records are needed to confirm that (1) an ocean circulation change and a rapid water temperature increase preceded the methane release (thermal dissociation) or (2) methane release preceded the water temperature increase (mechanical disruption). In addition, further documentation with seismic profiles and corroborative borehole data are needed to confirm the plausibility of erosion as the causal mechanism for the initial methane release.

## Appendix A

Paleobathymetric estimates were based on benthic foraminiferal faunas at Sites 605 [Hulsbos, 1987; Saint-Marc, 1987; van Hinte et al., 1987], 1051 [Norris et al., 1998; Katz, 2001], and 1052 [Norris et al., 1998; M. E. Katz, unpublished data, 1998] (Table A1). Paleodepth criteria are provided for the common occurrences of benthic foraminifera in the late Paleocene-early Eocene [Tjasma and Lohmann, 1983; van Morkhoven et al., 1986] (Table A1). Paleodepths of ~2000 m ( $\pm 100$  m) are indicated at Sites 605 and 1051 by the overlapping occurrences of species that are typically restricted to (or most abundant at) depths either shallower or deeper

than ~2000 m; furthermore, species typical of deeper water depths are rare or absent (e.g., *Clinapertina* spp., *Quadriformina profunda*). The faunal paleodepth estimates at Site 605 are supported by geophysical backstripping efforts that yield a paleodepth of 2000–2300 m for the early Eocene [Hulsbos, 1987].

Site 1052 is ~100 m downslope from the Blake Nose PETM release site and provides the best constraint on paleodepth estimates. Site 1052 faunas lack several deeper water indicators that are present at Sites 605 and 1051 (e.g., *Abyssamina* spp., *A. praeacuta*, and *C. havanensis*) and contain shallower water indicators that are absent from the deeper sites (e.g., *B. impendens*, *C. mexicanus*, *N. jarvisi*, and *P. costata*); these faunas place Site 1052 and the nearby methane release site in the upper half of the lower bathyal zone (1000–1500 m). This paleodepth range is consistent with the vertical displacement between the deeper Sites 605 and 1051 and the New Jersey margin and Blake Nose release sites.

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**Table A1.** Benthic Foraminiferal Occurrences at Sites 605, 1051, and 1052<sup>a</sup>

Species	Paleodepth, m	Site 605	Site 1051	Site 1052
<i>Abyssamina quadrata</i>	>2000		x	
<i>Abyssamina poagi</i>	>2000	x		
<i>Anomalinoidea danica</i>	<2000	x		
<i>Aragonia</i> spp.	>2000	x	x	x
<i>Anomalinoidea semicibratus</i>	>600	x		
<i>Anomalinoidea capitatus</i>	>600	x		x
<i>Anomalinoidea praeacuta</i>	>2000		x	
<i>Bolivinoidea delicatulus</i>	<2000	x	x	x
<i>Bulimina impendens</i>	500–2000			x
<i>Bulimina semicostata</i>	>1000	x	x	x
<i>Bulimina trinitatensis</i>	<2500	x	x	x
<i>Bulimina velascoensis</i>	>1000		x	
<i>Bulimina midwayensis</i>	<2500	x	x	
<i>Buliminella beaumonti</i>	<2000	x	x	x
<i>Buliminella grata</i>	<2000	x	x	x
<i>Cibicidoides eocaenus</i>	<2000	x		x
<i>Cibicidoides grimsdalei</i>	>1000		x	x
<i>Cibicidoides havanensis</i>	>2000	x		
<i>Cibicidoides hyphalus</i>	<2000		x	x
<i>Cibicidoides laurisae</i>	>600			x
<i>Cibicidoides mexicanus</i>	600–2000			x
<i>Cibicidoides praemundulus</i>	>1000	x	x	
<i>Coryphostoma midwayensis</i>	<2000		x	
<i>Gaudryina pyramidata</i>	<2000	x	x	x
<i>Gyroldinoidea globulosus</i>	>200			x
<i>Hanzawaia ammophila</i>	<2000	x		x
<i>Lenticulina</i> spp.	<2000	x	x	x
<i>Neoflabellina jarvisi</i>	<2000			x
<i>Nuttallinella florealis</i>	>1000	x	x	
<i>Nuttallides truempyi</i>	>1000	x	x	x
<i>Osangularia</i> spp.	<2000	x	x	x
<i>Planulina costata</i>	<1500			x
<i>Pullenia coryelli</i>	<2000	x	x	
<i>Pyramidina rutida</i>	<2000		x	x
<i>Quadriformina profunda</i>	>2000		x	
<i>Stensioina beccariiiformis</i>	<2000	x	x	
<i>Tappanina selmensis</i>	<2000		x	
<i>Uvigerina rippensis</i>	<2000		x	
<i>Vulvulina mexicana</i>	<2500	x		x
<i>Vulvulina spinosa</i>	<2500	x		x
Geophysical backstripping		2000–2300 m		

<sup>a</sup>See Sites 605 Hulsbos [1987], Saint-Marc [1987], and van Hinte et al. [1987] for Site 605; Norris et al. [1998] and Katz [2001] for Site 1051; and Norris et al. [1998] and M. E. Katz (unpublished data, 1998) for Site 1052. Paleodepth criteria are based on the common distributions of species in the late Paleocene-early Eocene [Tjasma and Lohmann, 1983; van Morkhoven et al., 1986]. Geophysical backstripping is for the early Eocene [Hulsbos, 1987].

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