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The Source and Fate of Massive Carbon Input During the Latest Paleocene Thermal Maximum

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Lithologic, faunal, seismic, and isotopic evidence from the Blake Nose (subtropical western North Atlantic) links a massive release of biogenic methane \sim 55.5 million years ago to a warming of deep-ocean and high-latitude surface waters, a large perturbation in the combined ocean-atmosphere carbon cycle (the largest of the past 90 million years), a mass extinction event in benthic faunas, and a radiation of mammalian orders. The deposition of a mud clast interval and seismic evidence for slope disturbance are associated with intermediate water warming, massive carbon input to the global exogenic carbon cycle, pelagic carbonate dissolution, a decrease in dissolved oxygen, and a benthic foraminiferal extinction event. These events provide evidence to confirm the gas hydrate dissociation hypothesis and identify the Blake Nose as a site of methane release.

Over a 10,000- to 20,000-year interval about 55.5 million years ago (1, 2), Earth's climate and oceans warmed as deep-ocean and highlatitude surface water temperatures soared by 4° to $8^{\circ}C$ (3-6), numerous mammalian orders (including primates) suddenly appeared in the geologic record (7), and many deep-sea species became extinct [foraminifera (3, 5, 8-12)] or disappeared temporarily [ostracodes (12)]. This extraordinary event, the latest Paleocene thermal maximum (LPTM) (4), coincided with a remarkable decrease in the ¹³C/¹²C ratio of global carbon reservoirs (2, 5, 8-11, 13-15) that has been explained by the addition of isotopically light CO₂ to the ocean, comparable to present-day fossil fuel input to the atmosphere (5, 15, 16). All of these observations have been linked by a single hypothesis (Fig. 1) involving a sudden change in ocean circulation and rapid escape of 1 \times 10¹⁸ to 2 \times 10¹⁸ g of CH₄ from marine gas hydrate reservoirs on continental slopes (11, 15-18). Nonetheless, without appropriate Paleocene continental slope sections, evidence for the theoretical CH₄ release has been lacking. Results presented here provide critical evidence to support rapid, massive CH₄ input to the ocean during the LPTM.

The "LPTM hydrate dissociation hypothesis" (15–18) can be summarized as follows (Fig. 1): Similar to the present day, vast quantities of CH_4 greatly enriched in ¹²C

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 $(\delta^{13}C \sim -60 \text{ per mil})$ were stored as gas hydrate in the upper few hundred meters of continental slope sediments (18-21) before the LPTM. Long-term global warming during the late Paleocene (22, 23) pushed the oceanatmosphere system past a critical threshold (4, 17, 18), causing warm surface waters to sink and intermediate to deep ocean temperatures to rise by $\sim 4^{\circ}$ to $8^{\circ}C$ (3, 8). This warming propagated into the sediments, converting once solid CH₄ hydrates into free gas bubbles (15). This dissociation resulted in an increase in pore pressure at depth, leading to sediment failure and the release of massive quantities of CH_4 into the ocean (19, 24, 25). Methane release would have occurred on continental slopes between 900 and 2000 m water depth because all gas hydrate in this sediment would be prone to dissociation in the Paleocene with a 4° to 8°C rise in bottom water temperature (Fig. 1) (15). The gaseous CH₄ reacted with dissolved O₂ [likely via bacterial activity (26)] to produce ¹²Cenriched CO₂, adding carbon to all reservoirs of the global exogenic carbon cycle and substantially shoaling the depth of carbonate dissolution in the ocean (15-18). Higher bottom

water temperature, lower dissolved O_2 , changes in surface water productivity, and more corrosive waters killed many of the deep-sea species (17). On land, higher partial pressure of CO_2 and elevated temperatures quickly opened high-latitude migration routes for the widespread dispersal of mammals (7). Over several hundred thousand years, global carbon and oxygen cycles gradually returned to equilibrium conditions after the LPTM (16, 18), although marine and terrestrial ecosystems were forever changed (7–12).

Ocean Drilling Program (ODP) Site 1051 on the Blake Nose (Fig. 2) recovered a continuous, expanded LPTM section (27, 28) that was deposited on the lower continental slope (present water depth, 1981 m). The unusually thick LPTM section yields sediment cycles that are caused by subtle lithologic variations and are best seen in magnetic susceptibility variations (Fig. 3). The cycles bundle into 100,000-year packages that each contain five shorter cycles, strongly suggesting a relationship to Earth's precessional frequencies of $\sim 20,000$ years (27, 28). The precessional cycles provide an opportunity to study rates and timing of chemical and faunal changes associated with the LPTM, and to address the source and fate of CH₄.

At Site 1051, ~55% of benthic foraminiferal taxa disappeared in the latest Paleocene within a fraction of a precessional cycle (<5000 years) (Fig. 3). The majority (60%) of these last appearances occurs immediately below the carbon isotope excursion (CIE) and within a mud clast interval where faunal diversity plummets from ~ 25 to 30 taxa to ~ 5 to 10 taxa per sample. Bulimina spp. dominate the surviving fauna, suggesting decreased dissolved O₂ conditions; at the same time, partly dissolved foraminiferal tests indicate increased ΣCO_2 and decreased CaCO₃ (Fig. 3). A similar rapid, pronounced benthic foraminiferal extinction event (BFEE) and environmental conditions mark the onset of the LPTM at other deep-sea locations (3, 5, 8, 10) and probably resulted from a combination of factors, including increased temperature, decreased dissolved O2, surface water productivity changes, and enhanced carbonate dissolution. Post-extinction reestablishment



Fig. 1. Schematic of the LPTM hydrate dissociation hypothesis (15). Model assumptions include a pure CH₄ hydrate/seawater system, hydrostatic pressure gradient = 0.10 MPa/m, geotherm = 0.03° C/m, and initial bottom water temperature = 11°C. Pal, Paleocene. Modified from (15, 18, 24).

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of benthic assemblages was gradual at Site 1051, with species originations occurring over a period of 200,000 years (Fig. 3).

Oxygen and carbon isotope records of a single benthic foraminiferal group (*Oridorsalis* spp.) display large negative excursions across the LPTM at Site 1051 (Fig. 3), with δ^{18} O and δ^{13} C decreases of ~1.5 and ~3.0 per mil, respectively, across a ~20-cm interval. Bulk sediment δ^{13} C values decrease by ~1.2 per mil across this interval (Fig. 3), although we did not measure bulk samples from the interval of peak δ^{13} C excursion. At Site 1051, the onset of the isotopic excursions coincides with the BFEE and is contemporaneous with similar isotopic changes in other deep-sea LPTM sections from around the world (3, 5, 17).

The benthic foraminiferal δ^{18} O decrease at Site 1051 indicates an increase of >6°C in bottom water temperature on the continental slope (29). The onset of the δ^{18} O change occurs over 20 cm (or one-quarter to onethird of a single precessional cycle; Fig. 3), indicating that substantial warming of intermediate water occurred within 5000 to 7000 years during the LPTM. The amount, duration, and location of bottom water warming inferred at Site 1051 is sufficient to dissociate large quantities of gas hydrate in middle to lower slope sediments (15, 30).

The benthic foraminiferal CIE at Site 1051 is similar in shape and magnitude to those in other LPTM deep-ocean sections (3, 5, 8, 17) and represents a decrease of 3 per mil in the δ^{13} C of Σ CO₂ in all water beneath the thermocline. Major decreases in $\delta^{13}C$ records of planktonic foraminifera or bulk sediment carbonate (dominated by tests of surface-dwelling organisms) at Site 1051 and other marine locations (3, 5, 10, 14) indicate a large decrease in the $\delta^{13}C$ of surface water ΣCO_2 . A decrease of 4 per mil in the $\delta^{13}C$ of terrestrial carbonate and organic carbon also has been documented (11, 13). Thus, the prominent CIE across the LPTM occurred in shallow marine, deep marine, and terrestrial reservoirs, indicating massive carbon addition to the global exogenic carbon cycle (5, 14-16), as opposed to carbon redistribution within this system (31-33). Pronounced carbonate dissolution on the sea floor (5, 9-11, 14, 17), including at Site 1051 (Fig. 3), is consistent with this interpretation (15-18). The duration of carbon input is expected to be equivalent to the onset time of the CIE (18), or about 5000 to 7000 years according to the δ^{13} C records at Site 1051 (Fig. 3). Release and oxidation of 1×10^{18} to 2×10^{18} g of CH₄, and the subsequent propagation of CO₂ through various carbon reservoirs, is the only known mechanism to explain the sudden, extreme, and global nature of the CIE (11, 15).

Model results (18) show that the release and oxidation of 1.2×10^{18} g of CH₄ over



Fig. 2. Multichannel seismics line TD-5. (**A**) Map showing location of inset (B). BBOR, Blake Bahama Outer Ridge. (**B**) Enlarged location map with drill sites and seismic lines shown in (C) and (D). (**C**) Chaotic reflections correlated with the CIE near an Aptian reef may be a CH_4 release site. (**D**) Erosional scarp and current-controlled sedimentation associated with a reflection correlated with the CIE; reflection A^b is the equivalent age to reflection A^b mapped on the western Bermuda Rise (37). Modified from (27).



Fig. 3. Benthic foraminiferal extinctions (HO, highest occurrence) and decrease in diversity (number of taxa per sample) are associated with the CIE and deep-water warming (indicated by benthic isotopes, *Oridorsalis* spp.), whereas originations (LO, lowest occurrence) are scattered throughout. Triangles were derived from a single large specimen and are considered outliers. Magnetic susceptibility (related to ~20,000-year precessional cycles) provides a chronology. Mud clasts indicate sediment failure that may have resulted from CH₄ release; CH₄ oxidation led to the overlying dissolution interval and low O₂ benthic fauna (mbsf, meters below sea floor).

7500 years in the present-day deep Atlantic would result in a rapid decrease of the δ^{13} C of Σ CO₂ in the deep Atlantic, followed by an exponential recovery over a period of about 140,000 years as excess carbon is eventually transferred to the rock cycle (Fig. 4). The temporal resolution afforded by precessional cyclicity in the expanded section at Site 1051



Fig. 4. Comparison of theoretical (*18*) and observed (Site 1051) LPTM carbon isotope changes.

allows a direct comparison between theoretical and observed δ^{13} C isotope changes during the LPTM with respect to age. The similarity between modeled and observed records (Fig. 4) provides evidence that massive quantities of CH₄ were released and oxidized in the deep Atlantic during the LPTM.

Methane can escape from buried gas hydrate reservoirs only through sediment failure (24, 25, 34, 35). Thus, widespread slumping and sediment disturbance should have occurred on the middle to lower slope at the onset of the LPTM (Fig. 1). Upper Paleocene sediment at Site 1051 yields benthic foraminifera consistent with deposition in the lower bathyal zone (1000 to 2000 m), which is at the deep end of the dissociation depth range (15, 16, 18) and hence is the ideal depth on a continental margin to monitor potential effects of CH_4 release recorded in marine sediments.

Further evidence linking global perturbations at the LPTM to CH_4 release via sediment failure from a continental slope location is provided by an intraformational mud clast interval immediately below the CIE at Site 1051 (Fig. 3). X-ray fluorescence analyses on the <63-µm fraction of bulk sediment show that matrix and clast sediments are very similar in major and trace element composition. Benthic foraminifera within the clast and matrix sediments are typical of pre-BFEE slope faunas (1000 to 2000 m) and record pre-CIE stable isotope values. Moreover, this layer lacks the coarse sediments and grading typical of a turbidity deposit derived from shal-

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low waters; instead, it contains partially compacted, fine-grained clasts up to 5 cm long and has a scour mark at its base (27). The lithologic, faunal, and geochemical evidence indicates that the intraformational mud clast layer was transported from a penecontemporaneous horizon just upslope from Site 1051 at the crucial time, precisely at the onset of the CIE (Fig. 3). The juxtaposition of the top of a mud clast layer and the base of the CIE in a sediment succession deposited on the lower slope is a compelling argument for CH4 release via sediment failure at the Blake Nose during the LPTM. Evidence for the requisite deep-water warming just before the CH₄ release is not evident in our data, but would have been erased by erosion that formed the scour mark at the base of the mud clast interval.

Seismic profiles across the Blake Nose (27) reveal three features (Fig. 2) associated with the CIE: an extensive interval of chaotic reflections above a buried Aptian reef, a prominent seismic reflection, and a scarp upslope from Site 1051. Buried reefs may serve as traps for overpressured gas and gas hydrate (36), and CH₄ could have vented from the region of chaotic reflections during the LPTM (Fig. 2). This area was at the appropriate depth given for slope failure caused by hydrate dissociation in the Paleocene (Fig. 1). The chaotic interval is associated with a seismic reflection traced to Site 1051 that correlates with the CIE. This seismic reflection apparently is caused by the impedance contrast between the mud clast layer and the overlying dissolution interval observed at Site 1051. The CIE reflection clearly postdates reflection A^{b} , a time when widespread current-controlled sedimentation began in the western North Atlantic (37). A scarp upslope from Site 1051 (Fig. 2) may be related to slope failure associated with CH₄ release or to erosion associated with current-controlled sedimentation. We cannot discriminate between the two possibilities with seismic profiles available at present, but we note that the chaotic zone, seismic reflection, and scarp can be traced to the depth of the CIE at Site 1051 (Fig. 2), indicating a temporal equivalency and suggesting a causal link.

Even though our results suggest that CH_4 was released from the Blake Nose region during the LPTM, the mass of CH_4 from this region alone is insufficient to explain the magnitude of global perturbations at the LPTM. Other sections deposited on the middle to lower slope during the LPTM also must exhibit features similar to those reported here.

References and Notes

- M.-P. Aubry, W. A. Berggren, L. D. Stott, A. Sinha, in Correlations of the Early Paleogene in Northwest Europe, R. O. Knox et al., Eds. (Spec. Publ. 101, Geological Society, London, 1996), p. 353.
- 2. T. J. Bralower, D. J. Thomas, E. Thomas, J. C. Zachos, *Geology* 26, 671 (1998).

- 3. J. P. Kennett and L. D. Stott, Nature 353, 225 (1991).
- 4. J. C. Zachos, K. C. Lohmann, J. C. G. Walker, S. W. Wise, J. Geol. 101, 191 (1993).
- E. Thomas and N. J. Shackleton, in *Correlations of the Early Paleogene in Northwest Europe*, R. O. Knox *et al.*, Eds. (Spec. Publ. 101, Geological Society, London, 1996), pp. 401–411.
- H. C. Fricke, W. C. Clyde, J. R. O'Neil, P. D. Gingerich, Earth Planet. Sci. Lett. 160, 193 (1998).
- J. J. Hooker, in *Correlations of the Early Paleogene in Northwest Europe*, R. O. Knox *et al.*, Eds. (Spec. Publ. 101, Geological Society, London, 1996), pp. 205–218;
 W. C. Clyde and P. D. Gingerich, *Geology* 26, 1011 (1998).
- 8. D. K. Pak and K. G. Miller, *Paleoceanography* 7, 405 (1992).
- J. I. Canudo, G. Keller, E. Molina, N. Ortiz, Palaeogeogr. Palaeoclimatol. Palaeoecol. 114, 75 (1995).
- 10. T. J. Bralower et al., Geology **25**, 963 (1997).
- 11. K. Kaiho et al., Paleoceanography 11, 447 (1996)
- 12. P. L. Steineck and E. Thomas, Geology 24, 583 (1996).
- 13. P. L. Koch, J. C. Zachos, P. Gingerich, Nature 358, 319
- (1992). 14. G. Lu and G. Keller, *Mar. Micropaleontol.* **21**, 101
- (1993).
 15. G. R. Dickens, J. R. O'Neil, D. K. Rea, R. M. Owen, Paleoceanography 10, 965 (1995).
- 16. G. R. Dickens, M. M. Castillo, J. C. G. Walker, *Geology* **25**, 259 (1997).
- E. Thomas, in *Late Palaeocene–Early Eocene Climatic* and *Biotic Events*, M.-P. Aubry, S. Lucas, W. A. Berggren, Eds. (Columbia Univ. Press, New York, 1998), pp. 214–243.
- 18. G. R. Dickens, Bull. Soc. Geol. France, in press.
- 19. K. A. Kvenvolden, Rev. Geophys. 31, 173 (1993).
- 20. W. S. Holbrook et al., Science 273, 1840 (1996).
- G. R. Dickens, C. K. Paull, P. Wallace, ODP Leg 164 Scientific Party, *Nature* 385, 426 (1997).
- N. J. Shacketon, M. A. Hall, A. Boersma, *Init. Rep. Deep Sea Drill. Proj.* 74, 599 (1984).
- K. G. Miller, R. G. Fairbanks, G. S. Mountain, Paleoceanography 2, 741 (1987).
- 24. R. D. McIver, AAPG Bull. 75, 910 (1982).
- 25. R. Kayen and H. Lee, Mar. Geotech. 10, 125 (1991).
- M. A. deAngelis, M. D. Lilley, E. J. Olson, J. A. Baross, Deep Sea Res. / 40, 1169 (1993); C. K. Paull, W. Ussler III, W. S. Borowski, F. N. Speiss, *Geology* 23, 89 (1995).
- R. D. Norris et al., Proceedings of the Ocean Drilling Program, Initial Reports, 171B (College Station, TX, 1998).
- R. Norris, Eos **78** (fall suppl.), F364 (1997); R. D. Norris, U. Rohl, S. Bains, Early Paleogene Warm Climates Abstracts, vol. C21 (1999); U. Rohl, R. D. Norris, T. J. Bralower, G. Wefer, Early Paleogene Warm Climates Abstracts, vol. C21 (1999); S. Bains, R. M. Coffield, R. D. Norris, Science **285**, 274 (1999).
- The late Paleocene was relatively ice-free (23) [J. C. Zachos, L. D. Stott, K. C. Lohmann, *Paleoceanography* 9, 353 (1994)]. Paleotemperature equations are from S. Epstein, R. Buchsbaum, H. Lowenstam, H. C. Urey, *Bull. Geol. Soc. Am.* 64, 1315 (1953); J. R. O'Neil, R. N. Clayton, T. K. Mayeda, *J. Chem. Phys.* 51, 5547 (1969). Because bioturbation and dissolution may obscure the full amplitude of temperature change, 6°C is a minimum estimate.
- 30. C. Ruppel and G. R. Dickens, *Eos* **80** (fall suppl.), S333 (1999).
- J. C. Zachos, M. A. Arthur, W. E. Dean, *Nature* 337, 61 (1989).
- A. H. Knoll, R. K. Bambach, D. Canfield, J. P. Grotzinger, *Science* 273, 452 (1996).
- 33. S. A. Bowring et al., Science 280, 1039 (1998).
- C. K. Paull, W. J. Buelow, W. Ussler III; W. S. Borowski, Geology 24, 143 (1996).
- W. P. Dillon et al., in Gas Hydrates, Relevance to World Margin Stability and Climatic Change, J.-P. Henriet and J. Mienert, Eds. (Spec. Publ. 137, Geological Society, London, 1998), p. 293.
- 36. E. D. Sloan *et al., Eos* **80** (spring suppl.), 247 (1999). 37. G. S. Mountain and K. G. Miller, *Paleoceanography* **7**,
- 423 (1992).

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References and Notes

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