

# A blast of gas in the latest Paleocene: Simulating first-order effects of massive dissociation of oceanic methane hydrate

Gerald R. Dickens\*

Department of Geological Sciences, University of Michigan, Ann Arbor, Michigan 48109

Maria M. Castillo

School of Natural Resources, University of Michigan, Ann Arbor, Michigan 48109

James C. G. Walker

Department of Atmospheric, Oceanic, and Space Sciences, University of Michigan, Ann Arbor, Michigan 48109

## ABSTRACT

Carbonate and organic matter deposited during the latest Paleocene thermal maximum is characterized by a remarkable  $-2.5\%$  excursion in  $\delta^{13}\text{C}$  that occurred over  $\sim 10^4$  yr and returned to near initial values in an exponential pattern over  $\sim 2 \times 10^5$  yr. It has been hypothesized that this excursion signifies transfer of  $1.4$  to  $2.8 \times 10^{18}$  g of  $\text{CH}_4$  from oceanic hydrates to the combined ocean-atmosphere inorganic carbon reservoir. A scenario with  $1.12 \times 10^{18}$  g of  $\text{CH}_4$  is numerically simulated here within the framework of the present-day global carbon cycle to test the plausibility of the hypothesis. We find that (1) the  $\delta^{13}\text{C}$  of the deep ocean, shallow ocean, and atmosphere decreases by  $-2.3\%$  over  $10^4$  yr and returns to initial values in an exponential pattern over  $\sim 2 \times 10^5$  yr; (2) the depth of the lysocline shoals by up to  $400$  m over  $10^4$  yr, and this rise is most pronounced in one ocean region; and (3) global surface temperature increases by  $\sim 2^\circ\text{C}$  over  $10^4$  yr and returns to initial values over  $\sim 2 \times 10^6$  yr. The first effect is quantitatively consistent with the geologic record; the latter two effects are qualitatively consistent with observations. Thus, significant  $\text{CH}_4$  release from oceanic hydrates is a plausible explanation for observed carbon cycle perturbations during the thermal maximum. This conclusion is of broad interest because the flux of  $\text{CH}_4$  invoked during the maximum is of similar magnitude to that released to the atmosphere from present-day anthropogenic  $\text{CH}_4$  sources.

## INTRODUCTION

The latest Paleocene thermal maximum (LPTM) was a time interval ca.  $55.5$  Ma when temperatures at high-latitude locations and in the deep ocean increased by  $>4^\circ\text{C}$  over  $<10^4$  yr (Kennett and Stott, 1991; Zachos et al., 1993). Primary evidence for this warming is a  $-2\%$  to  $-3\%$  excursion in  $\delta^{18}\text{O}$  of benthic foraminifera of all oceans and planktic foraminifera at high-latitude locations (Kennett and Stott, 1991; Bralower et al., 1995; Thomas and Shackleton, 1996; Schmitz et al., 1996). Likely ancillary support for the warming includes an extraordinary high-latitude interchange of terrestrial mammalian orders (Maas et al., 1995; Hooker, 1996), a prominent extinction of benthic fauna in neritic to abyssal environments (Kaiho et al., 1996; Steinbeck and Thomas, 1996; Thomas, 1996), and an input to the ocean of clay minerals indicative of humid conditions (Robert and Kennett, 1994; Kaiho et al., 1996). Cause of rapid warming during the LPTM remains unclear but probably involves changes in tectonism, thermohaline circulation, and atmospheric  $p\text{CO}_2$ .

Nearly coeval with evidence for LPTM warming is a  $\delta^{13}\text{C}$  excursion in carbonate and organic matter that, in high-resolution open-ocean ben-

thic foraminifera records, can be described as a rapid decrease of  $\sim -2.5\%$  over  $10^4$  yr followed by a return to near initial values in a roughly exponential pattern over  $\sim 2 \times 10^5$  yr (Fig. 1). This  $\delta^{13}\text{C}$  excursion has been documented in planktic and benthic foraminifera in sediment of all oceans (Kennett and Stott, 1991; Bralower et al., 1995; Thomas and Shackleton, 1996; Stott et al., 1996; Schmitz et al., 1996), in fossil tooth enamel and carbonate concretions in terrestrial sequences of North America (Koch et al., 1995), and in terrestrial organic carbon in sediment from Europe and New Zealand (Stott et al., 1996; Kaiho et al., 1996).

The magnitude, timing, and global nature of the  $\delta^{13}\text{C}$  excursion imply that an immense quantity of carbon greatly enriched in  $^{12}\text{C}$  was rapidly added to the combined ocean-atmosphere inorganic carbon reservoir (Zachos et al., 1993; Dickens et al., 1995; Thomas and Shackleton, 1996). However, the two conventional hypotheses for rapidly decreasing the mean  $\delta^{13}\text{C}$  of the ocean-atmosphere inorganic carbon reservoir (addition of volcanogenic  $\text{CO}_2$ ; transfer of terrestrial biomass) are untenable explanations for the observed excursion (Dickens et al., 1995; Thomas and Shackleton, 1996). Mantle  $\text{CO}_2$  is not sufficiently enriched in  $^{12}\text{C}$ ; the terrestrial biomass is not sufficiently large.

Clathrate hydrates of  $\text{CH}_4$  (methane hydrates) are solids composed of water and  $\text{CH}_4$  that occur

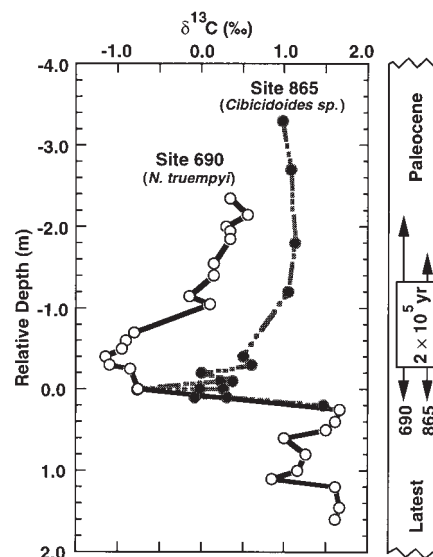


Figure 1. High-resolution carbon isotope records in benthic foraminifera at Ocean Drilling Program (ODP) Site 690 on Maud Rise in South Atlantic (Kennett and Stott, 1991), and Site 865 on Allison Guyot in Equatorial Pacific (Bralower et al., 1995). Both records have been placed on common depth scale;  $0.0$  m placed at  $\delta^{13}\text{C}$  minimum. Entire  $\delta^{13}\text{C}$  excursion (rapid decrease and return to near initial values) occurs within  $2$  m at both sites. This stratigraphy constrains duration of excursion to within  $2 \times 10^5$  yr (Kennett and Stott, 1991; Bralower et al., 1995).

\*Present address: Department of Earth Sciences, James Cook University, Townsville, Queensland 4811, Australia.

naturally in pore space of certain marine sediment sequences (Kvenvolden, 1993). The stability of these hydrates depends on temperature. Because current estimates for the mass ( $11 \times 10^{18}$  g of C) and isotopic composition ( $\delta^{13}\text{C}$  of  $-60\text{‰}$ ) of oceanic  $\text{CH}_4$  hydrates (Kvenvolden, 1993) make this a reservoir that can potentially transfer immense quantities of carbon greatly enriched in  $^{12}\text{C}$  to the combined ocean-atmosphere inorganic carbon reservoir over short ( $<10^4$  yr) time scales, a default hypothesis for the LPTM  $\delta^{13}\text{C}$  excursion has been proposed (Dickens et al., 1995): abrupt deep sea warming induced a shift in sediment geotherms and release of  $\text{CH}_4$  from oceanic hydrates.

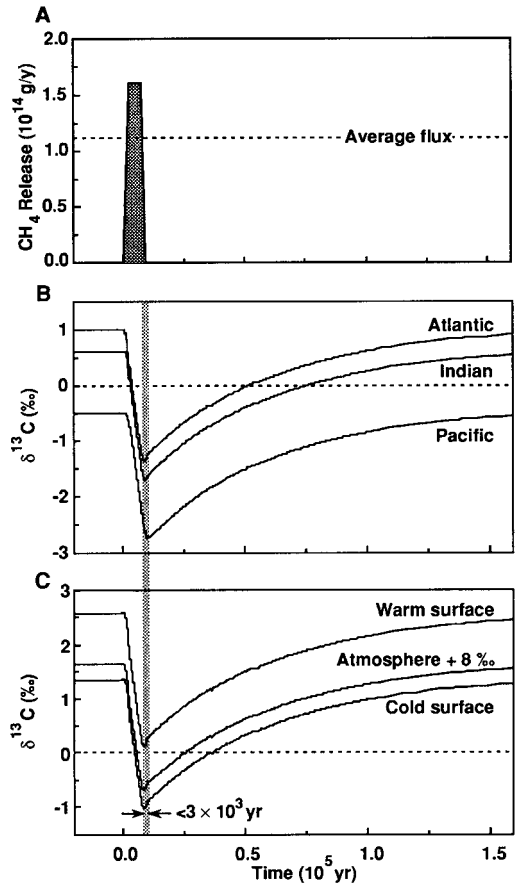
Mass-balance calculations suggest that transfer of  $1.4$  to  $2.8 \times 10^{18}$  g of  $\text{CH}_4$  from oceanic hydrates to the combined ocean-atmosphere inorganic reservoir would explain the observed  $\delta^{13}\text{C}$  excursion during the LPTM (Dickens et al., 1995). However, the plausibility of this suggestion has not been evaluated with a well-documented model of the carbon cycle. Here we numerically simulate the  $\text{CH}_4$  transfer scenario within the framework of the present-day global carbon cycle to show that the LPTM  $\delta^{13}\text{C}$  excursion can be explained by addition of  $\sim 1.12 \times 10^{18}$  g of  $\text{CH}_4$  with a  $\delta^{13}\text{C}$  of  $-60\text{‰}$ . We further demonstrate that such a simulation necessitates first-order changes in  $\text{CaCO}_3$  dissolution and global surface temperature that are consistent with geologic observations of the LPTM.

### CARBON MODEL FRAMEWORK

The model chosen to evaluate first-order effects of  $\text{CH}_4$  release during the LPTM was developed by Walker and Kasting (1992) to simulate the response of the present-day carbon cycle to variable inputs of  $\text{CO}_2$  over time intervals  $<10^7$  yr. The ocean is characterized by warm and cold shallow-water reservoirs, a thermocline reservoir, and deep Atlantic, Indian, and Pacific reservoirs, and the atmosphere and biomass are represented by single reservoirs. The model includes exchange with the rock cycle, distinguishes between shelf and pelagic carbonate precipitation, and has distinct lysocline depths in the three deep ocean reservoirs. Exchange fluxes between various reservoirs were determined (here and by Walker and Kasting, 1992) by tuning the model to reproduce the distribution of dissolved phosphate and total dissolved carbon between the ocean reservoirs and the distribution of  $^{13}\text{C}$  and  $^{14}\text{C}$  in the ocean and atmosphere (including radiocarbon from atomic weapons testing).

After tuning, the model can be used to simulate responses of initial values of carbon isotopes, lysocline depths, atmospheric  $p\text{CO}_2$ , and global average surface temperature to a given input of  $\text{CO}_2$ . Initial values used here are those for the preindustrial steady-state and were given by Walker and Kasting (1992). Equations linking atmospheric  $p\text{CO}_2$  and global surface temperature were also given by Walker and Kasting (1992).

**Figure 2.** Effect of releasing  $1.12 \times 10^{18}$  g of  $\text{CH}_4$  with  $\delta^{13}\text{C}$  of  $-60\text{‰}$  over  $10^4$  yr on  $\delta^{13}\text{C}$  value of present-day preindustrial carbon reservoirs. **A:** Assumed release of  $\text{CH}_4$  at average rate of  $1.12 \times 10^{14}$  g of  $\text{CH}_4/\text{yr}$  over  $10^4$  yr. **B:** Response of  $\delta^{13}\text{C}$  in deep water of Atlantic, Indian, and Pacific Oceans. Initial values are  $0.996\text{‰}$ ,  $0.620\text{‰}$ , and  $-0.508\text{‰}$ , respectively. **C:** Response of  $\delta^{13}\text{C}$  in warm surface water, cold surface water, and atmosphere (shifted by  $+8\text{‰}$ ). Initial values are  $2.577\text{‰}$ ,  $1.355\text{‰}$ , and  $-6.367\text{‰}$ , respectively.



We assume that the model provides a reasonable representation of how preindustrial steady-state conditions will be perturbed with a given input of  $\text{CO}_2$  (see discussion by Walker and Kasting, 1992). Indeed, Walker and Kasting (1992) demonstrated that the tuned model with initial conditions used here will reproduce observed records of atmospheric  $p\text{CO}_2$ ,  $^{13}\text{C}$ , and  $^{14}\text{C}$  caused by anthropogenic  $\text{CO}_2$  inputs and forest clearance.

The LPTM hydrate dissociation hypothesis was simulated here by adding  $\text{CO}_2$  with a  $\delta^{13}\text{C}$  of  $-60\text{‰}$  to the atmosphere at an average rate of  $3.08 \times 10^{14}$  g of  $\text{CO}_2/\text{yr}$  ( $1.12 \times 10^{14}$  g of  $\text{CH}_4/\text{yr}$ ) over  $10^4$  yr (Fig. 2). Justification for this approach is that  $\text{CH}_4$  in oceanic hydrates has an average  $\delta^{13}\text{C}$  of  $\sim -60\text{‰}$  (Kvenvolden, 1993),  $\text{CH}_4$  is rapidly ( $<10$  yr) oxidized to  $\text{CO}_2$  in the atmosphere and ocean (Ward et al., 1987; Khalil and Shearer, 1993), and isotopic and stratigraphic records (Fig. 1) constrain the duration of carbon release to  $\sim 10^4$  yr. A stepped release of  $\text{CH}_4$  with time (Fig. 2) and an input into the atmosphere (rather than into one of the ocean reservoirs) were assumed for the sake of modeling because information concerning these parameters is inconclusive or absent in the literature. Effects of  $\text{CH}_4$  (or  $\text{CO}_2$ ) release over  $10^4$  yr upon carbonate dissolution, atmospheric  $p\text{CO}_2$  and surface temperature are expected to be qualitatively similar regardless of which reservoir receives the additional carbon because carbon exchange fluxes between various

reservoirs are relatively large compared to carbon masses of each reservoir (e.g., Walker and Kasting, 1992). However, oxidation of a fraction of the  $\text{CH}_4$  in one or more of the ocean reservoirs should amplify effects on deep sea carbonate dissolution and dampen effects on atmospheric  $p\text{CO}_2$  and temperature.

Addition of significant  $\text{CO}_2$  to the atmosphere or ocean should dissolve some quantity of previously deposited  $\text{CaCO}_3$  in the ocean (Broecker and Peng, 1982; Walker and Kasting, 1992). The LPTM hydrate dissociation hypothesis was simulated here with and without dissolution of previously deposited  $\text{CaCO}_3$ . The simulation with dissolution of previously deposited  $\text{CaCO}_3$  involved  $\text{CaCO}_3$  dissolution in the top 30 cm of sediment over an area of sea floor above the lysocline (see Walker and Kasting, 1992). Global carbon system recovery was then evaluated for 5 m.y. after the initial  $10^4$  yr release of  $\text{CH}_4$  in both of these scenarios.

### RESULTS

Although initial  $\delta^{13}\text{C}$  values are different in warm surface water, cold surface water, deep ocean water, and the atmosphere (because of fractionation effects and the biological pump), the  $\delta^{13}\text{C}$  of carbon in each of these reservoirs responds similarly to the given input of  $\text{CH}_4$  over  $10^4$  yr. The model simulation results in a  $-2.2\text{‰}$  to  $-2.4\text{‰}$   $\delta^{13}\text{C}$  excursion in each reservoir over

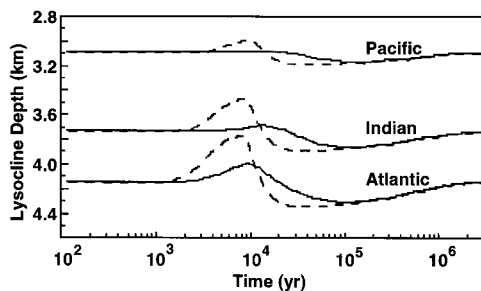
$10^4$  yr (Fig. 2). After the initial  $10^4$  yr input of carbon, the  $\delta^{13}\text{C}$  of each reservoir recovers to initial values in a roughly exponential pattern over  $\sim 2 \times 10^5$  yr (Fig. 2). This effect on the  $\delta^{13}\text{C}$  of various reservoirs is nearly independent of the amount of previously deposited carbonate that is dissolved upon addition of  $\text{CH}_4$ .

Addition of significant  $\text{CO}_2$  (or oxidized  $\text{CH}_4$ ) to the atmosphere or ocean should result in shoaling of lysocline depths followed by deepening of lysocline depths and gradual return to initial values (Broecker and Peng, 1982; Walker and Kasting, 1992). This effect on the lysocline is strongly dependent on the amount of previously deposited carbonate that is dissolved upon carbon addition, the location along deep ocean advective flow, and the relative sizes of deep ocean reservoirs (Broecker and Peng, 1982; Walker and Kasting, 1992). In the simulation without dissolution of previously deposited carbonate, lysocline depths shoal by  $\sim 420$  m in the Atlantic Ocean,  $\sim 300$  m in the Indian Ocean, and  $\sim 110$  m in the Pacific Ocean over  $10^4$  yr (Fig. 3). Lysocline depths then deepen over  $\sim 2 \times 10^5$  yr such that lysocline depths are deeper than initial values by  $\sim 200$  m in the Atlantic Ocean,  $\sim 140$  m in the Indian Ocean, and  $\sim 110$  m in the Pacific Ocean (Fig. 3). In the simulation with dissolution of previously deposited carbonate, lysocline depths shoal by  $\sim 160$  m in the Atlantic Ocean,  $\sim 50$  m in the Indian Ocean, and  $\sim 15$  m in the Pacific Ocean over  $10^4$  yr (Fig. 3). Lysocline depths then deepen over  $\sim 2 \times 10^5$  yr such that lysocline depths are deeper than initial values by  $\sim 180$  m in the Atlantic Ocean,  $\sim 130$  m in the Indian Ocean, and  $\sim 80$  m in the Pacific Ocean (Fig. 4). Lysocline depths return to initial values over  $\sim 5 \times 10^6$  yr in both simulations.

Atmospheric  $p\text{CO}_2$  will rise with addition of oxidized  $\text{CH}_4$  to the atmosphere or ocean. An expected effect of this elevated  $p\text{CO}_2$  will be a decrease in the outgoing flux of long-wave infrared radiation from the Earth and an increase in global surface temperature (Walker and Kasting, 1992). The model simulation results in a 70 to 85 ppmv (ppm by volume) rise in atmospheric  $p\text{CO}_2$  over  $10^4$  yr followed by a return to initial conditions over  $\sim 2 \times 10^6$  yr. The rise in  $p\text{CO}_2$  results in a 1.7 to 1.9 °C increase in global surface temperature over  $10^4$  yr (Fig. 4). A range in values exists because expected changes in atmospheric  $p\text{CO}_2$  depend on the amount of previously deposited  $\text{CaCO}_3$  that is dissolved upon addition of oxidized  $\text{CH}_4$ .

## DISCUSSION

A rapid negative excursion in the  $\delta^{13}\text{C}$  of global records of carbonate and organic matter implies that a mass of carbon enriched in  $^{12}\text{C}$  was added to the combined ocean-atmosphere inorganic carbon reservoir. The magnitude and duration of such an excursion depend on mass and isotope composition of carbon input, sizes of var-



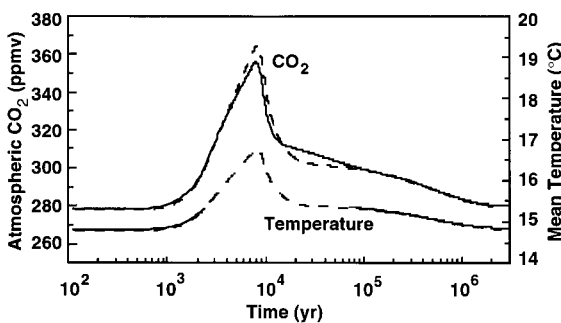
**Figure 3.** Response of present-day lysocline depths in Atlantic, Indian, and Pacific Oceans to  $\text{CH}_4$  release shown in Figure 2A. Dashed curves show response without dissolution of previously deposited  $\text{CaCO}_3$ . Solid curves show response when  $\text{CaCO}_3$  in upper 30 cm of sediment is dissolved upon addition of  $\text{CH}_4$  and introduction of newly corrosive water (Walker and Kasting, 1992). Initial values are 4.14, 3.73, and 3.09 km, respectively. Time scale is logarithmic.

ious global carbon reservoirs, and exchange fluxes between these reservoirs (Broecker and Peng, 1982; Walker and Kasting, 1992).

The pronounced and rapid  $\sim 2.5\%$  excursion in global  $\delta^{13}\text{C}$  records across the LPTM has been interpreted as representing release and oxidation of  $1.4$  to  $2.8 \times 10^{18}$  g of  $\text{CH}_4$  from oceanic hydrates (Dickens et al., 1995). Modeling results presented here support the plausibility of this hypothesis inasmuch as the observed  $\delta^{13}\text{C}$  excursion (Fig. 1) can be closely simulated within the framework of the present-day carbon cycle with addition of  $1.12 \times 10^{18}$  g of  $\text{CH}_4$  with a  $\delta^{13}\text{C}$  of  $-60\%$  (Fig. 2).

Addition of  $1.12 \times 10^{18}$  g of  $\text{CH}_4$  is also plausible considering the size of the oceanic  $\text{CH}_4$  hydrate reservoir and the inferred  $>4$  °C increase in bottom water temperature. A 4 °C increase in deep ocean temperature should shift sediment geotherms such that at least 14% of the present-day oceanic hydrate reservoir would be thermally dissociated and available for transfer to the atmosphere and ocean (Dickens et al., 1995). The simulation requires  $<8\%$  of the estimated  $11 \times 10^{18}$  g of C in the present-day oceanic hydrate reservoir.

Workers (Koch et al., 1995; Bralower et al., 1995; Thomas and Shackleton, 1996; Stott et al., 1996; Schmitz et al., 1996; Kaiho et al., 1996) have argued that the LPTM  $\delta^{13}\text{C}$  excursion is time coincident and of similar magnitude (although offset by fractionation) in terrestrial and marine records. This suggestion implies that the  $\delta^{13}\text{C}$  of the atmosphere and all ocean reservoirs respond simultaneously to a major input of carbon during the LPTM. Release and oxidation of  $1.12 \times 10^{18}$  g of  $\text{CH}_4$  over  $10^4$  yr provide a nearly simultaneous  $\delta^{13}\text{C}$  response (within  $3 \times 10^3$  yr) in all carbon reservoirs (Fig. 2).



**Figure 4.** Response of present-day atmospheric  $p\text{CO}_2$  and global average surface temperature to  $\text{CH}_4$  release shown in Figure 2A. Dashed curves show response without dissolution of previously deposited  $\text{CaCO}_3$ . Solid curves show response when  $\text{CaCO}_3$  in upper 30 cm of sediment is dissolved upon addition of  $\text{CH}_4$  and introduction of newly corrosive water (Walker and Kasting, 1992). Initial values are 279.25 ppmv and 14.84 °C, respectively. Time scale is logarithmic.

explain preferential warming at high latitudes (Sloan et al., 1992).

The simulation necessitates removal of  $4.5 \times 10^{18}$  g of  $O_2$  via oxidation of  $CH_4$ . Because terrestrial vertebrates and flora underwent high species origination in the latest Paleocene (Koch et al., 1995; Maas et al., 1995; Hooker, 1996; Thomas and Shackleton, 1996), any explanation for the LPTM  $\delta^{13}C$  excursion that results in appreciable depletion of atmospheric  $O_2$  would be inconsistent with the geologic record. Present-day atmospheric and combined ocean reservoirs contain  $\sim 1.2 \times 10^{21}$  g and  $\sim 6.8 \times 10^{18}$  g of  $O_2$ , respectively (Walker, 1980). Thus, addition of  $1.4 \times 10^{18}$  g of  $CH_4$  to the atmosphere or ocean would not significantly decrease the  $O_2$  content of the atmosphere. However, because  $O_2$  exchange fluxes between the deep ocean and atmosphere take on the order of  $10^3$  yr, if a substantial fraction of the  $CH_4$  was oxidized in the ocean, there should have been a brief time interval of significant oceanwide  $O_2$  depletion during the LPTM. Investigations of microfossil assemblages (Kaiho et al., 1996; Thomas, 1996) suggest that such  $O_2$  deficiency occurred during the LPTM, although this change might be related to other variables (e.g., decreased  $O_2$  solubility in warmer water, Kennett and Stott, 1991).

Although the LPTM hydrate dissociation hypothesis is modeled here with oxidation of  $CH_4$  in the atmosphere, alternatives involving substantial oxidation of  $CH_4$  in one or more ocean reservoirs are plausible with current assessments for latest Paleocene carbonate dissolution, atmospheric  $pCO_2$ , global surface temperature, and dissolved  $O_2$  in the ocean. Indeed, rigorous quantification of these variables may provide fundamental constraints on the location of  $CH_4$  oxidation as well as the viability of the overall hypothesis.

The LPTM hydrate dissociation hypothesis invokes three fundamental assumptions (Dickens et al., 1995): the estimated mass of the present-day oceanic hydrate reservoir ( $11 \times 10^{18}$  g of C) is the correct order of magnitude; processes controlling hydrate formation and distribution were the same in the Paleocene and present day; and carbon transfer can occur between oceanic hydrates and the ocean-atmosphere inorganic carbon reservoir during deep sea warming. None of these assumptions can be rigorously evaluated with current information. However, within the framework of the present-day carbon cycle, the hypothesis involving  $\sim 1.12 \times 10^{18}$  g of  $CH_4$  is the only hypothesis forwarded to date that (1) can explain the observed  $\delta^{13}C$  excursion in global carbon isotope records, and (2) is consistent with a series of observations concerning deep sea carbonate dissolution and global temperature. The importance of the hypothesis (if correct) is that it

necessitates a mean annual flux of  $CH_4$  to the ocean-atmosphere inorganic carbon reservoir during a brief time interval of rapid biotic and chemical change of a magnitude similar to present-day anthropogenic inputs of  $CH_4$  to the atmosphere ( $3.6 \times 10^{14}$  g of  $CH_4$ /yr; Khalil and Shearer, 1993). To some degree the LPTM may represent a past analog for certain future effects on global biogeochemical cycles.

#### ACKNOWLEDGMENTS

Funding for Dickens was furnished by the Department of Energy through the Graduate Fellowships for Global Change Program. Funding for Walker was supported in part by the National Aeronautics and Space Administration grant NAGW-176. J. Zachos and an anonymous reviewer contributed insightful comments. This paper is a contribution of IGCP Project 386.

#### REFERENCES CITED

- Bralower, T. J., and eight others, 1995, Late Paleocene to Eocene paleoceanography of the equatorial Pacific Ocean: Stable isotopes recorded at Ocean Drilling Program Site 865, Allison Guyot: *Paleoceanography*, v. 10, p. 841–865.
- Broecker, W. S., and Peng, T.-H., 1982, Tracers in the sea: New York, Eldigio Press, 690 p.
- Dickens, G. R., O'Neil, J. R., Rea, D. K., and Owen, R. M., 1995, Dissociation of oceanic methane hydrate as a cause of the carbon isotope excursion at the end of the Paleocene: *Paleoceanography*, v. 10, p. 965–971.
- Hooker, J. J., 1996, Mammalian biostratigraphy across the Paleocene-Eocene boundary in the Paris, London, and Belgian basins, *in* Knox, R. O., et al., eds., Correlations of the early Paleogene in Northwest Europe: Geological Society [London] Special Publication 101, p. 205–218.
- Kaiho, K., and twelve others, 1996, Latest Paleocene benthic foraminiferal extinction and environmental changes at Tawanui, New Zealand: *Paleoceanography*, v. 11, p. 447–465.
- Kennett, J. P., and Stott, L. D., 1991, Abrupt deep sea warming, paleoceanographic changes and benthic extinctions at the end of the Palaeocene: *Nature*, v. 353, p. 319–322.
- Khalil, M. A. K., and Shearer, M. J., 1993, Sources of methane: An overview, *in* Khalil, M. A. K., ed., Atmospheric methane: Sources, sinks, and role in global change: NATO ASI Series, v. 1-13, p. 180–198.
- Koch, P. L., Zachos, J. C., and Dettman, D. L., 1995, Stable isotope stratigraphy and paleoclimatology of the Paleogene Bighorn Basin: *Palaeogeography, Palaeoclimatology, Palaeoecology*, v. 115, p. 61–89.
- Kvenvolden, K. A., 1993, Gas hydrates: Geological perspective and global change: *Reviews of Geophysics*, v. 31, p. 173–187.
- Maas, M. C., Anthony, M. R. L., Gingerich, P. D., Gunnell, G. F., and Krause, D. K., 1995, Mammalian generic diversity and turnover in the late Paleocene and early Eocene of the Bighorn and Crazy

Mountains Basins, Wyoming and Montana: *Palaeogeography, Palaeoclimatology, Palaeoecology*, v. 115, p. 181–207.

- Robert, C., and Kennett, J. P., 1994, Antarctic subtropical humid episode at the Paleocene-Eocene boundary: Clay mineral evidence: *Geology*, v. 22, p. 211–214.
- Schmitz, B., Speijer, R., and Aubry, M.-P., 1996, Latest Paleocene benthic extinction event on the southern Tethyan shelf (Egypt): Foraminiferal stable isotope ( $\delta^{13}C$ ,  $\delta^{18}O$ ) record: *Geology*, v. 24, p. 347–350.
- Sloan, L. C., Walker, J. C. G., Moore, T. C., Jr., Rea, D. K., and Zachos, J. C., 1992, Possible methane-induced polar warming in the early Eocene: *Nature*, v. 357, p. 320–322.
- Steineck, P. L., and Thomas, E., 1996, The latest Paleocene crisis in the deep sea: Ostracode succession at Maud Rise, Southern Ocean: *Geology*, v. 24, p. 583–586.
- Stott, L. D., Sinha, A., Thiry, M., Aubry, M.-P., and Berggren, W. A., 1996, The transfer of  $^{12}C$  changes from the ocean to the terrestrial biosphere across the Paleocene/Eocene boundary: Criteria for terrestrial-marine correlations, *in* Knox, R. O., et al., eds., Correlations of the early Paleogene in Northwest Europe: Geological Society [London] Special Publication 101, p. 381–399.
- Thomas, E., 1996, Biogeography of the late Paleocene benthic foraminiferal extinction, *in* Aubry, M.-P., et al., eds., The Paleocene/Eocene boundary (IGCP Project 308): New York, Eldigio Press (in press).
- Thomas, E., and Shackleton, N. J., 1996, The Paleocene-Eocene benthic foraminiferal extinction and stable isotope anomalies, *in* Knox, R. O., et al., eds., Correlations of the early Paleogene in Northwest Europe: Geological Society [London] Special Publication 101, p. 401–411.
- Walker, J. C. G., 1980, The oxygen cycle, *in* Hutzinger, O., ed., Handbook of environmental chemistry, Volume 1, Part A: Berlin, Springer-Verlag, p. 85–104.
- Walker, J. C. G., and Kasting, J. F., 1992, Effects of fuel and forest conservation on future levels of atmospheric carbon dioxide: *Palaeogeography, Palaeoclimatology, Palaeoecology*, v. 97, p. 151–189.
- Ward, B. B., Kilpatrick, K. A., Novelli, P. C., and Scranton, M. I., 1987, Methane oxidation and methane fluxes in the ocean surface layer and deep anoxic waters: *Nature*, v. 327, p. 226–229.
- Zachos, J. C., Lohmann, K. C., Walker, J. C. G., and Wise, S. W., 1993, Abrupt climate change and transient climates during the Paleogene: A marine perspective: *Journal of Geology*, v. 101, p. 191–213.

Manuscript received August 23, 1996

Revised manuscript received December 2, 1996

Manuscript accepted December 10, 1996