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Dissociation of oceanic methane hydrate as a cause of the carbon isotope excursion at the end of the Paleocene

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Abstract. Isotopic records across the "Latest Paleocene Thermal Maximum" (LPTM) indicate that bottom water temperature increased by more than 4°C during a brief time interval ($<10^4$ years) of the latest Paleocene (~55.6 Ma). There also was a coeval -2 to -3‰ excursion in the δ^{13}C of the ocean/atmosphere inorganic carbon reservoir. Given the large mass of this reservoir, a rapid δ^{13}C shift of this magnitude is difficult to explain within the context of conventional hypotheses for changing the mean carbon isotope composition of the ocean and atmosphere. However, a direct consequence of warming bottom water temperature from 11 to 15°C over 10^4 years would be a significant change in sediment thermal gradients and dissociation of oceanic CH_4 hydrate at locations with intermediate water depths. In terms of the present-day oceanic CH_4 hydrate reservoir, thermal dissociation of oceanic CH_4 hydrate during the LPTM could have released greater than 1.1 to 2.1×10^{18} g of carbon with a δ^{13}C of approximately -60‰. The release and subsequent oxidation of this amount of carbon is sufficient to explain a -2 to -3‰ excursion in δ^{13}C across the LPTM. Fate of CH_4 in oceanic hydrates must be considered in developing models of the climatic and paleoceanographic regimes that operated during the LPTM.

Introduction

Understanding mechanisms and consequences of abrupt global change is a current focal point of many paleoceanographic investigations. The onset of the "Latest Paleocene Thermal Maximum" (LPTM) at ~55.6 Ma [*Aubry et al.*, 1995] is particularly intriguing because there are pronounced excursions in the δ^{13}C and δ^{18}O values of carbonate from widespread locations over less than 10^4 years [*Kennett and Stott*, 1991; *Barrera and Huber*, 1991; *Corfield and Cartlidge*, 1992; *Pak and Miller*, 1992; *Koch et al.*, 1992; *Zachos et al.*, 1993; *Corfield*, 1994; *Thomas and Shackleton*, 1995]. These excursions include a -2 to -3‰ shift in δ^{13}C and δ^{18}O values of deep-sea benthic foraminifera, a -4 to -5‰ shift in δ^{13}C values of planktonic foraminifera, a -2 to -3‰ shift in δ^{18}O values of planktonic foraminifera at high-latitude locations, and a -4.5‰ shift in δ^{13}C values of terrestrial paleosol carbonate. The isotope excursions are associated with a fundamental change in deep ocean conditions: the LPTM is marked by significant carbonate dissolution in pelagic sediment [e.g., *Lu and Keller*, 1993; *Thomas and Shackleton*, 1995] and is characterized by the most prominent benthic foraminiferal extinction of the Cenozoic [e.g., *Miller et al.*, 1987a; *Kaiho*, 1994].

The late Paleocene to middle Eocene is considered to be an "ice-free" world [e.g., *Miller et al.*, 1987b; *Zachos et al.*, 1994]. The decrease in δ^{18}O of benthic and high-latitude planktonic foraminifera during the onset of the LPTM thus has been interpreted as a rapid warming of deep and high-latitude waters, with ocean bottom water increasing from approximately 11°C to in excess of 15°C during the initial 10^4 years of the LPTM [*Kennett and Stott*, 1991; *Zachos et al.*, 1993; *Zachos et al.*, 1994; *Thomas and Shackleton*, 1995]. The differential change in the δ^{13}C between benthic and planktonic foraminifera also has been interpreted as a decrease in the δ^{13}C gradient of the water column, perhaps because of a decrease in productivity and/or change in oceanic circulation [e.g., *Kennett and Stott*, 1991; *Zachos et al.*, 1993; *Lu and Keller*, 1993; *Thomas and Shackleton*, 1995].

A satisfactory explanation for the "remaining" and relatively synchronous -2 to -3‰ shift in the δ^{13}C of global carbonate across the LPTM is more problematic [*Zachos et al.*, 1993; *Corfield*, 1994; *Thomas and Shackleton*, 1995]. The magnitude of this excursion within 10^4 years requires an immense and rapid transfer of reduced carbon to the ocean/atmosphere inorganic carbon reservoir, and, as discussed below, conventional hypotheses for changing the mean δ^{13}C of this reservoir may not be applicable. Here we propose a mechanism to explain the LPTM δ^{13}C excursion: the 4°C increase in bottom water temperature led to a significant change in sediment thermal gradients, dissociation of large quantities of oceanic hydrate, and release of CH_4 to the ocean/atmosphere inorganic carbon reservoir.

The LPTM Carbon Isotopic Excursion: The Problem

Previous authors [e.g., *Shackleton*, 1977; *Keigwin and Boyle*, 1985] have suggested that the decrease in carbonate δ^{13}C (~ -0.3 to -0.4‰) across interglacial-glacial transitions reflects net transfer of organic carbon to the ocean/atmosphere inorganic carbon reservoir. Simple mass balance

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calculations, however, demonstrate that this hypothesis is untenable as a sole cause for the $\delta^{13}C$ shift of -2 to -3‰ across the LPTM.

Over time frames significantly shorter than the residence time of carbon in the oceans (~1.4 × 10^5 years) and greater than the mixing time of the oceans (~10^3 years), the amount of carbon that can be redistributed between organic and inorganic carbon reservoirs can be evaluated via the following mass-balance equation:

$$M_{TX}(\delta^{13}C_{TX}) = M_O(\delta^{13}C_O) + M_I(\delta^{13}C_I), \quad (1)$$

where M_{TX}, M_O, M_I, $\delta^{13}C_{TX}$, $\delta^{13}C_O$, and $\delta^{13}C_I$ are the masses and $\delta^{13}C$ of carbon in the total, organic, and inorganic exchangeable carbon reservoirs, respectively. Here the organic carbon reservoir would include land biota, soil, humus, and dissolved marine organic carbon, and the inorganic carbon reservoir would include marine dissolved ΣCO_2 and atmospheric CO_2 (Table 1). Carbon stored in carbonate rocks and conventional fossil fuel reserves (e.g., coal deposits and oil) would not be included in the total exchangeable ocean/atmosphere/terrestrial carbon reservoir (TX) because these reservoirs cannot exchange significant amounts of carbon over rapid (~10^4 years) time frames.

Assuming that Paleocene carbon masses and isotope compositions of the above reservoirs were similar to present-day levels (Table 1), a -2 to -3‰ shift in the $\delta^{13}C$ of the ocean/atmosphere inorganic carbon reservoir can occur only if an enormous amount of the organic carbon reservoir is removed from the total exchangeable carbon reservoir. For example, to produce a shift of -2‰ in the $\delta^{13}C$ of the present-day ocean/atmosphere inorganic carbon reservoir, between 75 and 90% of the organic carbon reservoir would have to be transferred to the ocean/atmosphere inorganic carbon reservoir; likewise, for a $\delta^{13}C$ shift of -3‰ across the LPTM as suggested by certain isotopic records [see *Zachos et al.*, 1993; *Corfield*, 1994], an amount greater than the present-day organic carbon reservoir would have to be transferred (the given ranges reflect different estimates of the size of carbon reservoirs; Table 1). The geological record does not support such biomass destruction across the LPTM [e.g., *Thomas and Shackleton*, 1995]. Consequently, invoking a redistribution of carbon between organic and inorganic carbon reservoirs is untenable as a sole cause of the LPTM $\delta^{13}C$ excursion, unless future investigations can demonstrate that the Paleocene organic carbon reservoir was substantially greater in mass or much lower in $\delta^{13}C$ prior to the LPTM than it is today.

A -2 to -3‰ excursion in the $\delta^{13}C$ of the ocean/atmosphere inorganic carbon reservoir strongly indicates that at least one flux of carbon from a reservoir outside of the exchangeable ocean/atmosphere/terrestrial carbon reservoir (TX) experienced a fundamental change in magnitude (as also noted by *Thomas and Shackleton* [1995]). As evident by plateau basalts and anomalous metal accumulation in deep-sea sediment (especially in the North Atlantic), outgassing of CO_2 from volcanism and deep-sea hydrothermal activity was greater during the late Paleocene and early Eocene relative to present day [*Olivarez and Owen*, 1989; *Rea et al.*, 1990; *Eldholm and Thomas*, 1993]. This CO_2 outgassing may have reached a maximum near the LPTM [*Thomas and Shackleton*, 1995]. Simple mass balance calculations suggest, however, that an increase in mantle derived CO_2 probably was not the primary cause of the LPTM $\delta^{13}C$ shift.

Over time intervals much shorter than the residence time of carbon in the oceans, the mass of carbon transferred from an external reservoir necessary to cause a particular $\delta^{13}C$ excursion in the exchangeable carbon reservoir can be estimated to a first approximation with the following equation:

$$(M_{TX} + M_R)(\delta^{13}C_{TX'}) = (M_R)(\delta^{13}C_R) + (M_{TX})(\delta^{13}C_{TX}), \quad (2)$$

where M_{TX} and $\delta^{13}C_{TX}$ are defined as above, M_R and $\delta^{13}C_R$ are

Table 1. Short-Term (<10^4 years) Exchangeable Carbon Reservoirs (Present-Day)

Reservoir	Mass C, 10^{15}g		
	BP93 / K88	S93 / GF94	$\delta^{13}C_{PDB}$, ‰
Inorganic			
Atmosphere	500	750	
Ocean	30,000	38,000	
Combined inorganic	30,500	38,750	0
Organic			
Land biota	500	550	
Soil and humus	1500	1500	
Dissolved marine	1500	1600	
Combined organic	3500	3650	-25
Total exchangeable (excluding hydrate)	34,000	42,400	-2.1 to -2.6
Oceanic methane hydrate	8250	>10,500	-60

Estimates for the mass of various inorganic and organic C reservoirs are from *Broecker and Peng* [1993] and *Siegenthaler* [1993]; estimates for the mass of the oceanic methane hydrate reservoir are from *Kvenvolden* [1988] and *Gornitz and Fung* [1994]. A suggested range for the latter mass, however, is 7,500 to 15,000 x 10^{15} g (see *Kvenvolden* , 1993; *Gornitz and Fung* , 1994). The organic and inorganic reservoirs do not include conventional fossil fuels (coal deposits and oil reserves) and carbonate rocks.

the mass and $\delta^{13}C$ of carbon transferred from an external reservoir, and $\delta^{13}C_{TX'}$ is the $\delta^{13}C$ of carbon in the total exchangeable carbon reservoir after a mass transfer. Again assuming that Paleocene masses and carbon isotope compositions of various carbon reservoirs were similar to those of present day (Table 1), a -2 to -3‰ shift in the $\delta^{13}C$ of the present-day exchangeable carbon reservoir would require the addition of between approximately 1.0 and 2.5 × 10^{20} g of mantle CO_2 (2.7 to 6.8 × 10^{19} g of C) with a $\delta^{13}C$ value of -7‰. This outgassing over 10^4 years would correspond to a mean annual discharge (1.0 to 2.5 × 10^{16} g of CO_2) that is 25 to 125 times higher than "best" estimates of long-term (10^4 to 10^9 years) mantle CO_2 outgassing rates of 2 to 4 × 10^{14} g CO_2/yr [*Leavitt*, 1982; *Gregor et al.*, 1988; *Zhang and Zindler*, 1993]. Such high rates are improbable. For example, if Earth scientists [*Gregor et al.*, 1988, and references therein; *Zhang and Zindler*, 1993, and references therein] are correct in assuming that global rates of CO_2 outgassing are related largely to basalt production, then invoking mantle CO_2 as the sole cause of the LPTM $\delta^{13}C$ excursion would necessitate a rate of basalt production of the order of > 600 km^3/yr. This rate would be unprecedented in the geological record [e.g., *Leavitt*, 1982; *Larson*, 1991].

Making similar mass balance arguments, ***Thomas and Shackleton*** [1995] have concluded that a "complex combination" of rapid emission of volcanogenic CO_2, changes in oceanic circulation, variations in terrestrial and marine productivity, and changes in the size of exchangeable ocean, atmosphere, and terrestrial carbon reservoirs might have caused the LPTM $\delta^{13}C$ shift. These authors stress, however, that the observed $\delta^{13}C$ excursion is still difficult to explain. We suggest that there is a plausible explanation within the current paleoceanographic confines of the LPTM if an additional external carbon reservoir is considered.

The Hydrate Dissociation Hypothesis

Clathrate hydrates of CH_4 ("methane hydrates") are crystalline substances composed of cages of water molecules that host molecules of CH_4. The stability of these hydrates depends on temperature and pressure (as well as salinity and trace gas composition; Figure 1).

Methane hydrate is restricted to an uppermost depth zone of sediment columns in the marine environment. This zone, at any given location, lies between the sediment-water interface and the subbottom depth where the geotherm intersects the CH_4-hydrate-water equilibrium curve (Figure 2 [*Kvenvolden*, 1988]). On the basis of recent field work along the Cascadia Margin [*Westbrook et al.*, 1994], we assume that the appropriate CH_4-hydrate-water equilibrium curve in the marine environment approximates that of the CH_4-seawater system [*Dickens and Quinby-Hunt*, 1994]. The depth zone over which CH_4 hydrate is stable at a given location therefore depends largely on the profile and intercept (bottom water temperature) of the geotherm (Figure 2).

An enormous amount of reduced carbon is stored in CH_4 hydrate located along present-day continental margins

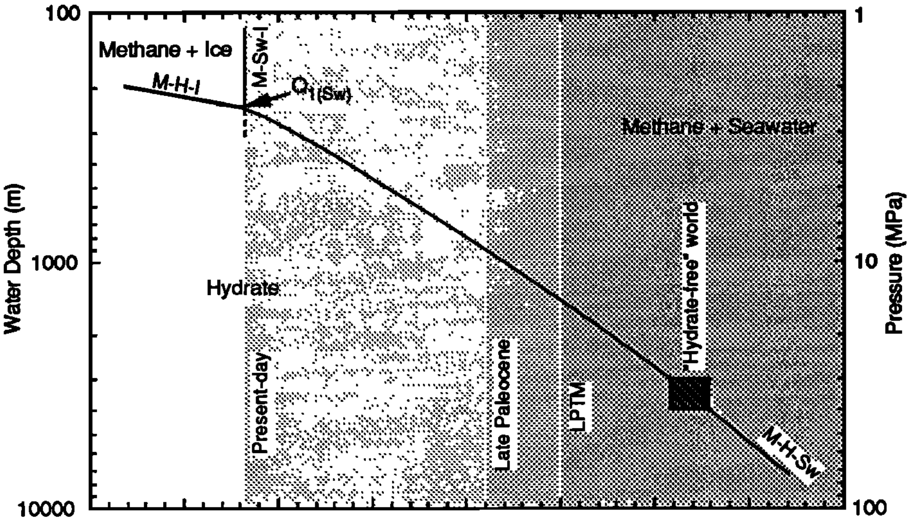
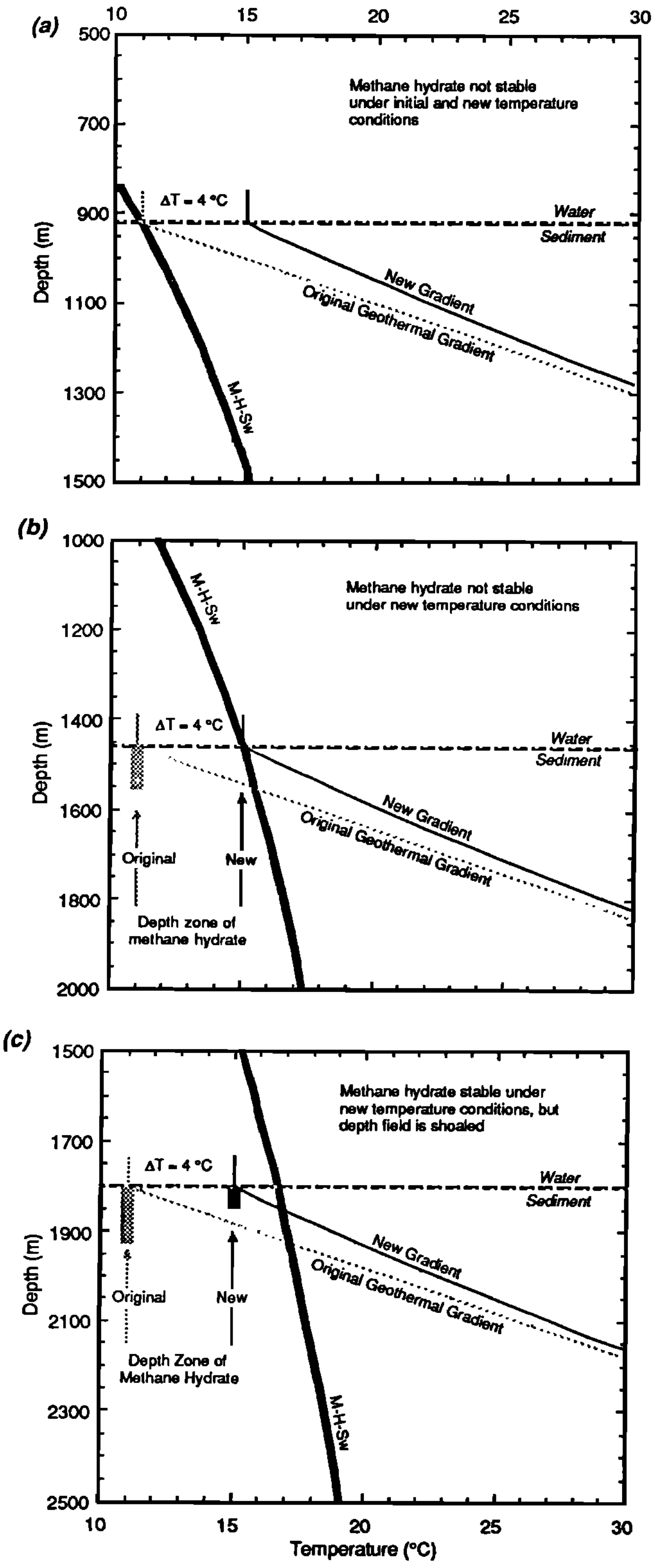


Figure 1. Methane hydrate temperature-depth (pressure) phase diagram for the CH_4-seawater system (extrapolated from *Dickens and Quinby-Hunt* [1994]). There are three fields of stability (CH_4-seawater; CH_4-ice; hydrate) separated by three equilibrium curves (CH_4-ice-seawater; CH_4-hydrate-ice; CH_4-hydrate-seawater). The point where all four phases are in equilibrium is the quadruple point (Q_1). The depth axis on this diagram assumes a hydrostatic pressure gradient of 0.010 MPa/m. In the present-day marine environment (bottom water temperatures to -1.5°C), CH_4 hydrate can exist in sediment where water depths exceed ~250 m. In the Late Paleocene marine environment (bottom water temperatures ~11°C), CH_4 hydrate could exist in sediment where water depths exceeded ~920 m. During the abrupt deep-sea warmth (bottom water temperature ~15°C) of the Latest Paleocene Thermal Maximum (LPTM), CH_4 hydrate could exist only in sediment where water depths exceeded ~1460 m. If essentially all hydrate occurs along continental margins where water depths are shallower than 3000 to 4000 m, a "hydrate-free world" will occur if bottom waters increase to about 21 to 23°C.



[*Kvenvolden*, 1988, 1993]. This hydrate occupies pore space (typically < 10%) in the aforementioned depth zone where there is a supply of methane via bacterial and/or thermogenic breakdown of organic matter [*Kvenvolden*, 1988, 1993]. Estimates from various independent calculations [e.g., *Kvenvolden*, 1988; 1993; *MacDonald*, 1990; *Gornitz and Fung*, 1994] suggest that the present-day oceanic hydrate reservoir contains approximately 7.5 to 15 × 10^{18} g of carbon (1 to 2 × 10^{19} g of CH_4). The $\delta^{13}C$ of CH_4 in this hydrate is highly variable but averages approximately -60‰ [*Kvenvolden*, 1993].

Deep-sea warming will induce a change in sediment geotherms such that pore waters will be warmer at subbottom depths (Figure 2). As suggested by several authors [*Kvenvolden*, 1988; 1993; *MacDonald*, 1990, *Nisbet*, 1990; *Paull et al.*, 1991; *Gornitz and Fung*, 1994] and recently observed at small scale in the Gulf of Mexico [*MacDonald et al.*, 1994], deep-sea warming (and thus a shift in the profile and intercept of sediment geotherms) will dissociate CH_4 hydrates and will reduce the mass of the oceanic hydrate reservoir. The CH_4 released upon hydrate dissociation then might be transferred to the exchangeable carbon reservoir (TX) via diffusion into the water column and/or ebullition into the atmosphere during sediment failure [*Paull et al.*, 1991; *Kvenvolden*, 1993]. Given that CH_4 is rapidly (within 10^1 years) oxidized to CO_2 in the ocean [e.g., *Ward et al.*, 1987; *deAngelis et al.*, 1993] and atmosphere [e.g., *Khalil et al.*, 1993] and that carbon exchange between the deep ocean, atmosphere, and terrestrial biomass is relatively fast (~10^3 years), release of significant CH_4 over 10^4 years would increase the mass of carbon in the exchangeable carbon reservoir. Such release of CH_4 also would decrease the $\delta^{13}C$ of this reservoir.

Within the context of our present understanding of the LPTM, explaining the LPTM $\delta^{13}C$ excursion via release of hydrate CH_4 is appealing because it is a direct and necessary consequence of inferred deep-sea warming. The question remains whether such a carbon transfer scenario is plausible. Specifically, (1) will a 4°C increase in bottom water temperature over 10^4 years significantly affect sediment geotherms and reduce the mass of the oceanic hydrate reservoir, and (2) can the oceanic hydrate reservoir within the above constraints supply enough carbon to explain a -2 to -3‰ excursion in the

Figure 2. The effect of an increase in bottom water temperature from 11°C to 15°C over 10^4 years upon CH_4 stability at locations with water depths of (a) 920 m, (b) 1460 m, and (c) 1800 m. The zone of CH_4 hydrate stability at each location (shaded rectangles) lies between the sediment-water interface and the intersection of the CH_4-hydrate-seawater equilibrium line (M-H-Sw) and the sediment thermal gradient. The effect of the prescribed increase in bottom water temperature is to shift the original geothermal gradient (shown here at 0.05 °C/m) to a new sediment gradient. This change in the sediment gradient dissociates all CH_4 hydrate within sediment at locations with water depths between 920 and 1460 m (Figure 2b). At locations with water depths greater than 1460 m (Figure 2c), the change in the sediment gradient shoals the zone of CH_4 hydrate stability. Methane hydrate is not stable at locations with water depths shallower than 920 m at bottom water temperatures greater than 11°C.

$\delta^{13}C$ of the exchangeable carbon reservoir? We address these questions in the following paragraphs.

The transient thermal regime in oceanic sediment induced by a change in bottom water temperature is a nonlinear and highly complex problem when the temperature change brings about a phase change (e.g., $\text{hydrate}_{(s)} \dashrightarrow CH_{4(g)} + H_2O_{(l)}$) in the sediment [*Carslaw and Jaeger*, 1959]. The problem, however, is greatly simplified if the additional heat required for the phase change is ignored. Given an "infinite" heat source (the ocean) and the small volume of hydrate in the sediment (< 5% for sediment with a porosity of 0.5), this simplification should be reasonable over long time frames (e.g., 10^4 years [*MacDonald* , 1990]). The effect of a gradual increase in bottom water temperature upon a geotherm in sediment (without a phase change) thus can be evaluated with the following equation [*Carslaw and Jaeger*, 1959]:

$$T(z) = T_o + G_o(z) + \Delta T 2^n \Gamma(n/2 + 1) i^n \operatorname{erfc}(z/(4\kappa t)^{1/2}), \qquad (3)$$

where $T(z)$ is the temperature at depth, z, T_o is the initial bottom water temperature, G_o is the initial geotherm, ΔT is the temperature increase, κ is the thermal diffusivity, t is the time over which ΔT occurred, and $2^n \Gamma(n/2 + 1) i^n \operatorname{erfc}(x)$ is the n^{th} repeated integral of the error function. An average value of κ for marine sediment along continental slopes and rises is about 3×10^{-7} m^2 (from the empirical relationship between κ and thermal conductivity [*Hyndman et al.*, 1979] and thermal conductivity measurements along continental slopes and rises [*Wright and Louden*, 1989]). For locations with initial geotherms of 0.05 °C/m, a linear increase (i.e., $n = 2$) in the bottom water temperature from 11 to 15°C over 10^4 years leads to the "new" geotherms shown in Figure 2. The expected temperature increase at a given depth (equation (3)) is independent of the initial thermal gradient; hence for a 4°C temperature increase in bottom water over 10^4 years, subbottom depths will remain warmer than bottom waters for all locations with initial geotherms greater than ~0.02 °C/m.

A change in bottom water temperature from 11 to 15°C over 10^4 years would maintain a positive slope in sediment geotherms because continental margins invariably have geotherms greater than 0.02 °C/m [e.g., *Wright and Louden*, 1989]. Inferred deep-sea warmth during the onset of the LPTM thus may have dissociated oceanic hydrate throughout sediment columns where the sediment/water interface lay between 920 and 1460 m below sea level (Figure 2). This depth range of locations where hydrate would become unstable throughout the sediment column is the difference between the upper stability depth of CH_4 hydrate at 11°C (~920 m) and at 15°C (~1460 m). During inferred LPTM deep-sea warmth, CH_4 hydrate would remain stable in uppermost sediment at locations deeper than 1460-m water depth; however, the depth zone over which CH_4 hydrate was stable at these locations would have shoaled (Figure 2).

A considerable quantity of carbon (as CH_4) might have been transferred from the oceanic hydrate reservoir to the exchangeable ocean/atmosphere/terrestrial carbon reservoir (TX) during the onset of the LPTM. Assuming that all present-day oceanic hydrate exists at continental margins where water depths are between 250 (the present-day upper stability depth of CH_4 hydrate in the ocean) and 4000 m and that areas of continental margins and volumes of hydrate are evenly distributed across this 3750-m depth range, then about 14% of the present-day oceanic hydrate reservoir lies in sediment columns where the sediment/water interface is between 920 and 1460 m below sea level. The above estimate is most likely too low, because mechanisms for hydrate formation preclude the existence of hydrate in many shallow (<1000 m) and deep water (>3000 m) locations [*MacDonald*, 1990; *Kvenvolden*, 1993; *Gornitz and Fung*, 1994]. Methane released at locations between 920 and 1460 m below sea level presumably would have transferred to the exchangeable carbon reservoir because the solubility of CH_4 in water is extremely low; that is, CH_4 would not remain in pore waters. Methane released upon basal hydrate dissociation at locations deeper than 1460-m water depth also might have transferred to the exchangeable carbon reservoir. This additional CH_4 input would depend on whether stable hydrate in the uppermost sediment served as an impermeable trap [cf. *Rowe and Gettrust*, 1993; *Kvenvolden*, 1993] and whether rates of CH_4 migration (upward through the hydrate stability zone) could exceed rates of hydrate formation.

Transfer and oxidation of 14% of the present-day hydrate reservoir (1.1 to 2.1×10^{18} g of C; 1.4 to 2.8×10^{18} g of CH_4) is just about the amount of CH_4 (with a $\delta^{13}C$ of -60‰) needed to explain a -2 to -3‰ excursion in the $\delta^{13}C$ of the exchangeable ocean/atmosphere/terrestrial carbon reservoir. For a -2‰ shift in the $\delta^{13}C$ of the present-day exchangeable carbon reservoir (Table 1; equation (2)), approximately 1.6 to 2.0×10^{18} g of CH_4 would have to be added; for a shift of -3‰, approximately 2.5 to 3.1×10^{18} g of CH_4 would have to be added. The mean annual fluxes of CH_4 necessary to obtain these amounts of carbon over 10^4 years also are plausible considering the present-day anthropogenic input of CH_4 to the atmosphere. The average rate of CH_4 release from hydrate dissociation necessary to explain a -2 to -3‰ $\delta^{13}C$ excursion in the present-day exchangeable ocean/atmosphere/terrestrial carbon reservoir over 10^4 years would have to be about 1.6 to 3.1×10^{14} g CH_4/yr. This rate is lower than the combined flux of present-day anthropogenic sources of methane (e.g., via rice agriculture and domestic animals) to the atmosphere (~3.6×10^{14} g CH_4/yr [*Khalil and Shearer*, 1993]). In fact, the above anthropogenic input of CH_4 explains in part the gradual lowering of $\delta^{13}C$ of atmospheric CO_2 that is taking place today.

Summary, Problems, and Implications of the Hydrate Dissociation Hypothesis

The observed -2 to -3‰ excursion in the $\delta^{13}C$ of global carbonate across the LPTM is difficult to explain with conventional hypotheses for changing the mean carbon isotope composition of the ocean/atmosphere inorganic carbon reservoir. Dissociation of oceanic hydrate and release of CH_4 upon a 4°C increase in bottom water temperature, however, is a plausible mechanism. An increase in bottom water temperature from 11°C to 15°C over 10^4 years is sufficient to change sediment thermal gradients so that all hydrate would have been dissociated within sediment columns where the water depths were between 920 and 1460 m. Within the framework of present-day estimates for the amount of carbon stored in the oceanic hydrate reservoir, the release (and subsequent oxidation) of CH_4 from sediment columns in this depth range explains the observed $\delta^{13}C$ excursion.

The CH_4 hydrate dissociation hypothesis invokes several fundamental assumptions, including (1) current estimates of the size of the present-day hydrate reservoir are the correct order of magnitude (see review by *Gornitz and Fung* [1994]), (2) processes controlling the formation and distribution of oceanic CH_4 hydrate were similar in the Paleocene and present day, and (3) CH_4 released from oceanic hydrate dissociation indeed can be added to the exchangeable carbon reservoir. We cannot rigorously evaluate any of these assumptions with information currently available.

Likewise, we are not aware of any current means to uniquely test the hypothesis; that is, proxy indicators for paleohydrate distribution and release have not been developed. The plausibility of the hypothesis, however, might be evaluated further. Addition of significant quantities of CO_2 to the ocean/atmosphere system over 10^4 years should result in deep-sea carbonate dissolution [e.g., *Broecker et al.*, 1971, 1993]. The distribution and magnitude of such dissolution also should be related to the quantity of added CO_2 [e.g., *Broecker et al.*, 1971, 1993]. If release of CH_4 (and its subsequent oxidation to CO_2) is the correct explanation for the LPTM $\delta^{13}C$ excursion, the distribution and magnitude of carbonate dissolution during the LPTM should be consistent with the addition of 1.1 to 2.1 $\times 10^{18}$ g of C (as CH_4) to the exchangeable carbon reservoir over 10^4 years. Although it is evident that carbonate dissolution indeed occurred during the LPTM [e.g., *Lu and Keller*, 1993; *Thomas and Shackleton*, 1995], its distribution and magnitude have yet to be quantified.

The hydrate dissociation hypothesis requires a triggering mechanism [*Nisbet*, 1990]; the rapid dissociation of oceanic hydrates would need to be triggered by an increase in deep-sea temperature. Here an idea of *Thomas and Shackleton* [1995] is particularly appealing: a rapid emission of CO_2 associated with a brief interval of explosive volcanism in the North Atlantic changed the source of ocean bottom water and induced LPTM deep-sea warmth.

Perhaps a greater problem with the hypothesis lies in stopping deep-sea warmth and hydrate dissociation. Once a significant increase in the CH_4 flux to the ocean/atmosphere system (via hydrate dissociation) was initiated, CO_2 concentrations would increase in both the ocean and atmosphere (via oxidation and ocean/atmosphere exchange). Atmospheric CH_4 concentrations also might have increased during the onset of the LPTM if ebullition of CH_4 was an important process during hydrate dissociation. The elevated atmospheric CO_2 (and CH_4) concentrations then might act as a positive feedback for further climatic and oceanic warmth [*Kvenvolden*, 1988, 1993; *Nisbet*, 1990]. Complete depletion of the oceanic hydrate reservoir would be a simple but implausible mechanism to stop a potential positive feedback loop. Assuming that essentially all hydrate occurs in sediment sequences where water depths are above 3000 to 4000 m, a "hydrate-free" world will occur at significantly higher bottom water temperatures (21 to 23°C) than those suggested for the LPTM (Figure 1). If a stopping mechanism is necessary, one idea is that the distribution of hydrate according to location water depth was skewed toward ~1460 m in the Paleocene, such that the flux of CH_4 from oceanic hydrates to the ocean/atmosphere system was at a maximum during the LPTM and that an incremental increase in bottom water temperature could not increase the flux of CH_4.

The hydrate dissociation hypothesis discussed here is specifically directed at explaining the carbon isotope excursion that occurred during the onset of the LPTM because this particular isotope excursion is well documented and difficult to explain by other hypotheses. The scenario (if correct), however, has a fundamental implication toward understanding the carbon isotope record of the ocean/atmosphere system through time: release of CH_4 from dissociation of oceanic hydrate must be considered as an explanation for negative excursions in the $\delta^{13}C$ of global carbonate when these excursions occur during time intervals of deep-sea warmth.

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