Available online at www.sciencedirect.com

Earth and Planetary Science Letters 213 (2003) 169–183

www.elsevier.com/locate/epsl

Frontiers

Rethinking the global carbon cycle with a large, dynamic and microbially mediated gas hydrate capacitor

Gerald R. Dickens *

Department of Earth Sciences, Rice University, Houston, TX, USA
Shell Center for Sustainability, Rice University, Houston, TX, USA

Received 17 December 2002; received in revised form 20 May 2003; accepted 10 June 2003

Abstract

Prominent negative δ^{13}C excursions characterize several past intervals of abrupt (<100 kyr) environmental change. These anomalies, best exemplified by the >2.5‰ drop across the Paleocene/Eocene thermal maximum (PETM) ca. 55.5 Ma, command our attention because they lack explanation with conventional models for global carbon cycling. Increasingly, Earth scientists have argued that they signify massive release of CH_4 from marine gas hydrates, although typically without considering the underlying process or the ensuing ramifications of such an interpretation. At the most basic level, a large, dynamic 'gas hydrate capacitor' stores and releases ^{13}C-depleted carbon at rates linked to external conditions such as deep ocean temperature. The capacitor contains three internal reservoirs: dissolved gas, gas hydrate, and free gas. Carbon enters and leaves these reservoirs through microbial decomposition of organic matter, anaerobic oxidation of CH_4 in shallow sediment, and seafloor gas venting; carbon cycles between these reservoirs through several processes, including fluid flow, precipitation and dissolution of gas hydrate, and burial. Numerical simulations show that simple gas hydrate capacitors driven by inferred changes in bottom water warming during the PETM can generate a global δ^{13}C excursion that mimics observations. The same modeling extended over longer time demonstrates that variable CH_4 fluxes to and from gas hydrates can partly explain other δ^{13}C excursions, rapid and slow, large and small, negative and positive. Although such modeling is rudimentary (because processes and variables in modern and ancient gas hydrate systems remain poorly constrained), acceptance of a vast, externally regulated gas hydrate capacitor forces us to rethink δ^{13}C records and the operation of the global carbon cycle throughout time.

© 2003 Elsevier B.V. All rights reserved.

Keywords: gashydrates; carbon cycle; methane; carbon isotopes; global change; Paleocene–Ecocene; Phanerozoic

1. Introduction

Secular changes in the stable carbon isotopic composition of primary carbonate and organic matter, as exemplified in newly compiled Cenozoic benthic foraminiferal δ^{13}C records (Fig. 1), lie at the heart of paleo-environmental reconstructions [1]. For decades, a common template for carbon cycling on Earth's surface (Fig. 2) has been used to understand these variations. According to this framework, widespread δ^{13}C changes

---

* Tel.: +1-713-348-5130; Fax: +1-713-348-5214.
E-mail address: jerry@rice.edu (G.R. Dickens).

0012-821X/03/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/S0012-821X(03)00325-X

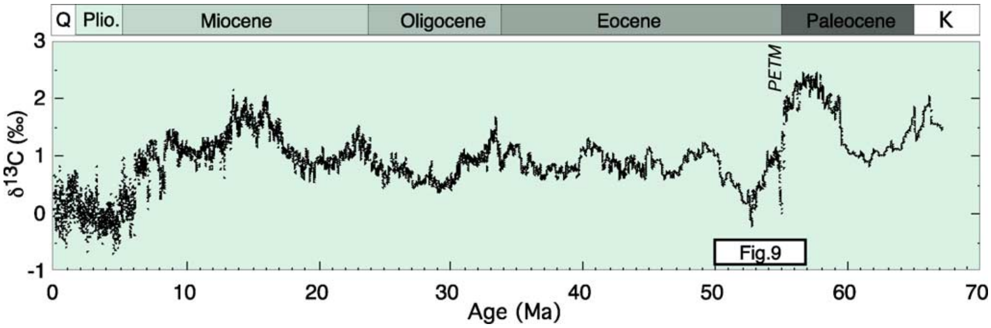

Fig. 1. The carbon isotopic composition ($\delta^{13}C$) of benthic foraminifera over the Cenozoic [1] showing secular changes in the exogenic carbon cycle (δ_{Ex}), including the abrupt negative excursion at the PETM. Note that $\delta^{13}C$ data have been averaged over 5000 yr increments so that the magnitude of change across the PETM is dampened. Also note that foraminiferal carbonate has a ~1.5‰ offset from δ_{Ex} (Fig. 2).

reflect differences in the fluxes or isotopic compositions of terrestrial carbon inputs (weathering and volcanism) or marine carbon outputs (carbonate and organic matter) [2–4].

Two wondrous discoveries challenge widely held views of global carbon cycling. First, $\delta^{13}C$ records display extraordinary >2‰ drops across several intervals of major environmental change [5–11]. For at least one of these events, the Paleocene/Eocene thermal maximum (PETM) ca. 55 Ma (Fig. 1), the $\delta^{13}C$ anomaly indicates an immense, <20 kyr input of ^{13}C-depleted carbon to the ocean and atmosphere, an addition impossible to explain with conventional carbon cycle models but analogous in several regards to anthropogenic fossil fuel emissions [12]. Second, sediment sequences along continental margins hold a tremendous amount of ^{13}C-depleted CH_4 as gas hydrate [13,14]. Current carbon cycle models neglect this CH_4 [2–4], although its distribution depends on fluxes to and from the ocean [15–20], and external conditions, especially deep ocean temperature [14].

Coupling these findings, numerous recent papers have argued that abrupt, negative $\delta^{13}C$ excursions signify bursts of CH_4 from marine gas hydrates [5–12,21–23]. But this literature almost invariably invokes CH_4 escape without accounting for its formation, storage and release, leaving us with a series of profound questions, namely why, how, where, and when should we incorporate gas hydrates into the global carbon cycle?

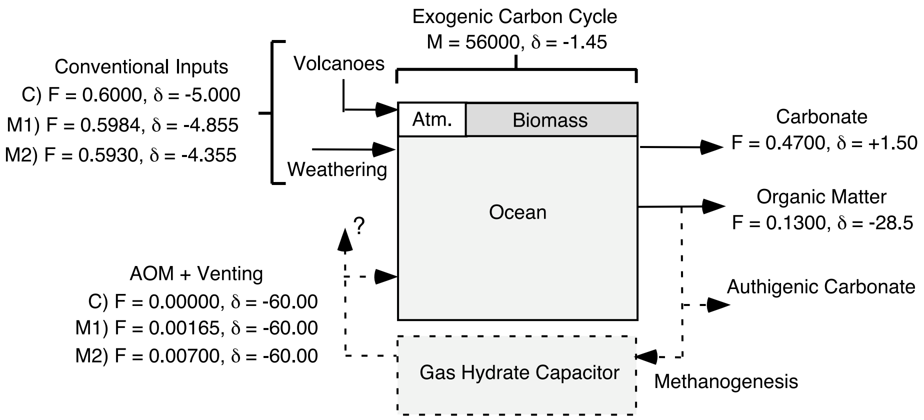
Exogenic Carbon Cycle
M = 56000, δ = -1.45
Conventional Inputs
C) F = 0.6000, δ = -5.000
M1) F = 0.5984, δ = -4.855
M2) F = 0.5930, δ = -4.355
Volcanoes
Weathering
Atm.
Biomass
Ocean
Carbonate
F = 0.4700, δ = +1.50
Organic Matter
F = 0.1300, δ = -28.5
Authigenic Carbonate
?
AOM + Venting
C) F = 0.00000, δ = -60.00
M1) F = 0.00165, δ = -60.00
M2) F = 0.00700, δ = -60.00
Gas Hydrate Capacitor
Methanogenesis

Fig. 2. A basic, steady-state model for the Phanerozoic exogenic carbon cycle (ocean, atmosphere and biomass) [2] with conventional (C) fluxes, and with postulated connections to gas hydrate capacitors (M1, M2, Fig. 7). Masses are in gigatons of carbon (Gt C); fluxes are in Gt C/yr δ values are in per mil.

Building on recent work [14,24], this paper explores these issues by attempting to satisfactorily explain the PETM $\delta^{13}C$ excursion within the context of existing carbon cycle models and gas hydrate knowledge. The assumptions, speculations, and unknowns inherent in such an exercise immediately highlight the frontier nature of gas hydrate studies and major research challenges.

2. Rapid, negative carbon isotope excursions and the PETM

Events of extreme environmental change punctuate Earth's history. Across some of these aberrations, carbonate and organic matter from widely separated locations display prominent (>2‰) drops in $\delta^{13}C$, indicating sudden perturbations in global carbon cycling. In the Phanerozoic, intervals include the Permian/Triassic Boundary ca. 252 Ma [11,21], Jurassic episodes ca. 183 and 157 Ma [9,10], the Aptian 'Selli' event ca. 120 Ma [7,8], and the PETM [5,6,25–28].

Of these events, the PETM warrants special attention because, unlike older intervals, stratigraphic relationships unequivocally demonstrate that its $\delta^{13}C$ excursion was global and rapid. At least 40 different Paleogene stable isotope records, constructed using deep and shallow marine carbonate, and terrestrial carbonate and organic matter, show a 2.5‰ or greater drop in $\delta^{13}C$ across the PETM [1,5,6,25–28]. In records from open ocean locations (Fig. 3), this decrease occurs over 10–40 cm and returns to near initial values in a roughly logarithmic pattern over 100–400 cm, depending on sedimentation rate. The exact shape and timing of the PETM $\delta^{13}C$ excursion remain open issues, even at the same location [5,6,29,30]. Nevertheless, on the basis of sedimentation rates, cyclostratigraphy, or He isotope accumulation [5,6,29–31], the decrease and return in $\delta^{13}C$ spanned <20 kyr and <220 kyr, respectively (Fig. 3). In striking contrast to the Cretaceous/Tertiary Boundary ~10 Myr before, the PETM precisely correlates to a prominent benthic foraminifera extinction [25] and an extraordinary terrestrial mammal diversification [27], suggesting an entirely different mechanism for extreme environmental change.

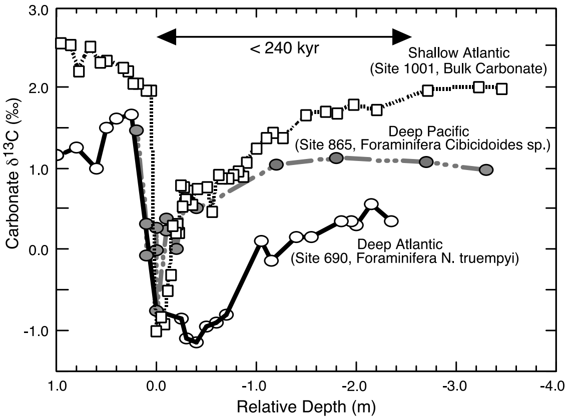

Fig. 3. Carbon isotope records across the PETM in different phases at three deep-sea locations. Original records have been placed on a common depth scale with the $\delta^{13}C$ minimum at 0.0 m [24]. Note that the sedimentation rates vary between sites, giving different shapes to the excursion.

3. A basic model for the global carbon cycle

Straightforward mass balance equations underpin any interpretation of 'global' $\delta^{13}C$ records (and, ultimately, any placement of seafloor CH_4 into the global carbon cycle). The exogenic carbon cycle includes all carbon in the ocean, atmosphere and biomass (Fig. 2). Carbon exchanges between these internal reservoirs within 2000 years (at least at the present day). Consequently, over longer time scales, the exogenic carbon cycle can be considered a single entity whose mass (M_{Ex}) and isotopic composition (δ_{Ex}) change because of variations in the flux or isotopic composition of external inputs or outputs [2–4].

The simplest useful expression for modeling δ_{Ex} over time is [2]:

$$\frac{d\delta_{Ex}}{dt} = \frac{F_{In}}{M_{Ex}}(\delta_{In} - \delta_{Ex}) - \frac{F_{Out}}{M_{Ex}}(\delta_{Out} - \delta_{Ex}) \qquad (1)$$

where F_{In}, F_{Out}, δ_{In} and δ_{Out} are the fluxes and $\delta^{13}C$ of external carbon inputs and outputs, and t is time. Both terms on the right can be expanded to include component fluxes. In particular, and for reasons clarified later, carbonate and organic matter outputs should be considered separately [2]:

$$\frac{d\delta_{Ex}}{dt}=\frac{F_{In}}{M_{Ex}}(\delta_{In}-\delta_{Ex})-\frac{F_{Carb}}{M_{Ex}}(\delta_{Carb}-\delta_{Ex})-\frac{F_{Org}}{M_{Ex}}(\delta_{Org}-\delta_{Ex}) \quad (2)$$

where F_{Carb}, F_{Org}, δ_{Carb}, and δ_{Org} are the fluxes and $\delta^{13}C$ of carbonate and organic matter outputs.

Carbonate and organic matter precipitate from reservoirs within the exogenic carbon cycle, so their fluxes and isotopic compositions relate to M_{Ex} and δ_{Ex}. At the simplest level, the mass–composition relationships are: $F_{Carb}=k_{Carb}M_{Ex}$, $F_{Org}=k_{Org}M_{Ex}$, $\delta_{Carb}=\delta_{Ex}+\Delta_{Carb}$, $\delta_{Org}=\delta_{Ex}+\Delta_{Org}$, where k_{Carb} and k_{Org} are reciprocal e-folding (residence) times, and Δ_{Carb} and Δ_{Org} are the broad isotopic fractionations between the exogenic carbon cycle and carbonate or organic matter. These relationships can be incorporated into Eq. 2 as follows [2]:

$$\frac{d\delta_{Ex}}{dt}=\frac{F_{In}}{M_{Ex}}(\delta_{In}-\delta_{Ex})-k_{Carb}(\Delta_{Carb})-k_{Org}(\Delta_{Org}) \quad (3)$$

Secular changes in δ_{Ex} can be simulated using this equation if appropriate parameters are known. A generic Phanerozoic exogenic carbon cycle with quantified masses and fluxes at steady-state conditions has been presented [2]. After modifications to include biomass and isotopic fractionation during carbonate precipitation [24], this carbon cycle (Fig. 2) provides a first-order foundation for understanding past global changes in stable carbon isotopes.

4. A carbon mass balance problem

The sharp drop and gradual recovery in δ_{Ex} across the PETM (Fig. 3) implies a massive injection of ^{13}C-depleted carbon to the ocean or atmosphere [1,12,31,32]. Such an input should have dissolved significant amounts of $CaCO_3$ on the deep seafloor [32], which indeed occurred during the PETM [25,26,28]. However, its source becomes hugely problematic if one considers the mass balance equations above and conventional carbon cycle models.

Theoretical carbon injections needed to cause a given global $\delta^{13}C$ excursion can be evaluated by modifying Eq. 3 [24]:

$$\frac{d\delta_{Ex}}{dt}=\frac{F_{Add}}{M_{Ex}}(\delta_{Add}-\delta_{Ex})+\frac{F_{In}}{M_{Ex}}(\delta_{In}-\delta_{Ex})-k_{Carb}(\Delta_{Carb})-k_{Org}(\Delta_{Org}) \quad (4)$$

where F_{Add} and δ_{Add} are the flux and $\delta^{13}C$ of the additional carbon. Solutions to this equation show that only implausibly large carbon inputs from rivers, volcanoes, or weathering can account for a global $-2.5‰$ excursion in δ_{Ex} within 20 kyr [24]. For example, average Phanerozoic volcanism (F_{Vol}) would have to increase >100 times [24], and no evidence supports such volcanism during the PETM. Excluding protracted anthropogenic emissions, conventional carbon cycle models cannot explain rapid, global $-2.0‰$ $\delta^{13}C$ excursions [12,24].

When considering possible sources for carbon input at the PETM, one observation seems particularly relevant: benthic foraminifera $\delta^{18}O$ records indicate a sudden 5–7°C warming of deep ocean water [25,26], an environmental change unparalleled in the last 70 Myr [1]. Massive carbon input at the PETM appears causally related to a rapid rise in seafloor temperatures.

5. Marine gas hydrates and free gas

At high gas concentration, certain low-molecular-weight gases (e.g., CH_4, CO_2, Xe) can combine with water to form crystalline clathrate hydrates of gas, or 'gas hydrates'. The stability of these compounds depends on gas composition, pressure, temperature, and the activity of water, a parameter inversely related to salinity. For a given gas composition, gas hydrates can dissociate to water and gas with a decrease in pressure or increase in temperature or salinity.

Gas hydrates can naturally occur in marine sediment when gas saturates pore water in the region of appropriate stability conditions, or gas

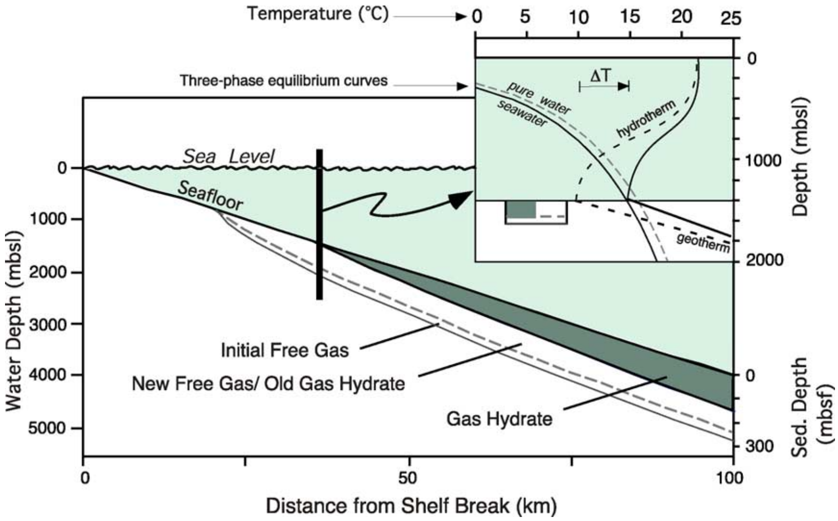
Temperature (°C)
0
5
10
15
20
25
Three-phase equilibrium curves
pure water
seawater
ΔT
hydrotherm
geotherm
Depth (mbsl)
0
1000
2000
Sea Level
Seafloor
Water Depth (mbsl)
0
1000
2000
3000
4000
5000
Initial Free Gas
New Free Gas/ Old Gas Hydrate
Gas Hydrate
Sed. Depth (mbsf)
0
300
Distance from Shelf Break (km)
0
50
100

Fig. 4. Theoretical GHSZ on a typical margin during the late Paleocene (dashed) and after 5°C warming (shaded) [14]. Also shown are locations of free gas before and after the thermal perturbation.

hydrate stability zone (GHSZ) [13]. At a single site, the GHSZ extends from the seafloor to a depth where pressure and temperature on the geotherm approximate those on a pore water–gas hydrate–free gas equilibrium curve (Fig. 4). When extrapolated across a continental margin, the GHSZ forms a lens starting at some shallow water depth (nominally 250–500 m at the present

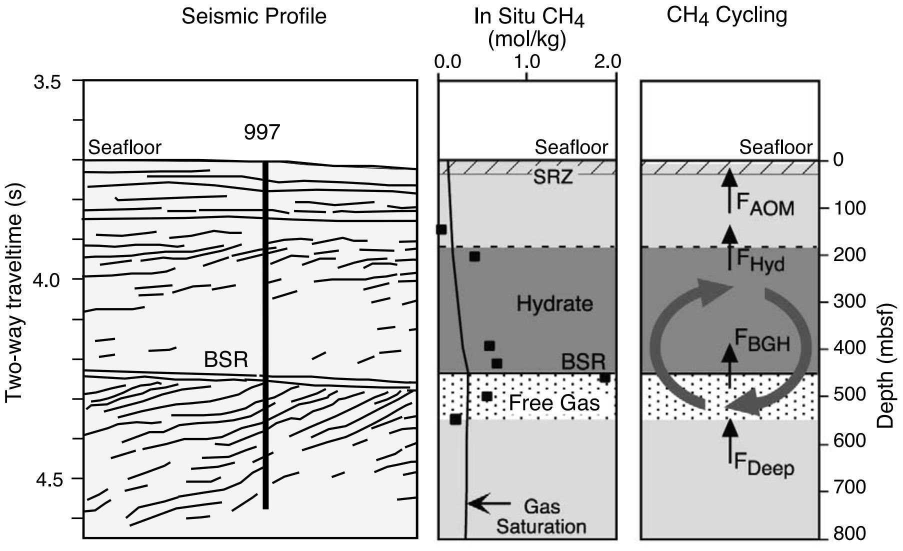
Seismic Profile
In Situ CH4 (mol/kg)
CH4 Cycling
0.0
1.0
2.0
3.5
4.0
4.5
Two-way traveltime (s)
Seafloor
997
BSR
Seafloor
SRZ
Hydrate
BSR
Free Gas
Gas Saturation
Seafloor
FAOM
FHyd
FBGH
FDeep
0
100
200
300
400
500
600
700
800
Depth (mbsf)

Fig. 5. Methane cycling in a modern gas hydrate reservoir, Ocean Drilling Program (ODP) Site 997, Blake Ridge, southeast USA margin (adapted from [65]). (Left) Schematic of seismic reflection profile showing the borehole and the bottom-simulating reflector (BSR), an acoustic interface between gas hydrate and free gas. (Middle) Methane solubility curves, in situ gas concentrations and the sulfate reduction zone (SRZ) at Site 997. (Right) Inferred 'high flux' CH_4 cycling at Site 997. Note that the gross fluxes between gas hydrate and free gas (gray arrows) greatly exceed the net fluxes (black arrows) and no venting occurs at or near this site.

day and 900 m in the Paleocene) and generally thickening beneath deeper water (Fig. 4), depending on local conditions [13,14,33].

Insufficient concentrations of requisite gases preclude gas hydrate formation in many deep-sea sediment sequences despite appropriate pressure, temperature and salinity. However, at numerous locations, particularly along continental slopes, decomposition of organic matter through microbial activity or to a lesser extent thermal cracking generates enough gas to saturate pore waters within portions of the GHSZ (Fig. 5). Because microbes produce much of the gas, it is generally greatly enriched in CH_4 (>99%) and very depleted in ^{13}C ($\delta^{13}C \approx -60$‰) [13].

An enormous volume of pore space can potentially host gas hydrates. By integrating cross-sectional areas (Fig. 4) along continental margins, this volume is likely $1–6 \times 10^6$ km^3 at the present day [14]. On average, pore space within the global GHSZ probably contains 1–10% gas hydrate, implying that present-day oceanic gas hydrates hold 1000–22 000 Gt C (Gt = 10^{15} g) [14], with current literature typically suggesting 10 000 Gt C [13,34]. Not included in this estimate is free gas, which exists when gas saturates pore waters beneath the GHSZ [35–37]. Oceanic gas hydrates and associated free gas constitute a substantial pool of pressure–temperature-sensitive, ^{13}C-depleted CH_4 somehow connected to the exogenic carbon cycle (Fig. 2).

6. The gas hydrate dissociation hypothesis

Sudden deep ocean warming and release of CH_4 from marine gas hydrate systems (Fig. 6) provides a general explanation for the $\delta^{13}C$ excursion and carbonate dissolution across the PETM [12,25,29,32] and perhaps older time intervals [9]. Similar to the present day, gas hydrate and underlying free gas stored enormous quantities of ^{13}C-depleted CH_4 in the upper few hundred meters of sediment on Paleocene continental margins [14]. However, some trigger (e.g., long-term late Paleocene global warming [1]) pushed ocean circulation past a critical threshold, causing relatively warm surface waters to sink into deep waters. This thermal perturbation steepened geotherms on continental margins, dissociating large amounts of gas hydrate to free gas, and injecting CH_4 into the ocean or atmosphere, perhaps through sediment failure (Figs. 4 and 6). In either reservoir, CH_4 would oxidize to ^{13}C-depleted CO_2 [17,38], which would propagate throughout the exogenic carbon cycle, causing a global negative $\delta^{13}C$ excursion and carbonate dissolution [32]. The external carbon inputs and outputs of conventional models (Fig. 2) then flushed the ^{13}C-depleted carbon from the exogenic carbon cycle over the next ~200 kyr [12,32].

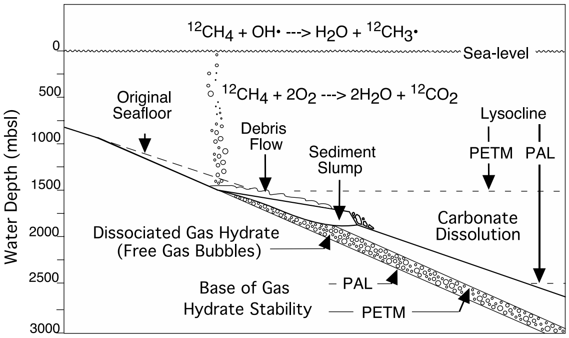
$^{12}CH_4 + OH\bullet \dashrightarrow H_2O + {}^{12}CH_3\bullet$
0
Sea-level
500
$^{12}CH_4 + 2O_2 \dashrightarrow 2H_2O + {}^{12}CO_2$
Original Seafloor
Lysocline
1000
Debris Flow
Sediment Slump
PETM
PAL
Water Depth (mbsl)
1500
2000
Dissociated Gas Hydrate (Free Gas Bubbles)
Carbonate Dissolution
2500
Base of Gas Hydrate Stability
PAL
PETM
3000

Fig. 6. Schematic highlighting the gas hydrate dissociation hypothesis for the PETM [25]. Significant quantities of CH_4 hydrate convert to free CH_4 gas, which escapes through sediment failure to form ^{13}C-depleted CO_2 in either the ocean or atmosphere.

Although other CH_4 release mechanisms have been proposed for the PETM (e.g., slope failure or erosion [39,40]), thermal dissociation of gas hydrates nicely explains the carbon cycle perturbation because the abrupt 5–7°C rise in bottom water temperature [1,25,26] should have shrunk the global GHSZ significantly (Fig. 4), even considering the time and energy required to heat deeply buried gas hydrate [41]. Assuming that late Paleocene and present-day continental margins were similar except for deep ocean temperature, which was ~9°C [1], the global GHSZ decreased >50% during the PETM, from ~1.5 to 0.7×10^6 km^3 [14]. Importantly, steady atmospheric warming can suddenly switch late Paleocene deep water sources from cold, southerly latitudes to relatively warm, northerly latitudes [42]. Equally important, isotopic records of single foraminifera specimens, albeit limited and controversial [43], indicate that abrupt surface warming at high latitudes (i.e., environmental change) preceded in part massive carbon input [29].

Barring a comet impact [43,44], which available records of fossil turnover, the onset of warmth [29], cosmogenic He accumulation [30], and marine osmium isotopic composition [45] do not support, only oceanic gas hydrates can supply enough ^{13}C-depleted carbon to cause the PETM δ^{13}C excursion. The same mass balance argument applies to other prominent negative δ^{13}C excursions [21–23], assuming they also represent rapid perturbations in δ_{Ex}. For the generic Phanerozoic exogenic carbon cycle (Fig. 2), release of ~2500 Gt C with a δ^{13}C of −60‰ over 20 kyr would cause a global −2.5‰ δ^{13}C excursion. Such carbon transfer compels us to incorporate gas hydrates into traditional carbon cycle models [24].

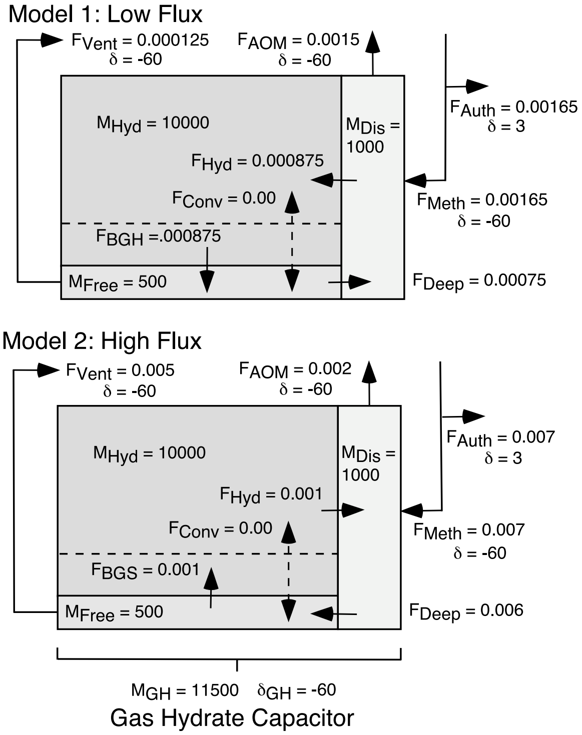

Fig. 7. Two plausible gas hydrate capacitors where ^{13}C-depleted CH_4 cycles through three reservoirs: dissolved gas, gas hydrate and free gas. Note the difference in the direction of CH_4 flow between the internal reservoirs. Masses are in gigatons of carbon (Gt C); fluxes are in Gt C/yr and represent net transport.

7. A large, dynamic gas hydrate capacitor

Marine gas hydrate systems probably serve as a large capacitor containing dissolved gas, gas hydrate and free gas, and exchanging carbon with the exogenic carbon cycle through methanogenesis and methanotrophy (Fig. 2). The capacitor concept arises because, in order to explain negative excursions in δ_{Ex}, carbon fluxes to and from gas hydrates must vary when external forcing changes the dimensions of the global GHSZ [24,32]. We are just beginning to appreciate the complex, dynamic cycling of carbon within individual gas hydrate systems [46–51]. Nonetheless, essential components of this cycling (Fig. 5) can be used to construct rudimentary global gas hydrate capacitors (Fig. 7) of mass M_{GH} and isotopic composition δ_{GH} that transfer CH_4 amongst three reservoirs: dissolved gas (M_{Diss}, δ_{Diss}), gas hydrate (M_{Hyd}, δ_{Hyd}), and free gas (M_{Free}, δ_{Free}) [24]. Available evidence suggests minimal carbon isotopic fractionation as CH_4 moves between dissolved gas, gas hydrate and free gas [52,53]. Hence, $\delta_{GH} = \delta_{Diss} = \delta_{Hyd} = \delta_{Free}$, and only carbon mass transfer expressions are developed below.

Carbon slowly enters most gas hydrate systems when archaea convert organic matter to dissolved CH_4 [54,55]. In established systems with significant free gas at depth, CH_4 generated in the past can also migrate to shallow depth [16,18,56–58]. High CH_4 concentrations at depth typically drive an upward dissolved CH_4 flux, which encounters downward diffusing SO_4^{2-} [15,59,60]. Carbon slowly leaves most systems when archaea–bacteria consortia consume both species via anaerobic oxidation of CH_4 (AOM) across a sulfate/methane transition (SMT) [61,62], usually within 40 m of the seafloor [15,60]. If CH_4 input exceeds CH_4 loss in shallow sediment, gas hydrate can eventually precipitate, provided ambient conditions lie within the GHSZ. The simplest equation to describe these processes is:

$$\frac{dM_{\mathrm{Diss}}}{dt} = F_{\mathrm{Meth}} + F_{\mathrm{Deep}} - F_{\mathrm{AOM}} - F_{\mathrm{Hyd}} \quad (5)$$

where F_{Meth} is methanogenesis, F_{Deep} is net CH_4 supply from depth, F_{AOM} is CH_4 flow to the SMT, and F_{Hyd} is net gas hydrate formation. Methanogenesis must depend on the organic carbon supply to sediment, so, at the most basic level, $F_{\mathrm{Meth}} = k_{\mathrm{Meth}} F_{\mathrm{Org}}$, where k_{Meth} represents the fraction of organic matter converted to CH_4. The CH_4 flux to the SMT probably depends on fluid flow and gas concentration at depth [15,46]. Hence, $F_{\mathrm{AOM}} = vM_{\mathrm{Diss}}$, where v is parameterized fluid flow. Net carbon transfer between dissolved CH_4 and the other reservoirs is more problematic because it depends on the overall flux regime (Fig. 7), and whether CH_4 dominantly moves from gas hydrate to free gas via sediment burial ('low flux'), or from free gas to gas hydrate via upward fluid flow ('high flux')[46–51]. In the first case, $F_{\mathrm{Hyd}} = 0$ when M_{Diss} is less than a critical mass representing saturation, and $F_{\mathrm{Hyd}} = F_{\mathrm{Meth}} + F_{\mathrm{Deep}} - F_{\mathrm{AOM}}$ when M_{Diss} exceeds this mass [24]. In the second case, $F_{\mathrm{Hyd}} = -rM_{\mathrm{Hyd}}$ where r is a parameterized rate for gas hydrate dissolution in shallow sediment. Both end-member regimes probably operate in various locations at different scales but it is unclear which better characterizes the global seafloor CH_4 cycle.

Once in gas hydrate, carbon moves through gas hydrate systems by three general processes, sediment burial and dissolution as noted above, and dissociation when the dimensions of the GHSZ change [14,41]. These processes can be described at the simplest level by:

$$\frac{dM_{\mathrm{Hyd}}}{dt} = F_{\mathrm{Hyd}} - F_{\mathrm{BGH}} - F_{\mathrm{Conv}} \quad (6)$$

where F_{BGH} is net gas hydrate burial, and F_{Conv} is net carbon transfer between gas hydrate and free gas when the GHSZ changes (Figs. 4 and 6). Burial of solid methane carbon at steady-state conditions probably depends on the sedimentation rate (SR) and the amount of gas hydrate in pore space [46,50,51]. Thus, in the 'low flux' model, $F_{\mathrm{BGH}} = sM_{\mathrm{Hyd}}$, where s is parameterized SR. The 'high flux' alternative is discussed below. The other flux, F_{Conv}, which can be positive or negative, can be calculated from average amounts of free gas and gas hydrate, and GHSZ dimensions before and after an environmental perturbation [14,24].

In several places, particularly where faults intersect the seafloor, free CH_4 gas vents to the water column [16–20]. Mass balance closure in gas hydrate systems occurs through the free gas reservoir, after including this venting. Considering the above, the appropriate equation is:

$$\frac{dM_{\mathrm{Free}}}{dt} = F_{\mathrm{BGH}} + F_{\mathrm{Conv}} - F_{\mathrm{Deep}} - F_{\mathrm{Vent}} \quad (7)$$

where F_{Vent} is seafloor venting. Carbon likely migrates between free gas and other sediment reservoirs via faults and gas chimneys [18,56–58]. In the simplest case, this transfer depends on fluid flow and free gas abundance, so that $F_{\mathrm{Deep}} = vM_{\mathrm{Free}}$ in the 'low flux' model, or $F_{\mathrm{BGH}} = -vM_{\mathrm{Free}}$ in the 'high flux' model. In addition to seafloor venting above faults, theoretical considerations and seismic studies suggest that CH_4 outgassing might occur through sediment slumping [63,64]. Thus, F_{Vent} depends on the amount of free gas and channeled fluid flow, which may be linked because excessive free gas could induce flow through fracturing or slumping [37,64]. A simple expression for this behavior is $F_{\mathrm{Vent}} = c(M_{\mathrm{Free}} - M_{\mathrm{Crit}})$ where c is directed flow, and M_{Crit} is the critical mass of free CH_4 above which free gas can escape.

8. Connecting the capacitor to the exogenic carbon cycle

Temporal changes in carbon masses within and from the global gas hydrate capacitor can be calculated from the above equations with four items: (1) initial amounts of CH_4 in dissolved gas, gas hydrate and free gas, (2) values of the rate parameters (e.g., r, v), (3) history of organic matter burial, and (4) evolution of the GHSZ. None are well constrained; indeed, they barely have been discussed in the literature from a perspective useful for modeling the seafloor CH_4 cycle. Assuming 10 000 Gt C in gas hydrate [34] within 3.5×10^6 km^3 of pore space [14], 1000 Gt C in dissolved gas, and 500 Gt C in free gas [24,37], speculative gas hydrate capacitors can be offered for the present day, depending on how carbon flows globally. These capacitors (Fig. 7) transfer ^{13}C-depleted CH$_4$ between the exogenic carbon cycle and gas hydrates through methanogenesis, AOM, and CH$_4$ venting, which can be bracketed crudely from the few available regional extrapolations [15,17,19,60] and an assumption of steady state, $F_{\mathrm{Meth}} = F_{\mathrm{AOM}} + F_{\mathrm{Vent}}$ [24].

Even at steady-state conditions – itself an open issue for the present day [60,65,66] – mass balance coupling between gas hydrates and the exogenic carbon cycle raises some intriguing problems mostly circumvented in the literature. First, carbon flux estimates for weathering and volcanoes need revision to account for the small but highly ^{13}C-depleted CH$_4$ inputs (Fig. 2). Second, some sedimentary component must remove significant quantities of relatively ^{13}C-enriched carbon from the exogenic carbon cycle to offset production and storage of CH$_4$ (Figs. 2 and 7). The ^{13}C-enriched authigenic carbonates found within gas hydrate systems [67] may provide this sink. Third, the residence time of CH$_4$ within the global gas hydrate capacitor must be fairly long, 1.5–7 Myr according to models presented here. This inference agrees with recent studies of individual gas hydrate systems [50,51]. Two conundrums also arise when connecting a present-day gas hydrate capacitor to a Phanerozoic carbon cycle. First, warmer bottom water temperatures and shorter continental margins would reduce the global GHSZ. In particular, the late Paleocene GHSZ was nominally half that of the present day, so that a gas hydrate capacitor with 11 500 Gt C presumes that gas hydrate occupied ~8.5% of pore space within the GHSZ [14]. This occupancy seems high but could reflect greater organic carbon burial in the past (and hence, increased F_{Meth}) as perhaps suggested by the δ^{13}C maximum ca. 58 Ma (Fig. 1). Second, the δ^{13}C of gas hydrates or the isotopic fractionation during methanogenesis must have been less in the past relative to the present day. The −60‰ CH$_4$ produced in modern gas hydrate systems derives dominantly from marine organic matter with a δ^{13}C of −22 to −25‰. However, a δ^{13}C of −27 to −30‰ characterizes marine organic matter for much of the Phanerozoic [68].

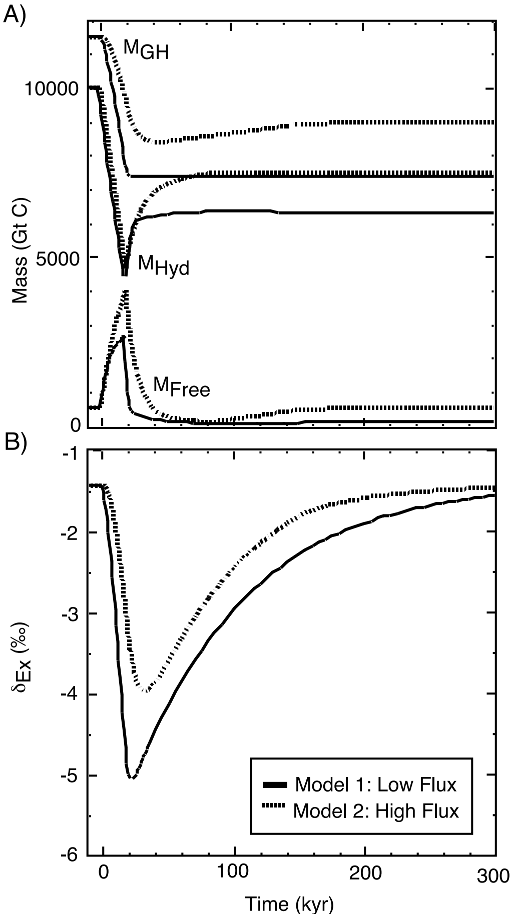

Fig. 8. (A) The predicted mass perturbation of the two gas hydrate capacitors (Fig. 7) with a 5°C warming of deep ocean water over 20 kyr. (B) The ensuing δ^{13}C excursions in the Phanerozoic exogenic carbon cycle (Fig. 2). Model 1 (solid); model 2 (dashed).

9. Simulating the PETM and the surrounding paleogene

The carbon cycle presented here (Figs. 2 and 7) transfers carbon between conventional reservoirs and a large, dynamic and microbially mediated seafloor CH$_4$ cycle. For generic Phanerozoic conditions with 10°C deep ocean temperatures (and caveats noted above), 1.65–7.0 × 10^{12} g C/yr of

$-60‰$ CH_4 enter and leave the exogenic carbon cycle by moving through dissolved gas, gas hydrate and free gas (Figs. 2 and 7). The enormous gas hydrate reservoir holds 10 000 Gt C within a lens that expands downward along continental margins starting at ~900 m water depth (Fig. 5). However, changes in external conditions, especially bottom water temperature, will reconfigure this volume, rearranging masses and fluxes within the circuit.

Benthic foraminifera $\delta^{18}O$ records across the PETM support a 5–7°C rise in deep ocean temperature within ~20 kyr, followed by a 5–7°C cooling over ~50 kyr [1,25,26]. This perturbation would profoundly impact carbon fluxes from any gas hydrate capacitor if AOM and CH_4 venting depend on the abundance of dissolved gas or free gas (Fig. 8). With models presented here, the GHSZ shrinks during initial warming (Fig. 4), and ~5500 Gt C of gas hydrate converts to free gas, of which >2600 Gt C escape from the seafloor, quickly depleting the capacitor and adding ^{13}C-depleted carbon to the exogenic carbon cycle. Once cooling begins, the GHSZ grows and remaining free gas reforms gas hydrate. Because so much carbon escaped, however, free gas abundance drops below steady-state conditions, and CH_4 discharge ($F_{AOM}+F_{Vent}$) drops below CH_4 production (F_{Meth}). The capacitor then recharges, effectively removing ^{13}C-depleted carbon from the exogenic carbon cycle. Consideration of a significant gas hydrate capacitor during the PETM necessarily results in a global $\delta^{13}C$ excursion that resembles isotopic records (Fig. 3), although the shape and magnitude of this excursion depend on parameters of the capacitor, such as initial masses and flow of CH_4 (Fig. 8).

With the models discussed here, only sudden, massive gas hydrate dissociation and free gas venting to the exogenic carbon cycle can explain rapid, negative excursions in δ_{Ex}. Such carbon transfer probably requires widespread sediment failure on continental slopes [63,64], which must have occurred at water depths >900 m during the PETM (Figs. 4 and 6). Slumping at the appropriate paleodepths during the PETM has been documented on the eastern USA margin [25,39].

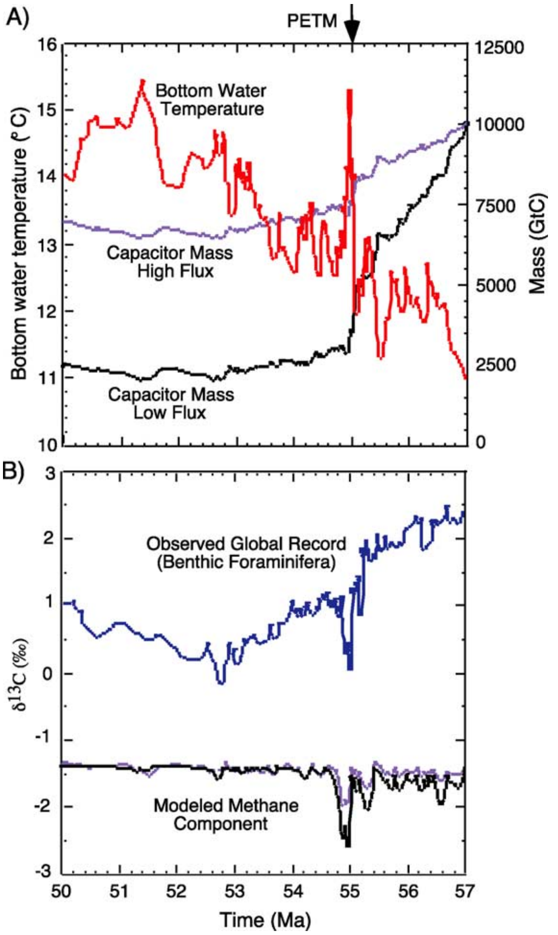

Fig. 9. (A) Inferred bottom water temperature changes between 57 and 50 Ma [1] and the predicted evolution of gas hydrate mass for the two gas hydrate capacitors (Fig. 7). (B) The modeled $\delta^{13}C$ record of the Phanerozoic exogenic carbon cycle assuming conventional carbon fluxes (Fig. 2) remain constant compared to the measured $\delta^{13}C$ of benthic foraminifera [1]. Model 1 (solid); model 2 (dashed). Note that temperature and $\delta^{13}C$ data have been averaged over 5000 yr increments [1] so that changes in mass and $\delta^{13}C$ are dampened across the PETM.

Most current literature has discussed prominent negative $\delta^{13}C$ excursions as isolated CH_4 bursts [5–11,21–24]. However, an integrated carbon cycle model allows us to appropriately assess these perturbations within the context of surrounding time. For example, consider the broad Paleocene–Eocene transition from 57 to 50 Ma (Fig. 1). Using benthic foraminifera $\delta^{18}O$ records as a proxy for deep ocean temperature [1] (and assuming other factors controlling gas hydrate distribution [14] remain constant), numerous brief intervals of accelerated CH_4 outgassing and storage occurred according to models presented here, collectively reducing the amount of gas hydrate from an assumed 10 000 Gt at 57 Ma to <7000 Gt at 53 Ma (Fig. 9). With this view, the PETM $\delta^{13}C$ excursion no longer represents an aberration requiring an extraordinary mechanism, but instead an outstanding example of a common phenomenon where seafloor CH_4 discharge exceeds CH_4 production. Paleogene benthic foraminifera assemblages, which appear to indicate multiple pulses of enhanced chemosynthetic activity [69], may support this interpretation.

10. Ten immediate challenges

A fundamental reconstruction of the global carbon cycle has been offered here to account for vast seafloor CH_4 reservoirs at the present day, and prominent negative $\delta^{13}C$ excursions in the past (Figs. 2 and 7). The most crucial insight from such a model is that CH_4 fluxes to and from gas hydrates continually vary, always contributing to changes in δ_{Ex}, large and small, negative and positive (Fig. 9). With the presented model, variable CH_4 fluxes adequately explain many short-term excursions in δ_{Ex}, but cannot cause long-term (>500 kyr) changes in δ_{Ex} (e.g., the 2.5‰ drop ca. 57–53 Ma, Fig. 1) because gas hydrates cannot excessively furnish CH_4 without recharge, and methanogenesis occurs slowly (Fig. 9). However, if past conditions (e.g., warmer water) accelerated CH_4 production, seafloor CH_4 fluxes could drive longer changes in δ_{Ex}.

The modified carbon cycle model of this paper is necessarily speculative, deterministic and simple. Indeed, the idea of an enormous marine gas hydrate capacitor, collecting and discharging variable amounts of CH_4 over time, should be highly controversial with available information. So, how can we build a more vinous model, sufficiently robust and complex to test?

1. Quantify the abundance of carbon residing in gas hydrate and free gas. Though widely cited, the 10 000 Gt estimate for the present-day mass of gas hydrates is wildly unconstrained [14,34]. No rigorous evaluation for the amount of free gas has been published [24,37].
2. Establish the flow of carbon through gas hydrate systems. Recent efforts to balance masses and fluxes within gas hydrate systems have focused on CH_4 [50,51]. No study has appropriately traced the flow of carbon, including in organic matter, dissolved phases, and authigenic carbonate.
3. Determine carbon outputs from modern gas hydrate systems. Quantified regional to global estimates for AOM and CH_4 venting are just surfacing [15,17,19,60]. These estimates vary significantly and it is not clear how much of the total fluxes apply to gas hydrate systems.
4. Connect other seafloor gas reservoirs. In addition to gas hydrate systems, large amounts of gas occur in conventional hydrocarbon plays and on continental shelves. These reservoirs and their fluxes might also vary considerably over time [33,66,70].
5. Incorporate triggers for variable CH_4 outputs. A complete model needs coupling to tectonism, Earth surface temperature, and environmental change (i.e., the underlying reasons for changing external conditions [42]) rather than simply inputting fluctuations in the GHSZ.
6. Track the oxidation of escaping CH_4. No significance has been placed on whether venting CH_4 is oxidized in the ocean or atmosphere (Fig. 6), although any consequential atmospheric warming, dissolved O_2 deficiency, and $CaCO_3$ dissolution strongly depend on this issue [32].
7. Include appropriate carbon cycle feedbacks. An advanced model must consider that CH_4 addition will increase $CaCO_3$ dissolution and weathering [32,45], which might enhance marine productivity [5], organic matter burial, and gas hydrate recharge [24].
8. Evaluate the impact on other geochemical cycles. AOM and CH_4 venting necessarily affect the marine sulfur, oxygen and perhaps barium cycles [17,32,60,71] but it remains unclear whether past perturbations in these other cycles are consistent with highly variable CH_4 release.

9. Develop tracers other than carbon isotopes for CH_4 fluxing. Oxidation of CH_4 should form authigenic minerals (e.g., calcite, barite) and organic compounds (e.g., hopanoids). We have only begun examining these phases in recent sediment to constrain past CH_4 fluxes [65,67,72].
10. Extend the model over the geological record. The ultimate challenge lies in building a global carbon cycle model that successfully accounts for the present-day mass of gas hydrate and agrees with the global $\delta^{13}C$ record after running from the Neoproterozoic, when conditions affecting gas hydrate distribution were perhaps the most dramatic [73], through the Neogene and Quaternary, when records for assessing seafloor CH_4 fluxes become most complete [72,74].

Acknowledgements

An NSF MESH sponsored workshop on gas hydrates and climate change provided the impetus for this paper. I thank the workshop participants for stimulating ideas, and K. Kvenvolden, A. Milkov, E. Thomas, and J. Zachos who, at various times, including as reviewers of this paper, have forced me to address key issues. I also thank A. Halliday for the challenge to put my thoughts on 10(+) pages! This writing was supported through U.S. NSF Grants (OCE 0117950, EAR 0120727). ***[AH]***

References

[1] J. Zachos, M. Pagani, L. Sloan, E. Thomas, K. Billups, Trends, rhythms, and aberrations in global climate 65 Ma to present, Science 292 (2001) 686–693.

[2] L.R. Kump, M.A. Arthur, Interpreting carbon-isotope excursions: Carbonates and organic matter, Chem. Geol. 161 (1999) 181–198.

[3] Y. Goddéris, L.M. François, J. Veizer, The early Paleozoic carbon cycle, Earth Planet. Sci. Lett. 190 (2001) 181–196.

[4] K. Wallmann, Controls on the Cretaceous and Cenozoic evolution of seawater composition, atmospheric CO_2 and climate, Geochim. Cosmochim. Acta 65 (2001) 3005–3025.

[5] S. Bains, R.M. Corfield, R.D. Norris, Mechanisms of climate warming at the end of the Paleocene, Science 285 (1999) 724–727.

[6] U. Röhl, T.J. Bralower, R.D. Norris, G. Wefer, New chronology for the late Paleocene thermal maximum and its environmental implications, Geology 28 (2000) 927–930.

[7] H.C. Jenkyns, P.A. Wilson, Stratigraphy, paleoceanography, and evolution of Cretaceous Pacific guyots: Relics from a greenhouse earth, Am. J. Sci. 299 (1999) 341–392.

[8] A.H. Jahren, N.C. Arens, G. Sarmiento, J. Guerrero, R. Amundson, Terrestrial record of methane hydrate dissociation in the Early Cretaceous, Geology 29 (2001) 159–162.

[9] S.P. Hesselbo, D.R. Gröcke, H.C. Jenkyns, C.J. Bjerrum, P. Farrimond, H.S.M. Bell, O.R. Green, Massive dissociation of gas hydrate during a Jurassic oceanic anoxic event, Nature 406 (2000) 392–395.

[10] M. Padden, H. Weissert, M. deRafelis, Evidence for Late Jurassic release of methane from gas hydrate, Geology 29 (2001) 223–226.

[11] E.S. Krull, G.J. Retallack, ^{13}C depth profiles from paleosols across the Permian-Triassic boundary: Evidence for methane release, Bull. Geol. Soc. Am. 112 (2000) 1459–1472.

[12] G.R. Dickens, The blast in the past, Nature 401 (1999) 752–755.

[13] K.A. Kvenvolden, T.D. Lorenson, The global occurrence of natural gas hydrate, in: C.K. Paull, W.P. Dillon (Eds.), Natural Gas Hydrates: Occurrence, Distribution and Detection, AGU Geophys. Monogr. Ser. 124 (2001) 3–18.

[14] G.R. Dickens, The potential volume of oceanic methane hydrates with variable external conditions, Org. Geochem. 32 (2001) 1132–1193.

[15] W.S. Borowski, C.K. Paull, W. Ussler III, Global and local variations of interstitial sulfate gradients in deep-water, continental margin sediments: Sensitivity to underlying methane and gas hydrates, Mar. Geol. 159 (1999) 131–154.

[16] E. Suess, M.E. Torres, G. Bohrmann, R.W. Collier, J. Greinerft, P. Linke, G. Rehder, A. Tréhu, K. Wallman, G. Winckler, E. Zuleger, Gas hydrate destabilization: Enhanced dewatering, benthic material turnover and large methane plumes at the Cascadia Margin, Earth Planet. Sci. Lett. 170 (1999) 1–15.

[17] D.L. Valentine, D.C. Blanton, W.S. Reeburgh, M. Kastner, Water column methane oxidation adjacent to an area of active hydrate dissociation, Eel River Basin, Geochim. Cosmochim. Acta 65 (2001) 2633–2640.

[18] M. Wiedicke, H. Sahling, G. Delisle, E. Faber, S. Neben, H. Beiersdorf, V. Marchig, W. Weiss, N. von Mirbach, A. Afiat, Characteristics of an active vent in the fore-arc basin of the Sunda Arc, Indonesia, Mar. Geol. 184 (2002) 121–141.

[19] M.E. Torres, J. McManus, D.E. Hammond, M.A. de

Angelis, K.U. Heeschen, S.L. Colbert, M.D. Tryon, K.M. Brown, E. Suess, Fluid and chemical fluxes in and out of sediments hosting methane hydrate deposits on Hydrate Ridge, OR, I: Hydrological provinces, Earth Planet. Sci. Lett. 201 (2002) 525–540.

[20] M.D. Tryon, K.M. Brown, M.E. Torres, Fluid and chemical flux in and out of sediments hosting methane hydrate deposits on Hydrate Ridge, OR, II: Hydrological processes, Earth Planet. Sci. Lett. 201 (2002) 541–557.

[21] M.J. de Wit, J.G. Ghosh, S. de Villiers, Multiple organic carbon isotope reversals across the Permo-Triassic boundary of terrestrial Gondwana sequences: Clues to extinction patterns and delayed ecosystem recovery, J. Geol. 110 (2002) 227–246.

[22] R.A. Berner, Examination of hypotheses for the Permo-Triassic boundary extinction by carbon cycle modeling, Proc. Natl. Acad. Sci. USA 99 (2002) 4172–4177.

[23] D.J. Beerling, M.R. Lomas, D.R. Gröcke, On the nature of methane gas-hydrate dissociation during the Toarcian and Aptian oceanic anoxic events, Am. J. Sci. 302 (2002) 28–49.

[24] G.R. Dickens, Modeling the global carbon cycle with a gas hydrate capacitor: Significance for the Latest Paleocene thermal maximum, in: C.K. Paull, W.P. Dillon (Eds.), Natural Gas Hydrates, Occurrence, Distribution and Detection, AGU Geophys. Monogr. Ser. 124 (2001) 19–38.

[25] M.E. Katz, D.K. Pak, G.R. Dickens, K.G. Miller, The source and fate of massive carbon input during the Latest Paleocene Thermal Maximum, Science 286 (1999) 1531–1533.

[26] D.J. Thomas, T.J. Bralower, J.C. Zachos, New evidence for subtropical warming during the late Paleocene thermal maximum Stable isotopes from Deep Sea Drilling Project Site 527, Walvis Ridge, Paleoceanography 14 (1999) 561–570.

[27] G.J. Bowen, W.C. Clyde, P.L. Koch, S.Y. Ting, J. Alroy, T. Tsubamoto, Y.Q. Wang, Y. Wang, Mammalian dispersal at the Paleocene/Eocene boundary, Science 295 (2002) 2062–2065.

[28] T.J. Bralower, I. Premoli-Silva, M.J. Malone, Scientific Participants of Leg 198, New evidence for abrupt climate change in the Cretaceous and Paleogene: An Ocean Drilling Program expedition to Shatsky Rise, northwest Pacific, GSA Today 12 (2002) 4–10.

[29] D.J. Thomas, J.C. Zachos, T.J. Bralower, E. Thomas, S. Bohaty, Warming the fuel for the fire: Evidence for the thermal dissocation of methane hydrate during the Paleocene-Eocene thermal maximum, Geology 30 (2002) 1067–1070.

[30] K.A. Farley, S.F. Eltgroth, An alternative age model for the Paleocene-Eocene thermal maximum using extraterrestrial ^{3}He, Earth Planet. Sci. Lett. 208 (2003) 135–148.

[31] R.D. Norris, U. Röhl, Carbon cycling and chronology of climate warming during the Palaeocene/Eocene transition, Nature 401 (1999) 775–778.

[32] G.R. Dickens, Methane oxidation during the late Palaeocene thermal maximum, Bull. Soc. Géol. Fr. 171 (2000) 37–49.

[33] A.V. Milkov, R. Sassen, Two-dimensional modeling of gas hydrate decomposition in the northwestern Gulf of Mexico: significance to global change assessment, Global Planet. Change 36 (2003) 31–46.

[34] K.A. Kvenvolden, Potential effects of gas hydrate on human welfare, Proc. Natl. Acad. Sci. USA 96 (1999) 3420–3426.

[35] I. Grevemeyer, A. Rosenberger, H. Villinger, Natural gas hydrate on the continental slope off Pakistan: Constraints from seismic techniques, Geophys. J. Int. 140 (2000) 295–310.

[36] A.M. Tréhu, E.R. Flueh, Estimating the thickness of the free gas zone beneath Hydrate Ridge, Oregon continental margin, from seismic velocities and attenuation, J. Geophys. Res. 106 (2001) 2035–2045.

[37] M. Hornbach, S. Holbrook, D. Saffer, A global, critically pressured free gas zone beneath methane hydrate provinces, EGS-AGU-EUG Assembly (2003) Abstract EAE03-A-08139.

[38] D.J. Wuebbles, K. Hayhoe, Atmospheric methane and global change, Earth-Sci. Rev. 57 (2002) 177–210.

[39] M.E. Katz, B.S. Cramer, G.S. Mountain, S. Katz, K.G. Miller, Uncorking the bottle: What triggered the Paleocene/Eocene thermal maximum methane release?, Paleoceanography 16 (2001) 549–562.

[40] W.S. Holbrook, D. Lizarralde, I.A. Pecher, A.R. Gorman, K.L. Hackwith, M. Hornbach, D. Saffer, Escape of methane gas through sediment waves in a large methane hydrate province, Geology 30 (2002) 467–470.

[41] W. Xu, R.P. Lowell, E.T. Peltzer, Effect of seafloor temperature and pressure variations on methane flux from a gas hydrate layer: Comparison between current and late Paleocene climate conditions, J. Geophys. Res. 106 (2001) 26413–26423.

[42] K.L. Bice, J. Marotzke, Could changing ocean circulation have destabilized methane hydrate at the Paleocene/Eocene boundary? Paleoceanography 17 (2002) 10.1029/2001PA000678.

[43] D.V. Kent, B.S. Cramer, L. Lanci, D. Wang, J.D. Wright, R. van der Voo, A case for a comet trigger for the Paleocene/Eocene thermal maximum and carbon isotope excursion, Earth Planet. Sci. Lett. 211 (2003) 13–26.

[44] D. Deming, On the possible influence of extraterrestrial volatiles on Earth's climate, the origin of the oceans, Palaeogeogr. Palaeoclimatol. Palaeoecol. 146 (1999) 33–51.

[45] G. Ravizza, R.N. Norris, J. Blusztajn, M.P. Aubry, An osmium isotope excursion associated with the late Paleocene thermal maximum: Evidence of intensified chemical weathering, Paleoceanography 16 (2001) 155–163.

[46] P.K. Egeberg, G.R. Dickens, Thermodynamic and pore water halogen constraints on gas hydrate distribution at ODP Site 997 (Blake Ridge), Chem. Geol. 153 (1999) 53–79.

[47] W. Xu, C. Ruppel, Predicting the occurrence, distribution, and evolution of methane gas hydrate in porous marine sediments, J. Geophys. Res. 104 (1999) 5081–5095.

[48] M.K. Davie, B.A. Buffett, A numerical model for the formation of gas hydrate below the seafloor, J. Geophys. Res. 106 (2001) 497–514.

[49] I.A. Pecher, N. Kukowski, C. Huebscher, J. Greinert, J. Bialas, GEOPECO Working Group, The link between bottom-simulating reflections and methane flux into the gas hydrate stability zone – new evidence from Lima Basin, Peru Margin, Earth Planet. Sci. Lett. 185 (2001) 343–354.

[50] M.K. Davie, B.A. Buffett, Sources of methane for marine gas hydrate: inferences from a comparison of observations and numerical models, Earth Planet. Sci. Lett. 206 (2003) 51–63.

[51] K.L. Gering, Simulations of methane hydrate phenomena over geologic timescales. Part I Effect of sediment compaction rates on methane hydrate and free gas accumulations, Earth Planet. Sci. Lett. 206 (2003) 65–81.

[52] C.K. Paull, T.D. Lorenson, W.S. Borowski, W. Ussler III, K. Olsen, N.M. Rodriguez, Isotopic composition of CH_4, CO_2 species, and sedimentary organic matter within samples from the Blake Ridge: Gas source implications, Proc. ODP Sci. Results. 164 (2000) 229–236.

[53] P.J. Wallace, G.R. Dickens, C.K. Paull, W. Ussler III, Carbon isotopic composition of methane in gas hydrates and free-gas-bearing sediments from the Blake Ridge: Effects of degassing on isotopic compositions of gas released from pressurized core samples, Proc. ODP Sci. Results 164 (2000) 101–112.

[54] K.A. Bidle, M. Kastner, D.H. Bartlett, A phylogenetic analysis of microbial communities associated with methane hydrate containing marine fluids and sediments in the Cascadia margin (ODP site 892B), FEMS Microbiol. Lett. 177 (1999) 101–108.

[55] J.R. Marchesi, A.J. Weightman, B.A. Cragg, R.J. Parkes, J.C. Fry, Methanogen and bacterial diversity and distribution in deep gas hydrate sediments from the Cascadia Margin as revealed by 16S rRNA molecular analysis, FEMS Microbiol. Ecol. 34 (2001) 221–228.

[56] A.R. Gorman, W.S. Holbrook, M.J. Hornbach, K.L. Hackwith, D. Lizarralde, I. Pecher, Migration of methane gas through the hydrate stability zone in a low-flux hydrate province, Geology 30 (2002) 327–330.

[57] C. Ruppel, M. Kinoshita, Fluid, methane, and energy flux in an active margin gas hydrate province, offshore Costa Rica, Earth Planet. Sci. Lett. 179 (2000) 153–165.

[58] W.T. Wood, J.F. Gettrust, N.R. Chapman, G.D. Spence, R.D. Hyndman, Decreased stability of methane hydrates in marine sediments owing to phase-boundary roughness, Nature 420 (2002) 656–660.

[59] H. Fossing, T.G. Ferdelman, P. Berg, Sulfate reduction and methane oxidation in continental margin sediments influenced by irrigation (South-East Atlantic off Namibia), Geochim. Cosmochim. Acta 64 (2000) 897–910.

[60] S. D'Hondt, S. Rutherford, A.J. Spivack, Metabolic activity of subsurface life in deep-sea sediments, Science 295 (2002) 2067–2070.

[61] K.-U. Hinrichs, J.M. Hayes, S.P. Sylva, P.G. Brewer, E.F. DeLong, Methane-consuming archaebacteria in marine sediments, Nature 398 (1999) 802–805.

[62] A. Boetius, K. Ravenschlag, C.J. Schubert, D. Rickert, F. Widdel, A. Gieseke, R. Amann, B.B. Jørgensen, U. Witte, O. Pfannkuche, A marine microbial consortium apparently mediating anaerobic oxidation of methane, Nature 407 (2000) 623–626.

[63] S. Bouriak, M. Vanneste, A. Saoutkine, Inferred gas hydrates and clay diapirs near the Storegga Slide on the southern edge of the Voring Plateau, offshore Norway, Mar. Geol. 163 (2000) 125–148.

[64] P. Cochonat, J.-P. Cadet, S.J. Lallemant, S. Mazzottid, H. Nouzéa, C. Foucheta, J.-P. Foucher, Slope instabilities and gravity processes in fluid migration and tectonically active environment in the eastern Nankai accretionary wedge (KAIKO-Tokai '96 cruise), Mar. Geol. 187 (2002) 193–202.

[65] G.R. Dickens, Sulfate profiles and barium fronts in sediment on the Blake Ridge: Present and past methane fluxes through a large gas hydrate reservoir, Geochim. Cosmochim. Acta 65 (2001) 529–543.

[66] R. Sassen, S.T. Sweet, A.V. Milkov, D.A. DeFreitas, M.C. Kennicutt, Thermogenic vent gas and gas hydrate in the Gulf of Mexico slope: Is gas hydrate decomposition significant?, Geology 29 (2001) 107–110.

[67] N.M. Rodriguez, C.K. Paull, W.S. Borowski, Zonation of authigenic carbonates within gas hydrate-bearing sedimentary sections on the Blake Ridge; offshore southeastern North America, Proc. ODP Sci. Results 164 (2000) 301–312.

[68] J.M. Hayes, H. Strauss, A.J. Kaufman, The abundance of ^{13}C in marine organic matter and isotopic fractionation in the global biogeochemical cycle of carbon during the past 800 Ma, Chem. Geol. 161 (1999) 103–125.

[69] E. Thomas, J.C. Zachos, Was the late Paleocene thermal maximum a unique event?, GFF 122 (2000) 169–170.

[70] M.J. Malone, G. Claypool, J.B. Martin, G.R. Dickens, Variable methane fluxes in shallow marine systems: The composition and origin of pore waters and authigenic carbonates on the New Jersey shelf, Mar. Geol. 189 (2002) 175–196.

[71] G.R Dickens, T. Fewless, E. Thomas, T.J. Bralower, Excess barite accumulation during the Paleocene-Eocene thermal maximum: Massive input of dissolved barium from seafloor gas hydrate reservoirs, in: S.L. Wing et al. (Eds.), Causes and Consequences of Globally Warm Climates of the Early Paleogene, Geol. Soc. Am. Spec. Pap. 369 (2003) 11–23.

[72] K.-U. Hinrichs, L.R. Hmelo, S.P. Sylva, Molecular fossil record of elevated methane levels in late Pleistocene coastal waters, Science (2003) 1214–1217.

[73] M.J. Kennedy, N. Christie-Blick, L.E. Sohl, Are Proterozoic cap carbonates and isotopic excursions a record of

gas hydrate destabilization following Earth's coldest intervals?, Geology 29 (2001) 443–446.

[74] J.P. Kennett, K.G. Cannariato, I.L. Hendy, R.J. Behl, Carbon isotopic evidence for methane hydrate instability during quaternary interstadials, Science 288 (2000) 128–133.

G.R. Dickens was raised in northern California. After obtaining a Chemistry BSc at the University of California, Davis, he honed his numerical skills dealing blackjack at Lake Tahoe. He then attended the University of Michigan, collecting an Oceanography PhD in 1996. Since, he has been a lecturer and senior lecturer at James Cook University, Australia, and associate professor at Rice University. His initial ideas for this paper were scrawled upon wet napkins in Charly's bar with J.R. O'Neil in 1994 after a summer DOE fellowship with M.S. Quinby-Hunt.