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

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## Abstract

Prominent negative  $\delta^{13}\text{C}$  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  $\text{CH}_4$  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  $^{13}\text{C}$ -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  $\text{CH}_4$  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  $\delta^{13}\text{C}$  excursion that mimics observations. The same modeling extended over longer time demonstrates that variable  $\text{CH}_4$  fluxes to and from gas hydrates can partly explain other  $\delta^{13}\text{C}$  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  $\delta^{13}\text{C}$  records and the operation of the global carbon cycle throughout time.

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## 1. Introduction

Secular changes in the stable carbon isotopic

composition of primary carbonate and organic matter, as exemplified in newly compiled Cenozoic benthic foraminiferal  $\delta^{13}\text{C}$  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  $\delta^{13}\text{C}$  changes

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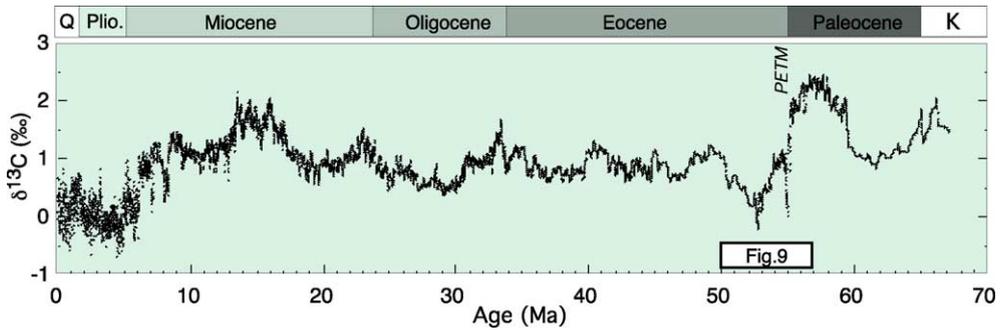


Fig. 1. The carbon isotopic composition ( $\delta^{13}\text{C}$ ) of benthic foraminifera over the Cenozoic [1] showing secular changes in the exogenic carbon cycle ( $\delta_{\text{Ex}}$ ), including the abrupt negative excursion at the PETM. Note that  $\delta^{13}\text{C}$  data have been averaged over 5000 yr increments so that the magnitude of change across the PETM is dampened. Also note that foraminiferal carbonate has a  $\sim 1.5\%$  offset from  $\delta_{\text{Ex}}$  (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,  $\delta^{13}\text{C}$  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  $\delta^{13}\text{C}$  anomaly indicates an immense,  $< 20$  kyr input of  $^{13}\text{C}$ -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 se-

quences along continental margins hold a tremendous amount of  $^{13}\text{C}$ -depleted  $\text{CH}_4$  as gas hydrate [13,14]. Current carbon cycle models neglect this  $\text{CH}_4$  [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  $\delta^{13}\text{C}$  excursions signify bursts of  $\text{CH}_4$  from marine gas hydrates [5–12,21–23]. But this literature almost invariably invokes  $\text{CH}_4$  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?

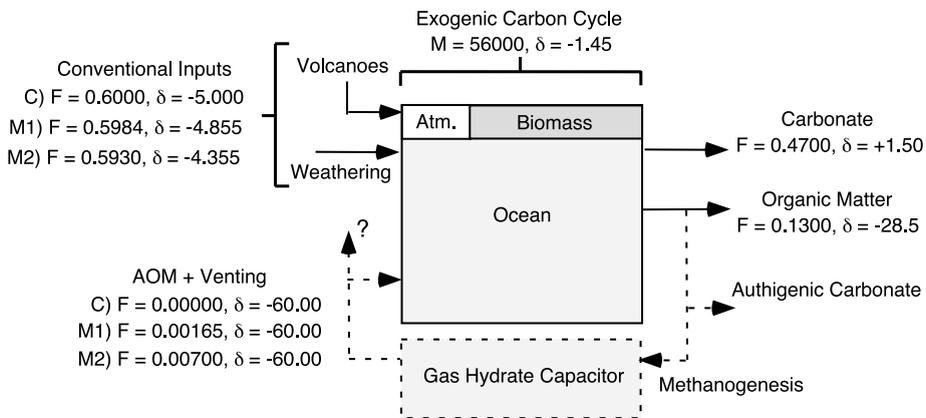


Fig. 2. A basic, steady-state model for the Phanerozoic exogenic carbon cycle (ocean, atmosphere and biomass) [2] with conventional (C) fluxes, and with postulated connections to gas hydrate capacitors (M1, M2, Fig. 7). Masses are in gigatons of carbon (Gt C); fluxes are in Gt C/yr  $\delta$  values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

Building on recent work [14,24], this paper explores these issues by attempting to satisfactorily explain the PETM  $\delta^{13}\text{C}$  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  $\delta^{13}\text{C}$ , 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  $\delta^{13}\text{C}$  excursion was global and rapid. At least 40 different Paleogene stable isotope records,

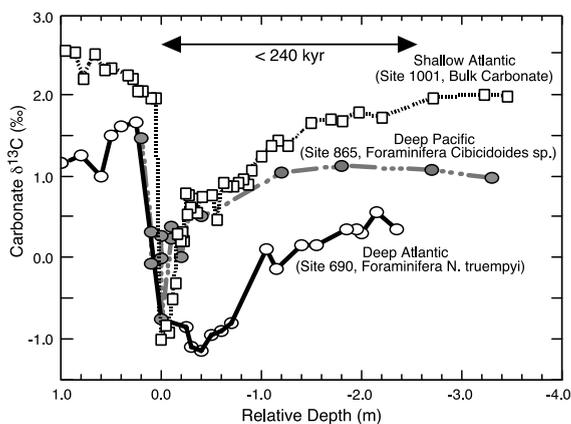


Fig. 3. Carbon isotope records across the PETM in different phases at three deep-sea locations. Original records have been placed on a common depth scale with the  $\delta^{13}\text{C}$  minimum at 0.0 m [24]. Note that the sedimentation rates vary between sites, giving different shapes to the excursion.

constructed using deep and shallow marine carbonate, and terrestrial carbonate and organic matter, show a 2.5‰ or greater drop in  $\delta^{13}\text{C}$  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  $\delta^{13}\text{C}$  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  $\delta^{13}\text{C}$  spanned  $<20$  kyr and  $<220$  kyr, respectively (Fig. 3). In striking contrast to the Cretaceous/Tertiary Boundary  $\sim 10$  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.

## 3. A basic model for the global carbon cycle

Straightforward mass balance equations underpin any interpretation of 'global'  $\delta^{13}\text{C}$  records (and, ultimately, any placement of seafloor  $\text{CH}_4$  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 ( $M_{\text{Ex}}$ ) and isotopic composition ( $\delta_{\text{Ex}}$ ) change because of variations in the flux or isotopic composition of external inputs or outputs [2–4].

The simplest useful expression for modeling  $\delta_{\text{Ex}}$  over time is [2]:

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

where  $F_{\text{In}}$ ,  $F_{\text{Out}}$ ,  $\delta_{\text{In}}$  and  $\delta_{\text{Out}}$  are the fluxes and  $\delta^{13}\text{C}$  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]:

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

where  $F_{\text{Carb}}$ ,  $F_{\text{Org}}$ ,  $\delta_{\text{Carb}}$ , and  $\delta_{\text{Org}}$  are the fluxes and  $\delta^{13}\text{C}$  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  $M_{\text{Ex}}$  and  $\delta_{\text{Ex}}$ . At the simplest level, the mass–composition relationships are:  $F_{\text{Carb}} = k_{\text{Carb}} M_{\text{Ex}}$ ,  $F_{\text{Org}} = k_{\text{Org}} M_{\text{Ex}}$ ,  $\delta_{\text{Carb}} = \delta_{\text{Ex}} + \Delta_{\text{Carb}}$ ,  $\delta_{\text{Org}} = \delta_{\text{Ex}} + \Delta_{\text{Org}}$ , where  $k_{\text{Carb}}$  and  $k_{\text{Org}}$  are reciprocal e-folding (residence) times, and  $\Delta_{\text{Carb}}$  and  $\Delta_{\text{Org}}$  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]:

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

Secular changes in  $\delta_{\text{Ex}}$  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  $\delta_{\text{Ex}}$  across the PETM (Fig. 3) implies a massive injection of  $^{13}\text{C}$ -depleted carbon to the ocean or atmosphere [1,12,31,32]. Such an input should have dissolved significant amounts of  $\text{CaCO}_3$  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  $\delta^{13}\text{C}$  excursion can be evaluated by modifying Eq. 3 [24]:

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

where  $F_{\text{Add}}$  and  $\delta_{\text{Add}}$  are the flux and  $\delta^{13}\text{C}$  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  $\delta_{\text{Ex}}$  within 20 kyr [24]. For example, average Phanerozoic volcanism ( $F_{\text{Vol}}$ ) 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  $-2.0\%$   $\delta^{13}\text{C}$  excursions [12,24].

When considering possible sources for carbon input at the PETM, one observation seems particularly relevant: benthic foraminifera  $\delta^{18}\text{O}$  records indicate a sudden  $5\text{--}7^\circ\text{C}$  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.,  $\text{CH}_4$ ,  $\text{CO}_2$ , 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

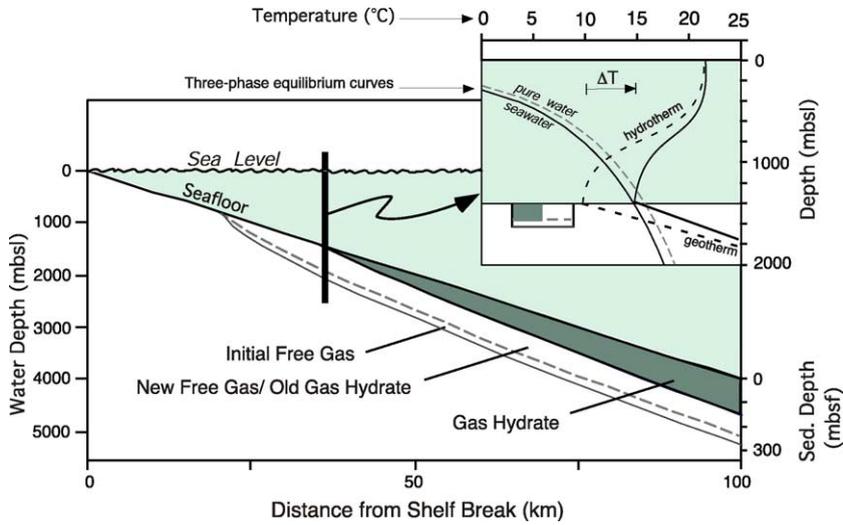


Fig. 4. Theoretical GHSZ on a typical margin during the late Paleocene (dashed) and after 5°C warming (shaded) [14]. Also shown are locations of free gas before and after the thermal perturbation.

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 hy-

drate–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

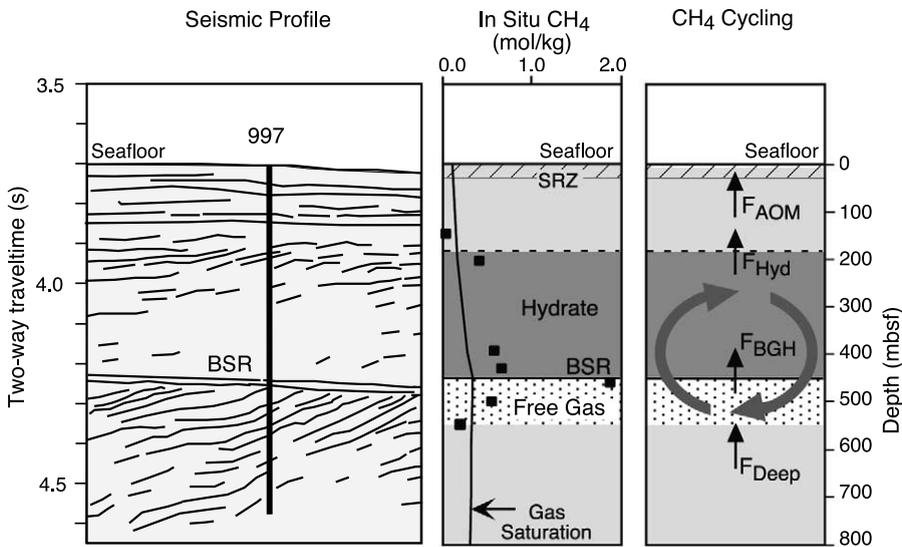


Fig. 5. Methane cycling in a modern gas hydrate reservoir, Ocean Drilling Program (ODP) Site 997, Blake Ridge, southeast USA margin (adapted from [65]). (Left) Schematic of seismic reflection profile showing the borehole and the bottom-simulating reflector (BSR), an acoustic interface between gas hydrate 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<sub>4</sub> 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  $\text{CH}_4$  (>99%) and very depleted in  $^{13}\text{C}$  ( $\delta^{13}\text{C} \approx -60\text{‰}$ ) [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  $1\text{--}6 \times 10^6 \text{ km}^3$  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,  $^{13}\text{C}$ -depleted  $\text{CH}_4$  somehow connected to the exogenic carbon cycle (Fig. 2).

## 6. The gas hydrate dissociation hypothesis

Sudden deep ocean warming and release of  $\text{CH}_4$  from marine gas hydrate systems (Fig. 6) provides a general explanation for the  $\delta^{13}\text{C}$  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  $^{13}\text{C}$ -depleted  $\text{CH}_4$  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 ther-

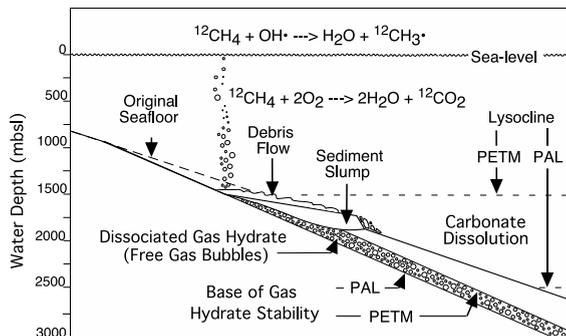


Fig. 6. Schematic highlighting the gas hydrate dissociation hypothesis for the PETM [25]. Significant quantities of  $\text{CH}_4$  hydrate convert to free  $\text{CH}_4$  gas, which escapes through sediment failure to form  $^{13}\text{C}$ -depleted  $\text{CO}_2$  in either the ocean or atmosphere.

mal perturbation steepened geotherms on continental margins, dissociating large amounts of gas hydrate to free gas, and injecting  $\text{CH}_4$  into the ocean or atmosphere, perhaps through sediment failure (Figs. 4 and 6). In either reservoir,  $\text{CH}_4$  would oxidize to  $^{13}\text{C}$ -depleted  $\text{CO}_2$  [17,38], which would propagate throughout the exogenic carbon cycle, causing a global negative  $\delta^{13}\text{C}$  excursion and carbonate dissolution [32]. The external carbon inputs and outputs of conventional models (Fig. 2) then flushed the  $^{13}\text{C}$ -depleted carbon from the exogenic carbon cycle over the next  $\sim 200$  kyr [12,32].

Although other  $\text{CH}_4$  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  $5\text{--}7^\circ\text{C}$  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  $\sim 9^\circ\text{C}$  [1], the global GHSZ decreased  $> 50\%$  during the PETM, from  $\sim 1.5$  to  $0.7 \times 10^6 \text{ km}^3$  [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 fo-

raminifera 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  $^{13}\text{C}$ -depleted carbon to cause the PETM  $\delta^{13}\text{C}$  excursion. The same mass balance argument applies to other prominent negative  $\delta^{13}\text{C}$  excursions [21–23], assuming they also represent rapid perturbations in  $\delta_{\text{Ex}}$ . For the generic Phanerozoic exogenic carbon cycle (Fig. 2), release of  $\sim 2500$  Gt C with a  $\delta^{13}\text{C}$  of  $-60\text{‰}$  over 20 kyr would cause a global  $-2.5\text{‰}$   $\delta^{13}\text{C}$  excursion. Such carbon transfer compels us to incorporate gas hydrates into traditional carbon cycle models [24].

## 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  $\delta_{\text{Ex}}$ , 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  $M_{\text{GH}}$  and isotopic composition  $\delta_{\text{GH}}$  that transfer  $\text{CH}_4$  amongst three reservoirs: dissolved gas ( $M_{\text{Diss}}$ ,  $\delta_{\text{Diss}}$ ), gas hydrate ( $M_{\text{Hyd}}$ ,  $\delta_{\text{Hyd}}$ ), and free gas ( $M_{\text{Free}}$ ,  $\delta_{\text{Free}}$ ) [24]. Available evidence suggests minimal carbon isotopic fractionation as  $\text{CH}_4$  moves between dissolved gas, gas hydrate and free gas [52,53]. Hence,  $\delta_{\text{GH}} = \delta_{\text{Diss}} = \delta_{\text{Hyd}} = \delta_{\text{Free}}$ , and only carbon mass transfer expressions are developed below.

Carbon slowly enters most gas hydrate systems

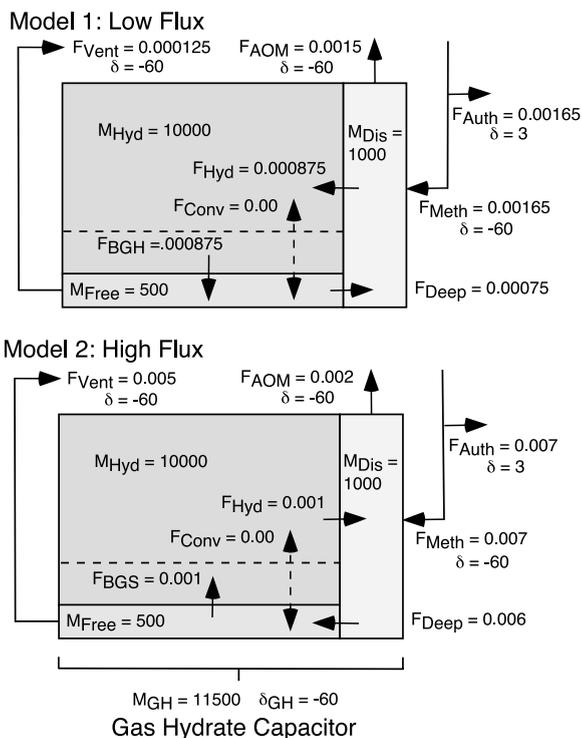


Fig. 7. Two plausible gas hydrate capacitors where  $^{13}\text{C}$ -depleted  $\text{CH}_4$  cycles through three reservoirs: dissolved gas, gas hydrate and free gas. Note the difference in the direction of  $\text{CH}_4$  flow between the internal reservoirs. Masses are in gigatons of carbon (Gt C); fluxes are in Gt C/yr and represent net transport.

when archaea convert organic matter to dissolved  $\text{CH}_4$  [54,55]. In established systems with significant free gas at depth,  $\text{CH}_4$  generated in the past can also migrate to shallow depth [16, 18,56–58]. High  $\text{CH}_4$  concentrations at depth typically drive an upward dissolved  $\text{CH}_4$  flux, which encounters downward diffusing  $\text{SO}_4^{2-}$  [15,59,60]. Carbon slowly leaves most systems when archaea–bacteria consortia consume both species via anaerobic oxidation of  $\text{CH}_4$  (AOM) across a sulfate/methane transition (SMT) [61, 62], usually within 40 m of the seafloor [15, 60]. If  $\text{CH}_4$  input exceeds  $\text{CH}_4$  loss in shallow sediment, gas hydrate can eventually precipitate, provided ambient conditions lie within the GHSZ. The simplest equation to describe these processes is:

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

where  $F_{\text{Meth}}$  is methanogenesis,  $F_{\text{Deep}}$  is net  $\text{CH}_4$  supply from depth,  $F_{\text{AOM}}$  is  $\text{CH}_4$  flow to the SMT, and  $F_{\text{Hyd}}$  is net gas hydrate formation. Methanogenesis must depend on the organic carbon supply to sediment, so, at the most basic level,  $F_{\text{Meth}} = k_{\text{Meth}} F_{\text{Org}}$ , where  $k_{\text{Meth}}$  represents the fraction of organic matter converted to  $\text{CH}_4$ . The  $\text{CH}_4$  flux to the SMT probably depends on fluid flow and gas concentration at depth [15,46]. Hence,  $F_{\text{AOM}} = \nu M_{\text{Diss}}$ , where  $\nu$  is parameterized fluid flow. Net carbon transfer between dissolved  $\text{CH}_4$  and the other reservoirs is more problematic because it depends on the overall flux regime (Fig. 7), and whether  $\text{CH}_4$  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,  $F_{\text{Hyd}} = 0$  when  $M_{\text{Diss}}$  is less than a critical mass representing saturation, and  $F_{\text{Hyd}} = F_{\text{Meth}} + F_{\text{Deep}} - F_{\text{AOM}}$  when  $M_{\text{Diss}}$  exceeds this mass [24]. In the second case,  $F_{\text{Hyd}} = -r M_{\text{Hyd}}$  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  $\text{CH}_4$  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:

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

where  $F_{\text{BGH}}$  is net gas hydrate burial, and  $F_{\text{Conv}}$  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,  $F_{\text{BGH}} = s M_{\text{Hyd}}$ , where  $s$  is parameterized SR. The 'high flux' alternative is discussed below. The other flux,  $F_{\text{Conv}}$ , 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  $\text{CH}_4$  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:

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

where  $F_{\text{Vent}}$  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  $F_{\text{Deep}} = \nu M_{\text{Free}}$  in the 'low flux' model, or  $F_{\text{BGH}} = -\nu M_{\text{Free}}$  in the 'high flux' model. In addition to seafloor venting above faults, theoretical considerations and seismic studies suggest that  $\text{CH}_4$  outgassing might occur through sediment slumping [63,64]. Thus,  $F_{\text{Vent}}$  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  $F_{\text{Vent}} = c(M_{\text{Free}} - M_{\text{Crit}})$  where  $c$  is directed flow, and  $M_{\text{Crit}}$  is the critical mass of free  $\text{CH}_4$  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  $\text{CH}_4$  in dissolved gas, gas hydrate and free gas, (2) values of the rate parameters (e.g.,  $r$ ,  $\nu$ ), (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  $\text{CH}_4$  cycle. Assuming 10 000 Gt C in gas hydrate [34] within  $3.5 \times 10^6 \text{ km}^3$  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  $^{13}\text{C}$ -depleted  $\text{CH}_4$  between the exogenic carbon cycle and gas hydrates through methanogenesis, AOM, and  $\text{CH}_4$  venting, which can be bracketed crudely from the few available regional extrapolations [15,17,19,60] and an assumption of steady state,  $F_{\text{Meth}} = F_{\text{AOM}} + F_{\text{Vent}}$  [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  $^{13}\text{C}$ -depleted  $\text{CH}_4$  inputs (Fig. 2). Second, some sedimentary component must remove significant quantities of relatively  $^{13}\text{C}$ -enriched carbon from the exogenic carbon cycle to offset production and storage of  $\text{CH}_4$  (Figs. 2 and 7). The  $^{13}\text{C}$ -enriched authigenic carbonates found within gas hydrate systems [67] may provide this sink. Third, the residence time of  $\text{CH}_4$  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  $\sim 8.5\%$  of pore space within the GHSZ [14]. This occupancy seems high but could reflect greater organic carbon burial in the past (and hence, increased  $F_{\text{Meth}}$ ) as perhaps suggested by the  $\delta^{13}\text{C}$  maximum ca. 58 Ma (Fig. 1). Second, the  $\delta^{13}\text{C}$  of gas hydrates or the isotopic fractionation during methanogenesis must have been less in the past relative to the present day. The  $-60\%$   $\text{CH}_4$  produced in modern gas hydrate systems derives dominantly from marine organic matter with a  $\delta^{13}\text{C}$  of  $-22$  to  $-25\%$ . However, a  $\delta^{13}\text{C}$  of  $-27$  to  $-30\%$  char-

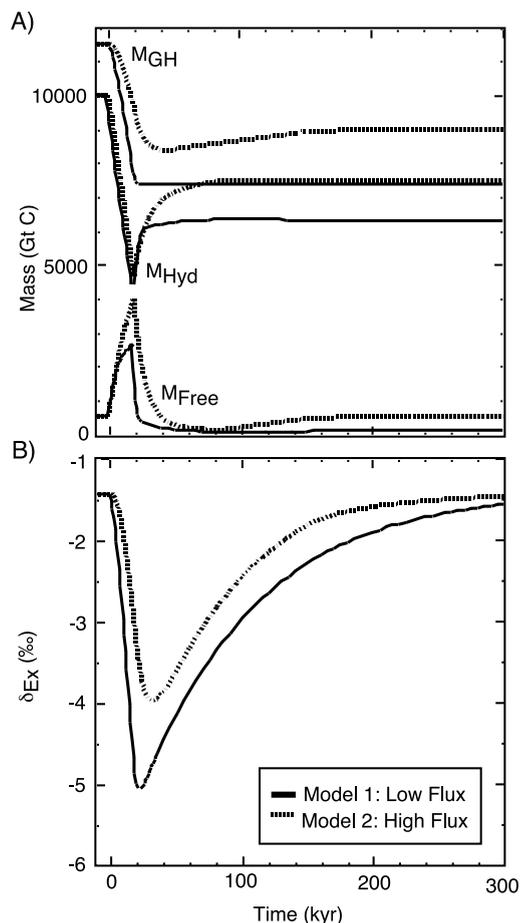


Fig. 8. (A) The predicted mass perturbation of the two gas hydrate capacitors (Fig. 7) with a  $5^\circ\text{C}$  warming of deep ocean water over 20 kyr. (B) The ensuing  $\delta^{13}\text{C}$  excursions in the Phanerozoic exogenic carbon cycle (Fig. 2). Model 1 (solid); model 2 (dashed).

acterizes marine organic matter for much of the Phanerozoic [68].

## 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  $\text{CH}_4$  cycle. For generic Phanerozoic conditions with  $10^\circ\text{C}$  deep ocean temperatures (and caveats noted above),  $1.65\text{--}7.0 \times 10^{12}$  g C/yr of

–60%  $\text{CH}_4$  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  $\sim 900$  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  $\delta^{18}\text{O}$  records across the PETM support a 5–7°C rise in deep ocean temperature within  $\sim 20$  kyr, followed by a 5–7°C cooling over  $\sim 50$  kyr [1,25,26]. This perturbation would profoundly impact carbon fluxes from any gas hydrate capacitor if AOM and  $\text{CH}_4$  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  $\sim 5500$  Gt C of gas hydrate converts to free gas, of which  $>2600$  Gt C escape from the seafloor, quickly depleting the capacitor and adding  $^{13}\text{C}$ -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  $\text{CH}_4$  discharge ( $F_{\text{AOM}} + F_{\text{Vent}}$ ) drops below  $\text{CH}_4$  production ( $F_{\text{Meth}}$ ). The capacitor then recharges, effectively removing  $^{13}\text{C}$ -depleted carbon from the exogenic carbon cycle. Consideration of a significant gas hydrate capacitor during the PETM necessarily results in a global  $\delta^{13}\text{C}$  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  $\text{CH}_4$  (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  $\delta_{\text{Ex}}$ . 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].

Most current literature has discussed prominent

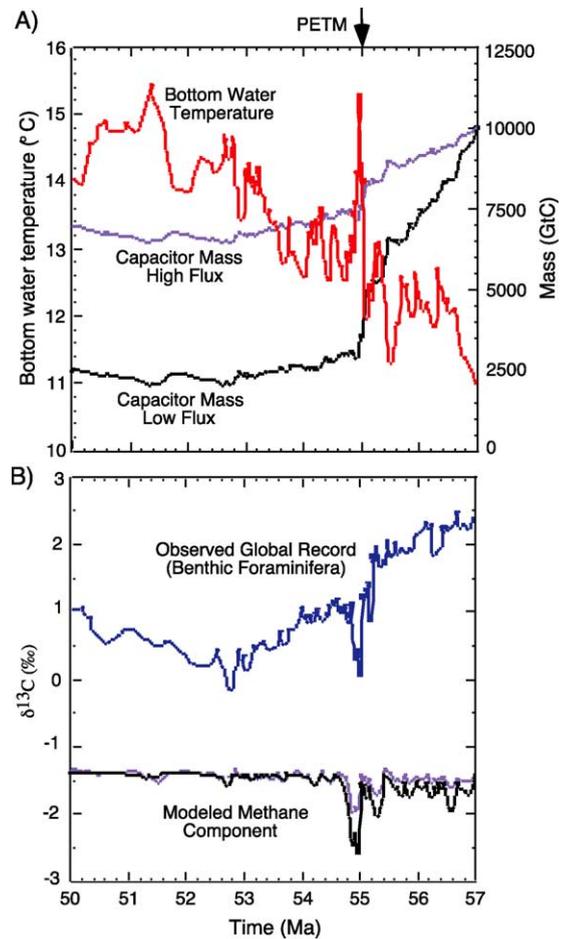


Fig. 9. (A) Inferred bottom water temperature changes between 57 and 50 Ma [1] and the predicted evolution of gas hydrate mass for the two gas hydrate capacitors (Fig. 7). (B) The modeled  $\delta^{13}\text{C}$  record of the Phanerozoic exogenic carbon cycle assuming conventional carbon fluxes (Fig.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

negative  $\delta^{13}\text{C}$  excursions as isolated  $\text{CH}_4$  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  $\delta^{18}\text{O}$  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<sub>4</sub> 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  $\delta^{13}\text{C}$  excursion no longer represents an aberration requiring an extraordinary mechanism, but instead an outstanding example of a common phenomenon where seafloor CH<sub>4</sub> discharge exceeds CH<sub>4</sub> 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<sub>4</sub> reservoirs at the present day, and prominent negative  $\delta^{13}\text{C}$  excursions in the past (Figs. 2 and 7). The most crucial insight from such a model is that CH<sub>4</sub> fluxes to and from gas hydrates continually vary, always contributing to changes in  $\delta_{\text{Ex}}$ , large and small, negative and positive (Fig. 9). With the presented model, variable CH<sub>4</sub> fluxes adequately explain many short-term excursions in  $\delta_{\text{Ex}}$ , but cannot cause long-term (> 500 kyr) changes in  $\delta_{\text{Ex}}$  (e.g., the 2.5‰ drop ca. 57–53 Ma, Fig. 1) because gas hydrates cannot excessively furnish CH<sub>4</sub> without recharge, and methanogenesis occurs slowly (Fig. 9). However, if past conditions (e.g., warmer water) accelerated CH<sub>4</sub> production, seafloor CH<sub>4</sub> fluxes could drive longer changes in  $\delta_{\text{Ex}}$ .

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<sub>4</sub> 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<sub>4</sub> [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<sub>4</sub> 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<sub>4</sub> 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<sub>4</sub>. No significance has been placed on whether venting CH<sub>4</sub> is oxidized in the ocean or atmosphere (Fig. 6), although any consequential atmospheric warming, dissolved O<sub>2</sub> deficiency, and CaCO<sub>3</sub> dissolution strongly depend on this issue [32].
7. Include appropriate carbon cycle feedbacks. An advanced model must consider that CH<sub>4</sub> addition will increase CaCO<sub>3</sub> 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<sub>4</sub> 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<sub>4</sub> release.

9. Develop tracers other than carbon isotopes for CH<sub>4</sub> fluxing. Oxidation of CH<sub>4</sub> 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<sub>4</sub> 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 δ<sup>13</sup>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<sub>4</sub> fluxes become most complete [72,74].

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