Climate of the Past Discussions

Methane release from gas hydrate systems during the Paleocene-Eocene thermal maximum and other past hyperthermal events: setting appropriate parameters for discussion

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Abstract

Enormous amounts of ^{13}C-depleted carbon rapidly entered the exogenic carbon cycle during the onset of the Paleocene-Eocene thermal maximum (PETM), as attested to by a prominent negative $\delta^{13}C$ excursion and widespread seafloor carbonate dissolution. A widely cited explanation for this carbon input has been thermal dissociation of gas hydrate, followed by release of massive CH_4 from the seafloor and its subsequent oxidation to CO_2 in the ocean or atmosphere. Increasingly, papers have argued against this mechanism, but without fully considering existing ideas and available data. Moreover, other explanations have been presented as plausible alternatives, even though they conflict with geological observations, they raise major conceptual problems, or both. Methane release from gas hydrates remains a congruous explanation for the $\delta^{13}C$ excursion across the PETM, although proof has not been provided and it would require a different framework for global geochemical cycling. These issues are addressed here in the hope that they will prompt appropriate discussions regarding the extraordinary carbon injection at the start of the PETM and during other events in Earth's history.

1 The Paleocene-Eocene thermal maximum

Earth's surface, including the ocean, warmed by 5–6 °C from the late Paleocene ca. 57.5 million years ago (Ma) through the Early Eocene climatic optimum (EECO) ca. 52–50 Ma (Zachos et al., 2008; Westerhold et al., 2011). During this long-term temperature rise, an additional 5–8 °C warming of the atmosphere and ocean occurred sometime between 55.5 and 56.3 Ma (Sluijs et al., 2007a; Zachos et al., 2010; McInerney and Wing, 2011; Westerhold et al., 2011). This event, which initiated within 60 kyr and lasted less than 200 kyr, is called the Paleocene-Eocene thermal maximum (PETM), and was associated with profound and widespread changes to the environment and biota (Sluijs et al., 2007a; McInerney and Wing, 2011).

The onset of the PETM is marked by a prominent negative excursion in the stable carbon isotope composition of carbon bearing phases across Earth (McInerney and Wing, 2011). The magnitude of the shift varies depending on location and material analyzed. In bulk marine carbonate and benthic foraminifera from open-ocean sites, the drop in δ^{13}C is typically 2.5–3.0‰; in mixed-layer planktonic foraminifera from open-ocean sites, it is often 3.0–4.5‰; in terrestrial carbonate and organic matter, it can exceed 5.0‰ (McInerney and Wing, 2011). Whatever the reasons for these differences (some discussed below), the entire exogenic carbon cycle, comprising the ocean, atmosphere, and biosphere, appears to have decreased by at least 2.5‰ within 60 kyr. This duration is given as a maximum because the timing of the δ^{13}C drop is a source of current debate (Murphy et al., 2010; Nicolo et al., 2010; McInerney and Wing, 2011); it could have been much faster (Zachos et al., 2007).

Considering their collective magnitude, rapid onset and global nature, both the warming and the carbon isotope excursion represent extreme Earth system anomalies (Kennett and Stott, 1991; McInerney and Wing, 2011). They clearly stand out in compiled records spanning the Cenozoic (Zachos et al., 2001, 2008).

2 General cause for the carbon isotope excursion at the PETM

For over 15 yr, the stable isotope anomaly has been regarded as representing a rapid and massive input of ^{13}C-depleted carbon to the entire exogenic carbon cycle (Dickens et al., 1995; Thomas and Shackleton, 1996). The inference is positively supported from numerous records of deep-sea sediment, which, in all ocean basins, display abrupt though highly variable carbonate dissolution at the start of PETM (Zachos et al., 2005; Zeebe and Zachos, 2007), as well as excess carbonate accumulation after the event (Kelly et al., 2005; Leon-Rodriguez et al., 2010). This is the expected and telltale signature for a rapid and massive carbon injection (Archer et al., 1997; Dickens et al., 1997a; Panchuk et al., 2008; Zeebe et al., 2008; Kump et al., 2009). The fact that the δ^{13}C excursion in numerous records recovers to a "baseline" within about 200 000 yr

after the onset is also consistent with models for how the carbon cycle should respond to a rapid and massive carbon input (Dickens et al., 1997; Dickens 2000). However, it should be stressed that a range of potential feedbacks complicates the details of this carbon isotope recovery (Dickens, 2001a, 2003; Higgins and Schrag, 2006; Bowen and Zachos, 2010).

Since the discovery of the PETM δ^{13}C excursion (Kennett and Stott, 1991; Koch et al., 1992), a fundamental issue has been one of carbon mass balance (Dickens et al., 1995; Thomas and Shackleton, 1996). The size and timing of the δ^{13}C excursion necessitate a tremendous addition of carbon, with the mass depending on the δ^{13}C composition of the source. In theory, a -2.5 to -3.0‰ excursion could be explained by an addition of $\sim$2000–3000 gigatonnes (Gt $= 10^{15}$ g) of C with a δ^{13}C of -60‰ or about $\sim$6000–10 000 Gt of C with a δ^{13}C of -25‰ (Dickens et al., 1995; Dickens, 2001a; Archer, 2007; Panchuk et al., 2008; Zeebe et al., 2009). As a comparison, unabated burning and near-complete consumption of all fossil fuel reserves will have added about 4000–5000 Gt by 2500 AD (Archer et al., 1997) with a δ^{13}C value of about -30‰. The amounts estimated above depend on various factors including the timing of the input, and the masses and fluxes within the exogenic carbon cycle (Dickens, 2001a; Archer, 2007; Carozza et al., 2011; McInerney and Wing, 2011). Note also that the relationship between carbon mass and δ^{13}C composition is non-linear, and the overall mass balance issue becomes more problematic with the size of the δ^{13}C excursion (Dickens et al., 1995; Dickens, 2001a; Archer, 2007; McInerney and Wing, 2011).

As Sundquist (1986) and others (Dickens et al., 1995; Thomas and Shackleton, 1996) emphasized, there is no mechanism for causing a geologically rapid and truly global > 2.5‰ negative δ^{13}C excursion with conventional models for carbon cycling on Earth's surface, except by human extraction and burning of most known fossil fuel resources. This problem regarding the PETM, nicely coined an "ancient carbon mystery" (Pagani et al., 2006a), forces the Earth science community to "think outside the box".

3 The gas hydrate dissociation hypothesis

The first plausible explanation given for the $\delta^{13}C$ excursion across the PETM was thermal dissociation of marine gas hydrates (Dickens et al., 1995). Gas hydrates are crystalline compounds comprised of water and low molecular weight gas that form at relatively high pressure and relatively low temperature. They are widespread along modern continental margins (Kvenvolden et al., 1993; Archer, 2007), where high concentrations of CH_4 have accumulated in pore space of a gas hydrate stability zone (GHSZ). This is a lens-shaped volume that expands down continental slopes between the seafloor and a sub-bottom horizon dictated by the intersection of the geotherm and the gas hydrate-free gas phase boundary. The dimensions of the GHSZ at present-day (and presumably throughout geological time) depend on several factors, but especially seafloor temperature (Dickens, 2001b).

According to the "gas hydrate dissociation" hypothesis (Dickens et al., 1995), some Earth system threshold was crossed, so that warm water began to sink, and intermediate to deep ocean temperatures rose rapidly. This warmth propagated into sediment on continental slopes, which shoaled the base of the GHSZ and converted large amounts of gas hydrate to free gas. On the order of 2000 Gt of CH_4, as free gas, then escaped from marine sediment into intermediate waters of the ocean. This could have occurred through slumping or venting (Dickens, 2003).

The mechanism remains appealing for five reasons. We know that temperature along continental slopes rose at the start of the PETM by at least 4 °C (Kennett and Stott, 1991; Zachos et al., 2001). We know that a 4 °C warming of seafloor temperatures on the 10 kyr time-scale would shrink the dimensions of the GHSZ by at least 50% (Dickens, 2001b). We know that CH_4 in modern gas hydrate systems is extremely depleted in ^{13}C ($\delta^{13}C$ typically $< -60‰$ at present-day; Milkov, 2005). We know that gas hydrate systems are "missing" from conventional models of carbon cycling on Earth (Dickens, 2003). We know that a source with an exceptionally low $\delta^{13}C$ composition makes the carbon mass balance problem more palatable.

It is important to re-emphasize two concepts concerning this potential explanation for the PETM δ^{13}C excursion (Dickens et al., 1995, 1997a; Dickens, 2000, 2003). First, CH$_4$ release would have operated as a feedback, such that some component of total global warming during the PETM preceded the carbon input associated with the δ^{13}C excursion. Second, the primary impact of CH$_4$ release from a geological perspective would be addition of CO$_2$ to the ocean and atmosphere, and modification of water chemistry, particularly a drop in pH and dissolved O$_2$. This is because CH$_4$ is rapidly oxidized to CO$_2$ in the ocean or atmosphere. There has never been a suggestion that CH$_4$ inputs from the seafloor entered the atmosphere and drove climate change during the PETM.

Arguments consistent with the gas hydrate dissociation hypothesis have been forwarded in the last few years. At several locations, the stratigraphic record suggests that environmental change preceded the δ^{13}C excursion (Thomas et al., 2002; Sluijs et al., 2007b; Harding et al., 2010; Secord et al., 2010; Handley et al., 2011). This includes ocean temperature, which may have been on the order of 4 °C and over several thousands of years before the onset of the CIE (Sluijs et al., 2007b). Recently constructed records show that dissolved oxygen concentrations in intermediate waters dropped precisely during the carbon input (Nicolo et al., 2010), as suspected for massive release of CH$_4$ from continental slopes and subsequent aerobic oxidation in the water column (Dickens, 2000). Model simulations have shown that intermediate waters can suddenly warm under early Paleogene boundary conditions when a threshold (sea-ice formation) is surpassed (Lunt et al., 2010). However, the data and modeling results should be questioned; they should not be taken as positive proof.

There is also a growing appreciation that the PETM is only the most prominent of a series of "self-similar" ^{13}C-depleted carbon injections that occurred during long-term deep-ocean warming of the early Paleogene (Lourens et al., 2005; Nicolo et al., 2007; Agnini et al., 2009; Stap et al., 2009; Leon-Rodriguez et al., 2010; Zachos et al., 2010; Westerhold et al., 2011). These inputs, in general, appear coupled to orbital forcing and to shrink over time (above references). Assuming they have a similar generic cause,

they almost demand inclusion of some large capacitor in the global carbon cycle that can release ^{13}C-depleted carbon fast in response to forcing, but that recharges more slowly (Dickens, 2000, 2003; Nicolo et al., 2007; Zachos et al., 2010; Westerhold et al., 2011). Models for the global carbon cycle that include large masses of seafloor CH_4,
5 although very primitive, have this very effect (Dickens, 2003; Archer et al., 2009).

4   Arguments against gas hydrate dissociation

Four arguments against gas hydrate dissociation for the cause of the $\delta^{13}C$ excursion across the PETM have emerged in recent literature (McInerney and Wing, 2011). All revolve around mass balance, and all were introduced when presenting the hypothesis
10 (Dickens et al., 1995, 1997a; Dickens 2000, 2001a,b, 2003).

One criticism has been that the ~6 °C warming of Earth's surface during the PETM exceeds that which would result from a 2000 Gt addition of carbon (Higgins and Schrag, 2006; Pagani et al., 2006a; Archer, 2007; Handley et al., 2011). This line of reasoning ignores the underlying idea that massive CH_4 input from the seafloor would have
15 been a feedback to warming caused by other mechanisms. In other words, addition of carbon from gas hydrate could not have caused all the warming and, in fact, this very point was made to support the gas hydrate dissociation hypothesis in the first place (Dickens et al., 1995, 1997a). The argument also assumes that we understand long-term (> 2000 yr) Earth climate system sensitivity at present-day and in the past, which
20 is certainly not the case, as emphasized by the wide range in temperature projections for our future.

A second criticism has been that carbonate dissolution on the seafloor was too intense for a 2000 Gt addition of carbon (Zachos et al., 2005; Higgins and Schrag, 2006; Pagani et al., 2006a; Archer, 2007). This idea was initially framed on records from
25 Walvis Ridge in the South-Central Atlantic Ocean, which suggest the calcite compensation depth (CCD) rose by > 2 km during the PETM (Zachos et al., 2005). For example, Archer (2007) suggested that a global 2 km rise in the CCD would implicate

a ~5000 Gt input of carbon, so dismissed gas hydrate dissociation as a cause for the δ^{13}C excursion.

The relationship between carbon input and carbonate dissolution during the PETM is not straightforward because it depends on a number of poorly constrained factors including the timing and location of carbon input, bathymetry, the chemistry of seawater, the initial position of the CCD, and the amount of previously deposited carbonate dissolved on the seafloor (Dickens et al., 1997a; Dickens, 2000, Higgins and Schrag, 2006; Panchuk et al., 2008; Zeebe et al., 2009; Leon-Rodriguez and Dickens, 2010). In any case, carbonate dissolution during the PETM was highly heterogeneous, with several sites in the Central and North Atlantic exhibiting extreme dissolution, and other sites in the South Atlantic, the Indian and especially the much larger Pacific showing much more modest dissolution (Dickens, 2000; Panchuk et al., 2008; Zeebe and Zachos, 2007; Zeebe et al., 2009; Leon-Rodriguez and Dickens, 2010). This may reflect differential carbon input to intermediate waters of the ocean, such as through aerobic oxidation of CH_4 in the water column above slopes, or changes in the direction of deepwater flow (Dickens, 2000, 2004; Zeebe and Zachos, 2007; Zeebe et al., 2009). Two studies have tried to model the overall carbonate dissolution during the PETM in terms of the required carbon input (Panchuk et al., 2008; Zeebe et al., 2009). These models disagree, as nicely discussed by McInerney and Wing (2011). Panchuk et al. (2008) suggested > 6800 Gt with a δ^{13}C composition of −22‰; Zeebe et al. (2008) suggested ~3000 Gt with a δ^{13}C of < −50‰. The latter is consistent with seafloor methane release. However, the second modeling effort did necessitate a "bleeding" of another 1500 Gt of carbon over about 60 kyr following the start of the PETM.

A third criticism has been that the magnitude of the δ^{13}C excursion across the PETM is much larger than 2.5–3.0‰ (Pagani et al., 2006a,b; Handley et al., 2008, 2011). If this represents the true change in the exogenic carbon cycle, it would indicate a carbon input much greater than 2000 Gt, unless the source was even more ^{13}C-depleted than CH_4 (Dickens et al., 1995; Dickens, 2001a). It is possible that CH_4 in marine sediment would have a δ^{13}C composition closer to −70‰ in the early Paleogene (Dickens,

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2003), because organic carbon landing on the seafloor was probably more depleted in ^{13}C during this time (Hayes et al., 1999). However, this would not impact mass balance calculations by very much.

The concept does come with two notions though (Zachos et al., 2007; McInerney and Wing, 2011): (1) the generally smaller shifts in individual bulk carbonate, benthic foraminifera and some planktonic foraminifera records (notably from the major pool of carbon on Earth's surface) reflect diagenesis, the mixing of carbonate phases with different isotope compositions, fractionation dampening by a major decrease in pH (Uchikawa and Zeebe, 2010), or their truncation because of carbonate dissolution; (2) The generally larger excursions in planktonic foraminifera, soil carbonate and alkane records more faithfully record the δ^{13}C of a fixed surface water horizon or the atmosphere. It is difficult to reject the first notion in many cases, but there are problems with the second notion (Bowen et al., 2004; Schouten et al., 2008; McInerney and Wing, 2011). It is worth highlighting a good example that has not been discussed previously.

Carbon isotope records of single species planktonic foraminifera and dinocysts of mostly a single genera (*Apectodinium*) both show a −4.5‰ δ^{13}C excursion across the PETM at the Bass River site, which was deposited in relatively shallow water on the ancient New Jersey shelf (Sluijs et al., 2007b; Zachos et al., 2007). The demonstration of a similar magnitude excursion in co-occurring marine carbonate and organic carbon seems to preclude differential carbon isotope fractionation for either phase, notably including by a large drop in pH (Uchikawa and Zeebe, 2010). That is, a 4.5‰ δ^{13}C excursion may be correct for the DIC of shallow mixed water at this location. However, the Bass River section has strong evidence for much greater river discharge and lowered salinity precisely during the onset of the PETM (Zachos et al., 2006; Kopp et al., 2009). This is important because the DIC of most river water is considerably depleted in δ^{13}C, and large gradients in salinity and δ^{13}C can occur along modern coasts (Chanton and Lewis, 1999; Fry, 2002).

The relationship between salinity and the δ^{13}C of DIC in coastal regions depends on the DIC concentration and the δ^{13}C of the DIC of the river water. Nonetheless, there are good examples at present-day where a shift from 35 to 30 ppt in salinity equates to a 1 to 2‰ drop in the δ^{13}C of DIC (Chanton and Lewis, 1999; Fry, 2002). Thus, it needs to be asked whether the δ^{13}C excursion at the Bass River site was amplified because of greater freshwater discharge (Uchikawa and Zeebe, 2010). Changes in TEX-86 at this location suggest a temperature rise of ∼7 °C across the PETM (Sluijs, 2007b), consistent with suggestions elsewhere, and implying that the planktonic foraminifera should exhibit a 1.8‰ decrease in δ^{18}O. In fact, they decrease by more than 2.5‰ across the PETM (Zachos et al., 2007), suggesting that a 3–4 ppt drop in salinity has magnified the δ^{18}O excursions in existing records from the New Jersey shelf (Zachos et al., 2006). Such freshening would have also magnified the δ^{13}C excursion. A correction for salinity, assuming a published relationship between salinity and the δ^{13}C of DIC (Fry, 2002), brings the magnitude of the change in the surface water, and by inference the exogenic carbon cycle, down to about 3‰.

If a 2.5–3.0‰ magnitude for the δ^{13}C excursion is correct, it will force the community to reconsider interpretations of δ^{13}C records across the PETM at many sites (McInerney and Wing, 2011). Basically, as stressed by Bowen et al. (2004), we should ask, at numerous locations, "why does the δ^{13}C anomaly exceed 3‰?" Bowen et al. (2004) offered several reasons, such as changes in relative humidity and soil productivity, for why terrestrial carbonate δ^{13}C excursions would be accentuated. Schouten et al. (2008) provided a good example of how mixing of sources can amplify alkane records. Similar thinking might be applied to marine records. For example, at ODP Site 690 in the South Atlantic, mixed layer planktonic foraminifera (*Acarinina*) exhibit a 4‰ excursion whereas themocline dwelling foraminifera (*Subbotina*) show a 2.5‰ excursion (Thomas et al., 2002). Rather than considering the latter record truncated, for which there is little evidence, we might consider the idea that, because of rapid warming at the start of the PETM, *Acarinina* started precipitating tests in deeper water, which would have DIC more depleted in ^{13}C. Interestingly, this might explain why the δ^{18}O values of these

two genera converged after the PETM at Site 690. That is, there was a downward migration of *Acarinina* rather than a collapse of the thermocline (Thomas et al., 2002), a notion that now seems inconsistent with evidence for greater water column stratification during the PETM (Lippert and Zachos, 2007; Nicolo et al., 2010) and in climate model simulations for warm worlds.

The current state of the literature regarding the magnitude of the PETM δ^{13}C excursion is wonderfully expressed in a recent paper. Jaramillo et al. (2010) document a 2–3‰ excursion in bulk organic carbon and specific alkanes across the PETM in a terrestrial sediment section from Venuzuela exclusively dominated by tropical flora. They systematically present and reject reasons for why this excursion might be too small at this location, and then conclude that this is difficult to explain. They omit the alternative: this is the magnitude of the δ^{13}C excursion when recorded by plants unaffected by processes that impact carbon isotope fractionation.

The fourth criticism against gas hydrate dissociation concerns the sizes of the modern and Paleogene gas hydrate reservoirs (Milkov, 2004; Higgins and Schrag, 2006; Pagani et al., 2006; Archer, 2007; Archer et al., 2009). Problems with estimates for the mass of the present-day gas hydrate reservoir are addressed in the next section, and problems with the mass of past gas hydrate reservoirs are considered later.

5 Methane masses in present-day marine gas hydrate systems

The total mass of carbon stored as CH_4 in present-day marine gas hydrates has been estimated numerous times using different approaches as reviewed in several papers (Dickens, 2001b; Milkov, 2004; Archer, 2007). Prior to 2001, several estimates converged on 10 000 Gt, and this "consensus mass" (Kvenvolden, 1993) was often cited in the literature. However, the convergence of estimates was fortuitous, because different authors arrived at nearly the same mass but with widely varying assumptions; an appropriate range across the studies was 5000–20 000 Gt (Dickens, 2001b). In the last ten years, estimates have ranged from 500–2500 Gt (Milkov, 2004) and 1600–2000 Gt

(Archer et al., 2009) to 74 400 Gt (Klauda and Sandler, 2005). The latter is almost assuredly too high (Archer, 2007). The others are probably too low.

The estimate of 500–2500 Gt C by Milkov (2004) was calculated as follows. He assumed a global volume for the modern marine GHSZ of $7 \times 10^6 \, \text{km}^3$. This number came from Dickens (2001b), who determined the cross-sectional area of the GHSZ for a hypothetical continental slope during a Pleistocene sealevel low-stand (35 km^2), and multiplied this by the approximate length of the world's continental margins (~200 000 km). Milkov (2004) then assumed that 10–30% of the area above this volume contains gas hydrate, and that this would have average gas hydrate contents of 0.9–1.5% (~1.8–3.0% of porosity) from the seafloor through the GHSZ. The latter range came from limited results of pressure cores at a few sites drilled with gas hydrate (Dickens et al., 1997b; Milkov et al., 2003).

Determining the mass of the present-day gas hydrate reservoir in this way is analogous to quantifying the mass of the present-day terrestrial biosphere by estimating the area which vegetation can grow across the globe and multiplying this by the mass of plants in a few hectares from a few scattered locations. Irrespective, the calculation by Milkov (2004) has three sources of error, each which render the estimated range too small. First, the global volume of sediment that can host gas hydrate lies at the low end of post-1990 estimates (~$5–30 \times 10^6 \, \text{km}^3$; Dickens, 2001b). As emphasized by Dickens (2001b) and Archer (2007), comparisons of GHSZ volumes are not straightforward because of different assumptions made by various workers. Nonetheless, this number is uncertain, and significantly higher values are plausible (Dickens, 2001b; Archer, 2007). Indeed, Dickens (2003) suggested that it could be closer to $12 \times 10^6 \, \text{km}^3$. Second, the $7 \times 10^6 \, \text{km}^3$ estimate pertains to bathymetric conditions during the last glacial maximum. The rationale for using this bathymetry to discuss gas hydrate accumulation is that modern sea level is anomalous compared to the recent geological record, and significant gas hydrate probably has not yet formed at shallow water depths on the slope, despite now being at appropriate stability conditions. Thus, some (~5–10%) of the assumed 70–90% of seafloor area without gas hydrate already has been "removed"

by using Pleistocene low-stand conditions. Third, average gas hydrate contents of 0.9–1.5% are at the low end for drill sites that have targeted gas hydrate and where their downhole abundance has been quantified. For example, the two primary sites drilled by IODP Expedition 311 to ascertain gas hydrate abundance (U1325 and U1326) have average gas hydrate contents across the GHSZ of somewhere between 1.5 and 3.0% (Malinverno et al., 2008). A value of between 1 and 3% has been suggested previously to represent the appropriate range for such a calculation (Archer, 2007).

The best estimates for the volume of the modern global GHSZ on continental margins probably come from Gornitz and Fung (1994) and Harvey and Huang (1995), who systematically tried to determine this quantity. Collectively, these authors provide a range of 4–16×10^6 km^3 (Dickens, 2001b). If we take the approach by Milkov (2004), but change this parameter accordingly, as well as the average gas hydrate content to 1–3%, consistent with drilling data, the total mass of carbon stored as CH$_4$ in present-day marine gas hydrates should be expressed as 170–12 700 Gt.

The estimate of 1600–2000 Gt C by Archer et al. (2009) was calculated in a more elegant manner. Following previous work (Buffett and Archer, 2004; Archer, 2007), they determined the volume of the GHSZ throughout the ocean (although unfortunately without stating and describing this volume, so comparisons to other work cannot be made). They then filled gridded portions of this volume over time by meshing a model for the supply of organic carbon to the seafloor with a one-dimensional model for the formation of gas hydrate in marine sediment. However, the estimate by Archer et al. (2009) has at least one major source of error that makes the amount too small. The supply of organic carbon landing on the seafloor and driving methanogenesis in their model is for present-day conditions. This is not appropriate because methanogenesis occurs well below the seafloor and depends on the integrated organic carbon input over time (Davie and Buffett, 2001; Dickens, 2003; Buffett and Archer, 2004; Archer, 2007; Bhatnagher et al., 2007). In general, far more organic carbon (perhaps more than twofold) accumulates on continental slopes during sealevel low-stands than at present-day (Muller and Suess, 1979; Jasper and Gagosian, 1990; Hall and McCave, 1998; Riedinger,

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et al., 2005), and low-stand conditions prevailed throughout most of the last 1 million years. Thus, the organic carbon input to sediment in the model is very likely too low. Buffett and Archer (2004) specifically noted that a 50% increase in organic carbon supply to the seafloor in their models would double the inventory of gas hydrate. In any case, predicted amounts at specific grid locations in the model have not been compared to estimates made by drilling at the same locations. From their maps, it is clear that too little gas hydrate occurs at Blake Ridge off the east coast of the US. It should be $\sim$400 kg m^{-2} seafloor (Dickens et al., 1997b) not <100 kg m^{-2} seafloor as modeled (Archer et al., 2009).

Importantly, the estimates discussed above pertain to gas hydrate alone, not the associated CH_4 dissolved in pore water or in free gas below the GHSZ. These amounts are likely very large (> 500–1000 Gt), and must be included in any dynamic model regarding past CH_4 release from the seafloor (Dickens, 2003). In other words, it is not the mass of gas hydrate that sets the bound on potential CH_4 input during a perturbation, but the sum of CH_4 in gas hydrate, free gas and dissolved gas (Dickens, 2003).

It should be obvious that, even with available information and modeling, we do not know the mass of carbon stored within present-day gas hydrate systems very well. Archer (2007) nicely summarized this problem after an earlier modeling effort, which unfortunately also included present-day organic carbon inputs to the seafloor. He suggested that modern gas hydrate systems contained 500–3000 Gt of carbon in gas hydrate and 500–3000 Gt of carbon in free gas, but these estimates could be significantly off target.

6 Other hypotheses for massive carbon input

Four other hypotheses for $\delta^{13}C$ excursion at the onset of the PETM have been published formally. Two conflict with available information; the other two not compatible with the dual notions that warming preceded carbon input, and that multiple carbon inputs occurred during the early Paleogene.

Kent et al. (2003) suggested that a large comet containing ^{13}C-depleted carbon impacted at the PETM, primarily on the basis of anomalous accumulation of single domain magnetite across the interval in sediment cores from New Jersey. This interpretation is wholly inconsistent with multiple geological observations, such as terrestrial
5 mammal migrations, He and Os isotope records, etc., as noted by Dickens (2003). Indeed, the incongruity prompted a comment arguing that bacteria likely produced the unusual magnetite on the New Jersey shelf because of greatly elevated terrigenous discharge and a change in redox conditions (Dickens and Francis, 2004). Subsequent work clearly shows this is the case (Lippert and Zachos, 2007; Kopp et al., 2009).
10 Kurtz et al. (2003) suggested that extensive burning of peat deposits released massive amounts of ^{13}C-depleted carbon during the PETM. However, this would necessitate an early Paleogene peat reservoir at least 10 times the mass of the modern peat reservoir (Higgins and Schrag, 2006), and there is no evidence for wholesale burning of peat (Collinson et al., 2007; Moore and Kurtz, 2008) or the total collapse of the
15 biosphere in general (Jaramillo et al., 2010; McInerney and Wing, 2011).
In framing their hypothesis, Kurtz et al. (2003) did emphasize a wonderful observation. The long-term Cenozoic δ^{13}C and δ^{34}S records (Zachos et al., 2001; Paytan et al., 1998), when coupled together on the same time scale, strongly suggest that an immense amount of organic carbon without Fe-sulfide minerals accumulated in the late
20 Paleocene (∼60–57 Ma), and a tremendous quantity of Fe-sulfides accumulated during the early Eocene (∼56–50 Ma). A huge mass of organic carbon placed into peat would provide a high C-low S reservoir, which then might have been "tapped" periodically to cause the PETM (Kurtz et al., 2003) and other negative carbon isotope excursions (Zachos et al., 2010). However, the estimated mass of peat (∼60 000 Gt) would be
25 extremely large compared to that of present-day (< 1000 Gt), and the subsequent precipitation of Fe-sulfides would require an ad hoc explanation. Kurtz et al. (2003) suggested massive burial of pyrite on the shelf during a major rise in sealevel during the early Eocene, but recent sealevel records do not support such a transgression (Müller et al., 2008). Indeed, the shelf is probably not a good place for long-term burial of

Fe-sulfides because of sulfide re-oxidation (Turchyn and Schrag, 2004).

Higgins and Schrag (2006) suggested that organic carbon deposited in one or more epicontinental seaways might have been subaerially exposed and rapidly oxidized during the PETM. However, sea level rose immediately before the CIE (Sluijs et al., 2008;

5 Harding et al., 2010; Handley et al., 2011), including in some epicontinental seaways (Iakovleva et al., 2001). They recognized this potential problem, and thus suggested tectonic uplift may have led to exposure. It is difficult to negate this hypothesis, although it would invoke a special set of circumstances given the short timing of the PETM δ^{13}C excursion. Certainly, organic-rich epicontinental seas have been exposed without mas-

10 sive carbon injections. In fact, parts of Turgay Strait, which accumulated organic-rich sediment during the PETM, were exposed < 1 million years afterward (Iakovleva et al., 2001), and there was no significant carbon injection during this time (Nicolo et al., 2007; Zachos et al., 2010).

In considering and rejecting CH_4 release, Higgins and Schrag (2006) raised a good

15 point overlooked in the original hypothesis (Dickens et al., 1995). Methanogenesis leads to ^{13}C-depleted CH_4 and ^{13}C-enriched bicarbonate, both which need to be accounted for in any model involving seafloor CH_4 release. Dickens (2003) had, in fact, incorporated this concept, suggesting that burial of authigenic carbonates removed the ^{13}C-enriched HCO_3^-. However, this is not how modern seafloor methane systems work:

20 most of the HCO_3^- produced during methanogenesis returns to the ocean through advection and diffusion (Luff and Wallmann, 2003; Snyder et al., 2007).

Svensen et al. (2004) presented geophysical evidence for extensive fluid output from the North Atlantic seafloor at about the time of the PETM. They suggested that rapid intrusion of magmatic sills into North Atlantic basins both heated sedimentary

25 organic carbon and released massive amounts of CH_4 precisely during the PETM. This idea remains plausible because the timing of sill intrusion and presumed fluid release from the seafloor is close to that of the PETM (Svensen et al., 2010), and it could account for certain observations, notably the greater amount carbonate dissolution and O_2-deficiency in this basin (Dickens, 2000, 2004). However, this idea

invokes "catastrophism"; essentially, most of the conventional hydrocarbon deposits in the modern world before human extraction (> 3000 Gt) would have to be produced, released, and oxidized all within 60 kyr (Dickens, 2004), and this is a challenge for several reasons (Higgins and Schrag, 2006). The age of the PETM must also precisely correspond to 55.9 Ma for this to be correct, because this is the specific overlap age of two zircons from the sills (Svensen et al., 2010). This is not the age of the PETM as presently presented (McInerney and Wing, 2011; Westerhold et al., 2011), although they could be the same, given existing problems with age models for the early Paleogene (Zachos et al., 2010). Such a mechanism further fails to explain the other likely early Paleogene carbon injection events, or why these might be paced by changes in Earth's orbital parameters. Lastly, the anomalous carbonate dissolution and O_2-deficiency in the North and Central Atlantic can be attributed to a change in ocean circulation during the PETM (Dickens, 2000; Zeebe and Zachos, 2007) – it does not demand volcanism.

A link between North Atlantic volcanism and massive carbon injection during the PETM has been suspected for a long time (Dickens et al., 1995; Thomas and Shackleton, 1996). The simplest explanation, however, is that North Atlantic volcanism pushed the long-term warming between 57.5 and ~50 Ma, and that variations in orbital parameters and heightened volcanism, including perhaps especially at 55.9 Ma, induced multiple short-term warming events, which initiated carbon cycle feedbacks (Westerhold et al., 2011). In other words, records of North Atlantic volcanism and the δ^{13}C of the carbon cycle might very well be coupled, but not directly.

7 Summary and progression

Somehow, four concepts have been muddled in recent literature:

1. The δ^{13}C excursions across the PETM and other hyperthermal events clearly show us that a major problem exists with conventional models of the global carbon cycle. Specifically, there must be a large reservoir of carbon that can rapidly

add large amounts of ^{13}C-depleted carbon to the exogenic carbon in response to environmental change, and probably repeatedly.

2. Incorporation of marine gas hydrate systems would solve this problem in a general sense. These systems are "missing" in conventional models of the global carbon cycle, contain exceptionally ^{13}C-depleted carbon, and should respond to rapid environmental change, notably deep-sea warming, which did occur during the PETM, and probably other hyperthermals of the early Paleogene.

3. The a priori assumption when examining data across the PETM should not be focused on reasons why a rapid 2000 Gt input of carbon is too small. Such an addition is already tremendously large and, in fact, was effectively deemed impossible before discovery of the CIE across the PETM (Sundquist, 1986).

4. Dismissal of gas hydrates on the grounds of present-day mass is not warranted, because it is large but poorly constrained. Equally important, this line of reasoning evades the overarching carbon mass balance issue for the PETM δ^{13}C excursion, because any viable alternative for the carbon injection probably faces a much greater problem (Dickens et al., 1995). No discussion should begin by rejecting seafloor CH_4 systems on reasons of mass balance, and then tout alternatives with worse mass balance considerations (e.g., McInerney and Wing, 2011).

We are in a quandary as a community. There is zero positive evidence that large amounts of CH_4 escaped the seafloor from gas hydrate systems during the onset of the PETM; the idea is entirely based on circumstantial reasoning and consistency with data. However, after 16 yr, there are no good arguments for dismissal, and there have been no better alternatives.

So, how should we progress? There are at least four obvious paths:

1. Ascertain whether the carbon input associated with the δ^{13}C excursion was a positive feedback to warming. Many papers concerning the PETM begin with the

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premise that the massive carbon input associated with the CIE drove the warming (e.g., Higgins and Schrag, 2006; Pagani et al., 2006a; Archer, 2007; Handley et al., 2011). There is no evidence to support this notion. Indeed, all information to date suggests the opposite.

5   2. Determine whether the PETM is a special case or the extreme example of a series of self-similar events during early Paleogene warming. Many papers have focused on the PETM as an isolated event (e.g., Kent et al., 2003; Svensen et al., 2004; Higgins and Schrag, 2006; Pagani et al., 2006a). Recent papers do not support this idea.

10   3. Entertain the idea that release of CH_4 from the seafloor might be the correct explanation for the $\delta^{13}C$ excursion across the PETM and other hyperthermal events of the early Paleogene (Dickens, 2003). This possibility is intriguing because it will demand some creativity to explain, to test, and to prove, and it would force the overturning of entrenched ideas.

15 As a start, the biggest problems with invoking successive massive releases of CH_4 from gas hydrate systems during the early Paleogene revolve around total mass and recharge (Dickens, 2003; Buffett and Archer, 2004; Higgins and Schrag, 2006). Seafloor temperatures on continental slopes increased from $\sim 7\,°C$ to $\sim 13\,°C$ between 58 and 50 Ma (Zachos et al., 2008). Thus, the dimensions of the GHSZ across the
20 world's oceans must have been smaller than at present-day (Dickens, 2001b), and must have generally decreased over this time interval (Dickens, 2003). A series of large ^{13}C-depleted carbon inputs appear to have occurred. Thus, large amounts of CH_4 carbon would have to reform relatively quickly to partly replenish carbon loss after an earlier injection (Dickens, 2003). The combination of both concepts almost necessi-
25 tates that, if seafloor CH_4 release were the culprit, carbon cycled through gas hydrate systems during "quiescent times" faster in the early Paleogene than at present-day (Dickens, 2003). So, does this make sense?

We know how carbon cycles through modern gas hydrate systems under steady-state conditions, at least at a rudimentary level (Davie and Buffett, 2001; Dickens, 2003; Luff and Wallman, 2003; Buffett and Archer, 2004, 2007; Bhatnagher et al., 2007). Organic carbon lands on the seafloor. During burial, it passes through a gauntlet of early

5 diagenetic reactions, including organoclastic sulfate reduction. Methanogens then utilize a fraction of remaining organic carbon to form ^{13}C-depleted CH_4 and ^{13}C-enriched HCO_3^-, the first that can cycle between dissolved gas, free gas and gas hydrate. Carbon returns to the ocean in most places as HCO_3^-. This includes HCO_3^- formed from methanogenesis and HCO_3^- formed when upward migrating CH_4 reacts with dissolved

10 SO_4^{2-} via anaerobic oxidation of methane (AOM: $CH_4 + SO_4^{2-} \rightarrow HCO_3^- + H_2S + H_2O$). Some amount of carbon also returns through CH_4 venting and aerobic oxidation in the water column. It should be stressed that it would have been a major change in the latter flux for massive carbon injections, otherwise seafloor carbonate dissolution would not have occurred.

15 Buffett and Archer (2004) suggested, using model simulations, that gas hydrate systems in the early Paleogene would have had a smaller mass than at present-day, but not as much as expected from phase boundary considerations, because the ocean would have had lowered dissolved O_2, which would increase organic carbon supply to slope sediments. However, the master variable is probably not dissolved O_2 but

20 dissolved SO_4^{2-}, because this limits organic carbon inputs and enhances CH_4 carbon outputs. Moreover, methanogenesis is highly sensitive to temperature (Zeikus and Winfrey, 1976; Price and Sowers, 2004) such that the rate of CH_4 production within the upper few hundred meters of sediment might be 3 times higher with a geothermal gradient shifted to warmer conditions by 10 °C.

25 Any discussion regarding large CH_4 masses and faster CH_4 cycling times in gas hydrate systems of the early Paleogene should begin with two basic questions (Dickens, 2003): were dissolved SO_4^{2-} concentrations in the ocean much less, and were bottom water temperatures much warmer relative to present-day? The answer to both is, almost assuredly, yes (Horita et al., 2002; Zachos et al., 2008). A model simulation of

gas hydrate and free gas distribution in a world with warmer bottom water, but lower dissolved O_2, lower dissolved SO_4^{2-}, and faster methanogenesis seems an appropriate target in which to frame future discussions regarding the possibility of a large and dynamic early Paleogene seafloor CH_4 cycle. This might especially include consideration of continental slopes in the Arctic (Archer, 2007), but not so much because of phase boundary considerations; rather, this large basin was euxinic and accumulating massive amounts of organic carbon during the Cretaceous and early Paleogene (Jenkyns et al., 2004; Moran et al., 2006).

A large seafloor CH_4 capacitor that diminishes in mass between 57 and 50 Ma because of deep-sea warming and successive short-term carbon injections, but partly refills because of deep-sea warming and increasingly higher carbon throughput is a testable hypothesis. For example, a predictable effect on $\delta^{13}C$ records must follow any postulated massive release of CH_4 (Dickens, 2003). During steady-state conditions, there would be a modest input of highly ^{13}C-depleted carbon from dissolved gas and free gas reservoirs to the ocean through AOM and venting. An initial estimate was $0.007\,\mathrm{Gt\,C\,yr^{-1}}$ ($0.62 \times 10^{12}\,\mathrm{mol\,C\,yr^{-1}}$; Dickens, 2003). After a massive injection of CH_4, this input would drop significantly. This is because, once deep-ocean temperatures stopped warming and they began cooling, gas hydrate would start re-forming from dissolved gas and free gas, effectively cannibalizing the CH_4 sources for return carbon outputs to the ocean under steady state conditions. The consequence would be a quasi-exponential rise in $\delta^{13}C$ sometime after the carbon input that is faster than predicted by weathering alone (Dickens, 2003). This effect appears to occur in $\delta^{13}C$ records following the PETM and other hyperthermals (Stap et al., 2009), although it might be attributed to massive uptake of carbon into organic carbon reservoirs in general (Dickens, 2001a), and a huge terrestrial biosphere more specifically (Bowen and Zachos, 2010).

Sulfate consumption by AOM produces H_2S (Borowski et al., 1996). Unlike during organoclastic sulfate reduction near the seafloor, where much of the H_2S is re-oxidized (Turchyn and Schrag, 2004), a good fraction of the H_2S produced by AOM precipitates

into Fe-sulfide minerals (Schultz et al., 1994; Hensen et al., 2003; Novosel et al., 2005; Riedinger et al., 2005; Snyder et al., 2007). Indeed, significant Fe-sulfide accumulation in shallow sediment above gas hydrate systems begins near the sulfate-methane transition, which is caused by AOM (above references). This is interesting because
5   it suggests that, on continental slopes, Fe-sulfide minerals do not accumulate with organic carbon burial, but they do accumulate with CH_4 output.

Burial of organic carbon on continental slopes during the late Paleocene, and the build-up of a large, dynamic gas hydrate capacitor, would not require concomitant sulfur accumulation. However, high carbon outputs through AOM during "steady-state" con-
10   ditions and its decay between 57 and 50 Ma would necessitate a large accumulation of Fe-sulfide minerals. It is intriguing to compare two independently derived mass fluxes: Kurtz et al. (2003) speculated that, in a low SO_4^{2-} ocean, Fe-sulfide outputs increased by $\sim 1 \times 10^{12}$ mol S yr^{-1} via excess pyrite burial between 56 and 50 Ma; Dickens (2003) speculated that CH_4 outputs from a diminishing "high flux gas hydrate system" be-
15   tween 57 and 50 Ma might have averaged $\sim 0.62 \times 10^{12}$ mol C yr^{-1}, with a good fraction of this occurring via AOM and, by inference, production of sulfide. The numbers do not agree if consumption of CH_4 through AOM drove the production of Fe-sulfide minerals in shallow marine sediment on continental slopes. However, given the assumptions behind the estimates, and the wildly different conceptual frameworks for arriving at these
20   fluxes, it is an idea worth pondering.

A highly speculative view of the early Paleogene carbon and sulfur cycles (Fig. 1) can be offered by trying to merge various models (Kump and Arthur, 1999; Dickens, 2003; Kurtz et al., 2003; Turchyn and Schrag, 2004). This is a curious machine. During organic carbon burial and the growth of large amounts of gas hydrate, the $\delta^{13}C$ of the
25   exogenic carbon cycle rises and the $\delta^{34}S$ of the exogenic sulfur cycle decreases. The first occurs because of organic carbon removal from the ocean, but more importantly because the products of methanogenesis are being separated: ^{13}C-depleted CH_4 is being stored into gas hydrate; ^{13}C-enriched HCO_3^- is returning to the ocean. The second occurs because the output of CH_4 through AOM is less. During the slow decay

of gas hydrates, especially with accelerated fluxes, the δ^{13}C of the exogenic carbon cycle drops and the δ^{34}S of the exogenic sulfur cycle rises because of AOM and the production of ^{13}C-depleted HCO_3^- and the precipitation of Fe-sulfide minerals. During rapid bottom water warming, massive amounts of ^{13}C-depleted CH_4 are released as free gas. The long-term δ^{13}C and δ^{34}S records between 62 and 50 Ma need not reflect enormous terrestrial peat formation serendipitously followed by immense marine accumulation of Fe-sulfide minerals. Rather, they could reflect the direct and necessary consequences of filling and sporadically emptying much smaller dynamic gas hydrate systems on continental slopes. Modest amounts of organic carbon were buried but without Fe-sulfide minerals accumulating; after three million of years, the carbon inputs developed large amounts of CH_4 (in the "model", Fig. 1, at least 10 000 Gt C); upon return of CH_4 toward the seafloor during "steady-state" conditions, large amounts of ^{13}C-depleted HCO_3^- and Fe-sulfides formed through AOM; superimposed on this framework were massive fluxes of CH_4 to the ocean through venting when bottom water warmed rapidly. With this perspective, the unusual long-term drop in the CCD between 57 and 50 Ma (Hancock et al., 2007; Leon-Rodriguez and Dickens, 2010) could have been caused by deep-sea HCO_3^- production.

It is difficult to fall down this rabbit hole further. There are uncertainties in the timing of available δ^{13}C and δ^{34}S records. The masses and fluxes in making such a model are essentially guess-work (although with some constraints; Dickens, 2003; Kurtz et al., 2003). Far more crucially, conventional models for the global sulfur cycle (Turchyn and Schrag, 2004), like those for carbon, do not explicitly include seafloor CH_4 systems and a deep-sea sulfur output driven by AOM, even though AOM in shallow sediment on modern continental slopes very likely consumes large amounts of SO_4^{2-} (Hinrichs and Boetius, 2002; D'Hondt et al, 2002), and this reaction produces large quantities of Fe-sulfides (Hensen et al., 2003).

As stated for a long time, there would remain the issues as to what drove the initial warming of the PETM and why a large, dynamic gas hydrate capacitor would have formed in the first place (Dickens et al., 1995; Dickens, 2003). Volcanic outputs are

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appealing in the first regard because CO_2 contributions would not manifest in $\delta^{13}C$ records (Sluijs et al., 2007; Carozza et al., 2011). This might also explain why carbonate dissolution appears to have begun before the CIE (Leon-Rodriguez and Dickens, 2010). The second problem is a challenge. Long-term $\delta^{13}C$ records strongly suggest that a massive storage of organic carbon occurred somewhere during the late Paleocene (Shackleton and Hall, 1984), so the answer may lie at the start of the positive $\delta^{13}C$ excursion, at about 62 Ma (Westerhold et al., 2011). It is important to stress, though, that the building of a huge organic carbon reservoir during the late Paleocene that can subsequently discharge carbon rapidly during the early Eocene presents a conceptual problem to any interpretation for the PETM $\delta^{13}C$ excursion, if it represents the extreme case of multiple events linked to environmental forcing.

(4) Provide and test a compelling alternative explanation for carbon inputs across the PETM and, likely, other related hyperthermal events of the early Paleogene that is consistent with available data. Assuming the PETM $\delta^{13}C$ excursion represents an incredibly large (> 5000 Gt) carbon mass transfer, assuming that it is the extreme case of multiple carbon injection events during the early Paleogene, and assuming these are positive feedbacks to environmental change, the answer would seemingly lie in a dynamic terrestrial organic carbon reservoir that was much larger and much different than at present-day (Kurtz et al., 2003). In fact, in presenting the carbon mass balance problem for the PETM, and excluding terrestrial sources, it was stated "a redistribution of carbon between organic and inorganic reservoirs is untenable as a sole cause... unless future investigations can demonstrate that the Paleocene organic carbon reservoir was substantially greater in mass..." (Dickens et al., 1995).

Within the context of at least a 5–10 fold increase of terrestrial carbon reservoirs relative to present-day, the hypothesis of Kurtz et al. (2003) remains entirely plausible, if it was the drying and oxidation of peat (Ise et al., 2008; Dorrepaal et al., 2009), rather than the burning of peat. Another candidate is organic carbon in permafrost (Zimov et al., 2006), which has now also been suggested as a possible explanation for the carbon inputs of the early Paleogene (DeConto et al., 2010).

The overall notion of several rapid and tremendously large carbon injections coming from land during the early Paleogene is exciting, including because it faces challenges similar to those regarding invocation of seafloor gas hydrates (Dickens, 2003). As hinted at by Bowen and Zachos (2010), it would require a wholesale rethinking of the global carbon cycle with one or more large and dynamic terrestrial "capacitors" that accumulate and release ^{13}C-depleted organic carbon throughout time, with carbon inputs and outputs somehow coupled to conventional reservoirs, and responding to environmental change. It would also necessitate imagination as to how and why hugely greater quantities of mobile terrestrial organic carbon existed in the past. For example, the present-day amount of organic carbon stored in permafrost regions is probably large, but less than 1000 Gt (Zimov et al., 2006). Moreover, this total is high only because approximately 500 Gt is associated with thick, organic-rich deposits of frozen wind-blown loess spread over $\sim 1 \times 10^6$ km^2 (Zimov et al., 2006). Can much greater quantities of these sort of deposits form and re-form when high-latitudes were much warmer than today?

With any terrestrial carbon source for the δ^{13}C excursions of the early Paleogene, however, there will be a tricky sulfur problem to pocket away: where and why did an excess of $\sim 1 \times 10^{12}$ mol S yr^{-1} accumulate as Fe sulfides during the early Eocene? One might suggest the happenstance development of a euxinic Arctic accumulating large amounts of pyrite (Ogawa et al., 2009), although, given the very limited records, the mass and timing of Fe-sulfide accumulation in this basin compared to changes in the global sulfur isotope curve are open to debate. Such questioning will also only beg the issue as to whether the pyrite reflects a past Arctic Ocean with enormous amounts of CH$_4$ in sediment and high rates of AOM.

It should be emphasized that other Myr-scale intervals of the Phanerozoic appear to have had Earth system changes similar to those of the Early Paleogene. The most notable example is the early Toarcian (Cohen et al., 2007). Much of the commentary presented here probably applies to debates concerning records across these other time intervals.

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Methane release from gas hydrate systems during the Paleocene-Eocene

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Interactive Discussion

Masses: 10^{18} moles   Fluxes: 10^{12} moles/yr

Rivers
F_{SIn} = 3.0
δ_{SIn} = +1‰

Rivers
F_{CIn} = 49
δ_{CIn} = -4.4‰

Weathering

Venting
F_{Vent} = 0.1
δ_{Vent} = -60‰

Carbonate
F_{Carb} = 39
δ_{Carb} = +2‰

Sulfur
M_{SEx} = 13.0
δ_{SEx} = +18‰

F_{AOM} = 0.4
δ_{AOM} = -60‰

Carbon
M_{CEx} = 4.67
δ_{CEx} = -1.45‰

Organic
F_{Org} = 11
δ_{Org} = -28‰

AOM

$F_{Dp\text{-}Bicarb}$ = 0.5
$\delta_{Dp\text{-}Bicarb}$ = +4‰

Meth

Seafloor T

Alteration
F_{Alt} = 2.0
$\delta_{Alt} = \delta_{Sulf}$ = 18‰

Pyrite
F_{Pyrite} = 1.0
δ_{Pyrite} = -35‰
(50% through AOM)

Seafloor T

Gas
Hydrate

Dissolved

Free Gas

Methane
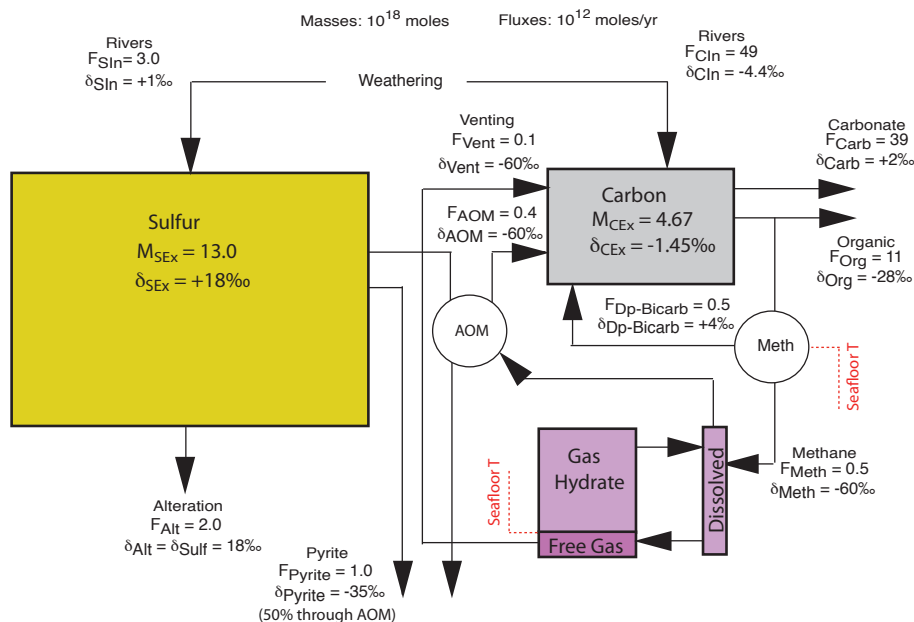F_{Meth} = 0.5
δ_{Meth} = -60‰

Fig. 1. A "steady-state" Paleogene machine with coupled carbon and sulfur fluxes. M = Mass; F = Flux; δ = delta. Postulated masses and fluxes are my best effort at trying to merge those presented in previous work (Kump and Arthur, 1999; Dickens, 2003; Kurtz et al., 2003; Turchyn and Schrag, 2004). The exogenic carbon cycle has $\sim$50 000 Gt in the ocean, $\sim$1400 Gt in the atmosphere (x2 pre-industrial), and $\sim$3600 Gt in the biosphere. The sulfur cycle pertains to SO_4^{2-} concentrations of $\sim$10 mM. This should not be taken as any specific point in time of the early Paleogene, but an effort to get the carbon and sulfur cycles coupled conceptually at some time within the early Paleogene.