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Climate of the Past

Down the Rabbit Hole: toward appropriate discussion of methane release from gas hydrate systems during the Paleocene-Eocene thermal maximum and other past hyperthermal events

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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 carbon isotope (δ^{13}C) excursion and deep-sea carbonate dissolution. A widely cited explanation for this carbon input has been thermal dissociation of gas hydrate on continental slopes, followed by release of 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 δ^{13}C excursion across the PETM, although it requires an unconventional framework for global carbon and sulfur cycling, and it lacks proof. 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, at least at high-latitudes and in the deep ocean, warmed by at least 5°C from the late Paleocene ca. 57.5 million years ago (Ma) through the Early Eocene climatic optimum (EECO) ca. 52–50 Ma (Bijl et al., 2009; 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; Charles et al., 2011; 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; Cui et al., 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 (CIE) across the PETM 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).

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2 General cause for the carbon isotope excursion at the PETM

For about 17 years, the CIE 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). Positive support for this inference comes 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 and Dickens, 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., 2009; Kump et al., 2009). In multiple δ^{13}C records, values return to near-initial ones within about 200 000 years after the onset (e.g. McInerney and Wing, 2011; Cui et al., 2011). This also agrees with model simulations for the long-term response of the exogenic carbon cycle following a rapid and massive carbon input (Archer et al., 1997; Dickens et al., 1997a). However, it should be stressed that a range of potential feedbacks, one re-introduced later, complicates details of the carbon isotope recovery (Dickens, 2001a, 2003; Higgins and Schrag, 2006; Bowen and Zachos, 2010; Cui et al., 2011).

Since discovery of the global 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 CIE 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 -4.0 ‰ excursion could be explained by an addition of ~2000–3500 gigatonnes (Gt = 10^{15}g) of C with a δ^{13}C of -60 ‰ or about ~6000–12 000 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; Cui et al., 2011). For comparison, unabated burning and near-complete consumption of all fossil fuel reserves will emit about 4000–5000 Gt of C by 2500 AD (Archer et al., 1997) with a δ^{13}C value of about -30 ‰, the latter value depending on ultimate inputs from coal, oil and natural gas (Anders et al., 2000). The amounts estimated for the PETM depend on various factors including the timing of the input, masses within the exogenic carbon cycle, and external fluxes to and from this cycle (Dickens, 2001a; Archer, 2007; Carozza et al., 2011; McInerney and Wing, 2011; Cui et al., 2011). Note that the relationship between carbon addition and resulting CIE is non-linear; 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; Cui et al., 2011).

As Sundquist (1986) and others (Dickens et al., 1995; Thomas and Shackleton, 1996) emphasized, there is no mechanism within the framework of conventional carbon cycle models to explain a geologically rapid and truly global >2.5 ‰ negative δ^{13}C excursion, except by human extraction and burning of most known fossil fuel resources. This problem regarding the PETM, nicely re-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 δ^{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, 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 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. Nominally 2000–3000 Gt C, as free CH_4 gas, then escaped from marine sediment through slumping or venting (Dickens, 2003). Importantly, CH_4 release must have occurred at water depths below 900 m, given phase boundary constraints for methane hydrate in seawater, and deep-ocean temperature values (~9 °C) before the PETM (Dickens et al., 1995; Dickens, 2001b).

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 (δ^{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 δ^{13}C composition makes the carbon mass balance problem more palatable.

Three concepts concerning the gas hydrate dissociation hypothesis warrant re-emphasis because many articles consistently overlook them. First, CH_4 release would have operated as a positive feedback to climate change. Specifically, some component of total global warming during the

PETM (perhaps 2 to 4 °C) must have preceded the carbon input associated with the δ^{13}C excursion, probably by at least 1000 years (Dickens et al., 1995). This is because temperature on the seafloor overlying the GHSZ (>900 m water depth in the late Paleocene) needs to rise significantly, and because heat needs to propagate into the GHSZ and dissociate gas hydrate, an endothermic reaction. Second, the primary impact of seafloor CH_4 release from a long-term carbon cycle perspective would have been addition of ^{13}C-depleted CO_2 to the ocean and atmosphere (Dickens et al., 1997a). This is because CH_4 rapidly oxidizes to CO_2 in the ocean or atmosphere, and because carbon cycles between the ocean and atmosphere much faster than the duration of the PETM. Third, a good fraction of CH_4 oxidation may have occurred within or below the thermocline (Dickens, 2000). This is because significant amounts of CH_4 escaping present-day continental slopes either dissolves in water or reacts with dissolved O_2 via microbial activity (e.g. Valentine et al., 2001; Tavormina et al., 2008; Kessler et al., 2011). There was never a suggestion in original works that all CH_4 inputs from the seafloor entered the atmosphere and drove all climate change during the PETM (Dickens et al., 1995, 1997a; Dickens, 2000, 2003). However, some CH_4 could have escaped the ocean and enhanced warming (as CH_4) during the PETM (Dickens et al., 1995; Schmidt and Shindell, 2003).

Support for the overall hypothesis has 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., 2011; 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). Dissolved oxygen concentrations likely decreased at intermediate water depths in the ocean (e.g. Thomas, 2003; Chun et al., 2010; Nicolo et al., 2010). This may have occurred 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 modelling 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 "hyperthermal" events 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, 2010; Leon-Rodriguez and Dickens, 2010; Zachos et al., 2010). At least five other events, presently called ETM2/H1, H2, I1, I2, and K/X (following Cramer et al., 2003), have been identified in multiple records and follow the PETM at approximately 53.7, 53.6, 53.3, 53.2, and 52.5 Ma. Like the PETM, these events display evidence for Earth surface warming (including in the deep-sea) and massive injection of ^{13}C-depleted carbon to the ocean and atmosphere; more interestingly, with available data, they appear coupled to orbital forcing and to have a relationship between magnitude and time (above references). Specifically, there seems to be a decrease in the magnitude of the δ^{13}C excursion with a shorter duration since the previous event (i.e. PETM > ETM2/H1 > K/X > I1 > H2 ∼ I2). Assuming the PETM and the other events have a similar generic cause, their characteristics 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, 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 δ^{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 (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 2000–3000 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 been a feedback to warming initiated 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 is certainly not the case, as emphasized by the wide range of possible temperature increases in our future (Roe and Baker, 2007).

A second criticism has been that carbonate dissolution on the seafloor was too intense for a 2000–3000 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 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; Carozza et al., 2011). 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 continental slopes, or changes in the direction of deepwater flow (Dickens, 2000, 2004; Zeebe and Zachos, 2007; Zeebe et al., 2009). Three 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; Cui et al., 2011). The first two model simulations disagree, as discussed by McInerney and Wing (2011). Panchuk et al. (2008) suggested >6800 Gt with a δ^{13}C composition of −22; Zeebe et al. (2009) 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. The most recent study (Cui et al., 2011) suggests that both explanations are plausible with available data.

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 likely that CH_4 in marine sediment would have a δ^{13}C composition closer to −70 ‰ in the early Paleogene (Dickens, 2003), because organic carbon landing on the seafloor was 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., 2007; 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 imply 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 also would have 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 ‰. This effect, compounded by water column stratification, probably needs consideration when examining δ^{13}C records of marine carbon bearing phases deposited along continental shelves during the PETM.

If the δ^{13}C of the exogenic carbon cycle, as a whole, changed by only 2.5–3.0 ‰ during the PETM, it forces the community to contemplate interpretations of δ^{13}C records across the event. Basically, as stressed by Bowen et al. (2004), we should ask at numerous locations, "why does the δ^{13}C anomaly differ from 3 ‰?" A model showing how δ^{13}C of seawater DIC and δ^{13}C of atmospheric CO_2 varied across the globe during the PETM would be very helpful.

Excepting regional deviations in the δ^{13}C of CO_2, Bowen et al. (2004) suggested that changes in relative humidity and soil productivity would accentuate terrestrial carbonate δ^{13}C excursions. Schouten et al. (2007) provided a good example of how mixing of plant sources can amplify the PETM δ^{13}C excursion in alkanes. 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, planktonic foraminifera (in this case, *Acarinina*) started precipitating tests in deeper water (Handley et al., 2008), 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 seems inconsistent in light of 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 is too small, 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 during the PETM.

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). 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), ∼700–1200 Gt (Archer et al., 2009), and 4–995 Gt (Burwicz et al., 2011) 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 7×10^6 km^3. This number came from Dickens (2001b), who determined the cross-sectional area of the GHSZ for a hypothetical 100 km-wide continental slope during a Pleistocene sea level 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 uncertainty, 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 × 10^6 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 12×10^6 km^3. Second, the 7×10^6 km^3 estimate pertains to bathymetric conditions during the last glacial maximum. The rationale for using this bathymetry to discuss gas hydrate accumulation comes from considerations of sea level (hydrostatic pressure) and the relatively slow cycling time of CH_4 in gas hydrate systems (>10 000 yr; Davie and Buffett, 2001; Bhatnagar et al., 2007). Sea level during the Holocene is much higher than that spanning most of the late Pleistocene. As such, significant gas hydrate probably has not yet formed at shallow water depths on the slope, despite now being at appropriate pressure. Some (∼5–10 %) of the assumed 70–90 % of seafloor area without gas hydrate already has been "removed" by using Pleistocene low-stand conditions. In fact, the combination of numbers used by Milkov (2004) implies that present-day gas hydrates only occur in sediment beneath 2–6 × 10^6 km^2 (0.5 to 1.7 %) of the present seafloor. 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 down-hole 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 $\times 10^6$ 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 ∼700–1200 Gt C by Archer et al. (2009) was calculated in a different manner. Following previous work (Buffett and Archer, 2004; Archer, 2007), they determined the volume of the GHSZ throughout the ocean (although 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 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 (i.e. surface sediment). 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; Bhatnagar et al., 2007). In general, far more organic carbon (perhaps more than twofold) accumulates on continental slopes during sea level low-stands than at present-day (Müller and Suess, 1979; Jasper and Gagosian, 1990; Hall and McCave, 1998; Riedinger 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 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 United States. It should be $\sim$400kg m^{-2} seafloor (Dickens et al., 1997b), not $<$100kg m^{-2} seafloor as modelled (Archer et al., 2009).

The estimate of 4–995 Gt C by Burwicz et al. (2011) was also determined through modelling. These authors recognized that long-term (rather than Holocene) sediment supply to continental slopes is crucial to understanding present-day gas hydrate distribution, and they incorporated this concept into their modelling. However, they appear to have awkwardly combined modern seafloor organic carbon contents with much higher rates for long-term sedimentation. This leads to organic carbon dilution and faster burial of smaller organic carbon contents through the GHSZ. Previous modelling has demonstrated that this will lower estimates for the amount of gas hydrate significantly (Bhatnaghar et al., 2007). More crucially, Burwicz et al. (2011) have not compared their modelling results to field data. In this case, it is egregious: their predictive maps suggest that no gas hydrate occurs at numerous locations where gas hydrate has been recovered or inferred from seismic information.

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; Archer, 2007; Archer et al., 2009) 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 modelling, 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 modelling 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 the δ^{13}C excursion at the onset of the PETM have been published formally. Two conflict with available information; the other two are 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 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 to be the case (Lippert and Zachos, 2007; Kopp et al., 2009).

Kurtz et al. (2003) suggested that extensive burning of peat deposits released massive amounts of ^{13}C-depleted carbon (∼10 000 Gt) 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; Page et al., 2011), and there is no evidence for wholesale burning of peat (Collinson et al., 2007; Moore and Kurtz, 2008) or the total collapse of the 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 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 late Paleocene peat (∼60 000 Gt C) would be extremely large considering masses of present-day peat (<700 Gt C; Page et al., 2011), or coal reserves and coal resources in sedimentary strata of all ages (<1000 Gt C and <21 000 Gt C, respectively; Höök et al., 2010). Moreover, the "flip-side" of this idea – subsequent precipitation of Fe-sulfides without significant carbon burial – mandates an ad hoc explanation. Kurtz et al. (2003) suggested massive burial of pyrite on the shelf during a major rise in sea level during the early Eocene, but recent sea level 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 reoxidation (Turchyn and Schrag, 2004; Bottrell and Newton, 2006).

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; Harding et al., 2011; Handley et al., 2011), including in some epi-continental 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 massive 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 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; much of the HCO_3^- produced during methanogenesis returns to the ocean through advection and diffusion (Luff and Wallmann, 2003; Snyder et al., 2007; Chaterjee et al., 2011).

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 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 of 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 (4000–5000 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; Charles et al., 2011). 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 or differential CH_4 release during the PETM (Dickens, 2000; Zeebe and Zachos, 2007) – it does not demand volcanism.

A link between North Atlantic volcanism and the PETM has been suspected for a long time (Eldholm and Thomas, 1993; 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 that 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 The croquet ground: 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 strongly suggest a major problem with conventional models of the global carbon cycle. Specifically, there likely exists at least one large reservoir that can rapidly add tremendous 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 2000–3000 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 grounds of present-day mass is not justified because it is large but poorly constrained. Certainly, gas hydrate estimates determined through models that do not replicate basic gas hydrate field-data should not be used to discount the idea. 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 almost assuredly 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.

We are in a quandary as a community. There is zero positive evidence that large amounts of CH_4 escaped the seafloor from gas hydrates during the onset of the PETM; the idea is entirely based on circumstantial reasoning and consistency with data. However, after 16 years, there are no good arguments for dismissal, and there are 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 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 support for this notion. Indeed, all information to date suggests the opposite (Thomas et al., 2002; Sluijs et al., 2007b; Harding et al., 2011; Secord et al., 2010; Handley et al., 2011).

2. Determine whether the PETM is a special case or the extreme example of a more common process, one especially apparent during early Paleogene warming. Many papers have focused on the PETM as an isolated event (e.g. Dickens et al., 1995; Kent et al., 2003; Svensen et al., 2004; Higgins and Schrag, 2006; Pagani et al., 2006a). Recent papers do not back this idea (Lourens et al., 2005; Nicolo et al., 2007; Agnini et al., 2009; Stap et al., 2009; Leon-Rodriguez and Dickens, 2010; Zachos et al., 2010).

3. Entertain the idea that CH_4 release from the seafloor might correctly explain much of the δ^{13}C excursion across the PETM and other hyperthermal events of the early Paleogene (Dickens, 2003). This possibility is intriguing because it demands some creativity to explain, to test, and to prove, and it forces the overturning of entrenched ideas.

   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 ∼7 °C to ∼13 °C between 58 and 50 Ma (Zachos et al., 2008). Thus, the dimensions of the GHSZ across the world's oceans must have been smaller than at present-day (Dickens, 2001b), and generally must have 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 fairly quickly to partly replenish carbon loss after an earlier injection (Dickens, 2003). The combination of both concepts almost necessitates that, if seafloor CH_4 release were the culprit, carbon cycled through gas hydrate systems during "quiescent times" relatively fast in the early Paleogene (Dickens, 2003). So, does this make sense?

   We have a basic concept for how carbon cycles through modern gas hydrate systems under steady-state conditions (Davie and Buffett, 2001; Dickens, 2003; Luff and Wallman, 2003; Buffett and Archer, 2004; Archer, 2007; Bhatnagher et al., 2007; Chaterjee et al., 2011). Solid organic carbon lands on the seafloor. During burial, it passes through a gauntlet of early diagenetic reactions, especially including organoclastic sulfate reduction ($CH_2O + SO_4^{2-} \longrightarrow 2HCO_3^- + H_2S$). Methanogens then utilize a fraction of remaining solid organic carbon to form ^{13}C-depleted CH_4

(typically $\delta^{13}C < -60$ ‰) and ^{13}C-enriched HCO_3^- (often $\delta^{13}C > +10$ ‰) in the upper few hundreds of meters of sediment. The ^{13}C-depleted CH_4 can cycle between dissolved gas, free gas, and gas hydrate within the sediment column, whereas much of the ^{13}C-enriched HCO_3^- produced by methanogenesis slowly returns to the ocean. However, ^{13}C-depleted HCO_3^- also slowly returns to the ocean in most places when upward migrating CH_4 reacts with dissolved SO_4^{2-} in shallow sediment via anaerobic oxidation of methane (AOM: $CH_4 + SO_4^{2-} \longrightarrow HCO_3^- + H_2S + H_2O$). Thus, there is a HCO_3^- flux from gas hydrate systems to the ocean that represents a mixture of products from methanogenesis and AOM. Some amount of carbon also returns to the ocean through CH_4 venting and aerobic oxidation in the water column ($CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$). It should be stressed that there would have been major changes in the latter flux to cause massive short-term carbon injections, otherwise seafloor carbonate dissolution would not have occurred.

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 (Dickens, 2001b), 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 dissolved SO_4^{2-}, because high SO_4^{2-} concentrations restrict organic carbon inputs into deep sediment via organoclastic sulfate reduction, and enhance CH_4 carbon outputs to the ocean via AOM. 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.

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: (1) Were dissolved SO_4^{2-} concentrations in the ocean much less? (2) Were bottom water temperatures much warmer relative to present-day? The answer to both is, most probably, 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 accumulated 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 after these losses because of high 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 "quasi steady state" conditions, a modest input of exceptionally ^{13}C-depleted carbon would enter the ocean from dissolved gas and free gas reservoirs through AOM and CH_4 venting. An initial estimate was 0.007 Gt C yr^{-1} (0.62×10^{12} 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 "quasi steady state" carbon outputs from these sources to the ocean. The consequence would be a logarithmic rise in the $\delta^{13}C$ of the exogenic carbon cycle 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, 2010), although it might be attributed to excess uptake of carbon into organic carbon reservoirs in general (Dickens, 2001a; Cui et al., 2011), or 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 reoxidized (Bottrell and Newton, 2006), a good fraction of H_2S produced by AOM precipitates into Fe-sulfide minerals (Schulz 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 it suggests that, on continental slopes, Fe-sulfide minerals do not accumulate with organic carbon burial, but they do accumulate with CH_4 output through AOM.

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 sulfide accumulation. However, high carbon outputs through AOM during 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

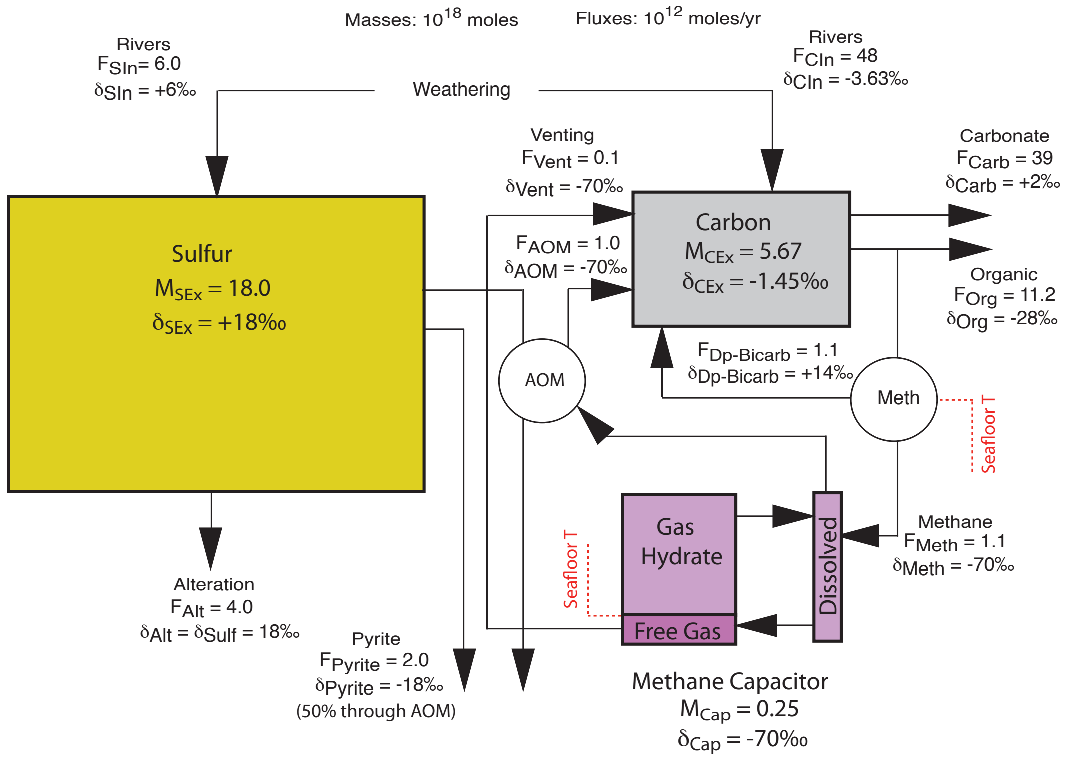

Fig. 1. A "steady-state" Paleogene machine with coupled carbon and sulfur fluxes. M = Mass; F = Flux; δ = delta. Postulated masses and fluxes are my best effort at trying to merge those presented in previous work (Kump and Arthur, 1999; Dickens, 2003; Kurtz et al., 2003; Turchyn and Schrag, 2004; Bottrell and Newton, 2006). The exogenic carbon cycle pertains to a world with nominally three times pre-industrial atmospheric CO_2. The sulfur cycle pertains to SO_4^{2-} concentrations of ~14 mM. This should be taken as initial effort to get the carbon and sulfur cycles coupled conceptually at some time within the late Paleocene.

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" between 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.

A highly speculative view of the early Paleogene carbon and sulfur cycles (Fig. 1) can be offered by trying to merge various models (Garrels and Lerman, 1984; Kump and Arthur, 1999; Dickens, 2003; Kurtz et al., 2003; Turchyn and Schrag, 2004; Bottrell and Newton, 2006). This is a curious machine. During organic carbon burial and the growth of gas hydrate, the δ^{13}C of the exogenic carbon cycle increases while the δ^{34}S of the exogenic sulfur cycle decreases. This occurs because ^{13}C-depleted CH_2O is removed from the ocean when the products of methanogenesis are being separated (^{13}C-depleted CH_4 stored into gas hydrate; ^{13}C-enriched HCO_3^- returning to the ocean), and because the output of CH_4 through AOM is lowered. During the slow decay of gas hydrates, the δ^{13}C of the exogenic carbon cycle drops while the δ^{34}S of the exogenic sulfur cycle rises. This is because of enhanced AOM in shallow sediment, which produces ^{13}C-depleted HCO_3^- and precipitates Fe-sulfide minerals. During rapid bottom water warming, massive amounts of ^{13}C-depleted CH_4 are released from the seafloor 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 emptying much smaller dynamic gas hydrate systems on continental slopes. From about 62 to 57 Ma, modest amounts of organic carbon were buried but without significant Fe-sulfide mineral accumulation; during this time, organic carbon generated CH_4 and ^{13}C-enriched HCO_3^-, but much of the CH_4 formed gas hydrate and remained in sediment. From about 57 to 50 Ma, long-term deep-ocean warming induced slow gas hydrate dissociation; during this time, CH_4 previously produced returned toward the seafloor, generating large amounts of ^{13}C-depleted HCO_3^- and Fe-sulfides through AOM. Superimposed on this framework were times of massive CH_4 release to the ocean through venting when bottom waters warmed rapidly; these were followed by times of reduced CH_4 outputs (partial recharge) when bottom waters cooled. Interestingly, 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) might reflect enhanced HCO_3^- inputs from AOM instead of weathering or volcanism.

The plausibility of the model (Fig. 1), with regards to the Early Paleogene, can be evaluated with a few mass balance calculations. For example, a modest increase in organic carbon burial over 5 million years (to $11.4\,\mathrm{mol\,C\,yr^{-1}}$), coupled with increases in ^{13}C-enriched HCO_3^- (to $1.15\,\mathrm{mol\,C\,yr^{-1}}$) and decreases in AOM and CH_4 venting (to $0.7\,\mathrm{mol\,C\,yr^{-1}}$ and $0.07\,\mathrm{mol\,C\,yr^{-1}}$), stores $\sim$12 000 Gt C as CH_4. It also causes a +0.9 ‰ excursion in δ^{13}C and a -1.5 ‰ excursion in δ^{34}S, as observed in records (Shackleton and Hall, 1984; Paytan et al., 1998). If CH_4 outputs halve following 200 000 years of cooling after a major CH_4 discharge (to $0.5\,\mathrm{mol\,C\,yr^{-1}}$), seafloor methane systems partly recharge, accumulating $\sim$1200 Gt C. However, a model that truly couples global C and S cycles through AOM and CH_4 cycling has not been developed.

It is difficult to fall down the rabbit hole further. There remain uncertainties in the timing and magnitude of changes in δ^{13}C and δ^{34}S records. The masses and fluxes behind such a coupled C and S model are mostly best guesses with limited constraints. Indeed, there are no good estimates for global fluxes of carbon passing in and out of modern gas hydrate systems. Far more crucially, conventional models for the global sulfur cycle (Garrels and Lerman, 1984; Turchyn and Schrag, 2004; Bottrell and Newton, 2006), like those for carbon, do not include seafloor CH_4 systems and pertinent fluxes, especially AOM. Almost certainly, however, AOM in shallow sediment on modern continental slopes consumes large amounts of SO_4^{2-} (Hinrichs and Boetius, 2002; D'Hondt et al., 2002) and produces substantial quantities of HCO_3^- and Fe-sulfides (Hensen et al., 2003).

Even if the overall idea of major gas hydrate dissociation during the PETM is correct, a longstanding issue remains: what drove deep sea warming at the start of the event? It could have been the crossing of a threshold during long-term warming, as originally argued and now modelled (Lunt et al., 2010). Alternatively, volcanic outputs are appealing, at least for the PETM, because CO_2 contributions would not manifest in δ^{13}C records (Sluijs et al., 2007b; Carozza et al., 2011). This might also explain why carbonate dissolution appears to have begun before the CIE (Leon-Rodriguez and Dickens, 2010b).

The present work raises a far more vexing problem: why would a large, dynamic gas hydrate capacitor form in the first place? Long-term δ^{13}C and δ^{18}O records strongly suggest cooling, including in the deep-ocean, and massive storage of organic carbon somewhere during the late Paleocene (Shackleton and Hall, 1984; Zachos et al., 2001, 2008). The answer, therefore, might be found at the start of these changes, nominally 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 with triggering (e.g. Kurtz et al., 2003) presents a conceptual problem facing any interpretation for the PETM δ^{13}C excursion, if it represents the extreme case of multiple events linked to environmental forcing.

With available information, models and arguments, the sedimentary record is the "Achilles Heel" to the overall notion that seafloor CH_4 systems are crucial to understanding Early Paleogene climate and geochemical cycling. If CH_4 outputs and inputs on continental slopes changed significantly during the Late Paleocene and Early Eocene, there should be evidence of this in appropriate sediment sequences.

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 δ^{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 other possibility seems to be a dynamic terrestrial organic carbon reservoir that was much larger and much different than at present-day (Kurtz et al., 2003; Cui et al., 2011). When presenting the carbon mass balance problem for the PETM, and excluding terrestrial sources, it was stated that "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. 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 $\sim 1 \times 10^6\,\mathrm{km}^2$ (Zimov et al., 2006). Can much greater quantities of these sort of deposits form and reform 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 $\sim 1 \times 10^{12}\,\mathrm{mol\,S\,yr^{-1}}$ accumulate, presumably as Fe sulfides, during the early Eocene? One might suggest the happenstance development of an 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 a pursuit 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.

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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