LETTER • OPEN ACCESS

New constraints on massive carbon release and recovery processes during the Paleocene-Eocene Thermal Maximum

To cite this article: Donald E Penman and James C Zachos 2018 Environ. Res. Lett. 13 105008

View the article online for updates and enhancements.
LETTER

New constraints on massive carbon release and recovery processes during the Paleocene-Eocene Thermal Maximum

Donald E Penman1* and James C Zachos2

1 Department of Geology & Geophysics, Yale University, New Haven, CT 06511, United States of America
2 Earth and Planetary Science, University of California, Santa Cruz, CA 95060, United States of America
E-mail: donald.penman@yale.edu

Keywords: PETM, carbon cycle, ocean acidification

Supplementary material for this article is available online

Abstract

Recent geochemical and sedimentological evidence constrains the response of seawater chemistry to carbon injection during the Paleocene-Eocene Thermal Maximum (PETM): foraminiferal boron-based proxy records constrain the magnitude and duration of surface ocean acidification, while new deep sea records document a carbonate compensation depth (CCD) over-shoot during the recovery. Such features can be used to more tightly constrain simulations of the event within carbon cycle models, and thus test mechanisms for carbon release, buffering, and sequestration. We use the LOSCAR carbon cycle model to examine first the onset of, and then recovery from the PETM. We systematically varied the mass, rate, and location of C release along with changes in ocean circulation patterns as well as initial conditions such as pre-event pCO2 and the strength of weathering feedbacks. A range of input parameters produced output that successfully conformed to observational constraints on the event’s onset. However, none of the successful scenarios featured surface seawater aragonite or calcite undersaturation at even peak PETM conditions (in contrast to anthropogenic acidification projections), and most runs featured approximately a doubling of pCO2 relative to pre-event conditions (suggesting a high PETM climate sensitivity). Further runs test scenarios of the body and recovery of the PETM against records of sustained acidification followed by rapid pH recovery in boron records, as well as the timing and depth of the CCD overshoot. Successful scenarios all require a sustained release of carbon over many tens of thousands of years following the onset (comparable to the mass released during the onset) and removal of carbon (likely as burial of organic carbon in addition to elevated chemical weathering rates) during the recovery. This sequence of events is consistent with a short-lived feedback involving the release of 13C-depleted C in response to initial warming followed by its subsequent sequestration during the cooling phase.

Introduction

The Paleocene-Eocene Thermal Maximum (PETM, ∼56 Ma) involved the geologically rapid release of thousands of petagrams of 12C-enriched carbon (Dickens et al 1997, Panchuk et al 2008, Zeebe et al 2009, Cui et al 2011) into the ocean-atmosphere system, resulting in global warming (Dunkley-Jones et al 2013), ocean acidification (Zachos et al 2005, Penman et al 2014, Babila et al 2016, Babila et al 2018), and varied yet pronounced impacts on marine and terrestrial biota (Thomas and Shackleton 1996, Wing et al 2005, Gibbs et al 2016). The event is often considered a geologic point of comparison to current anthropogenic CO2 release, offering the opportunity to improve our understanding of the response of climate, biota, and the carbon cycle to rapid carbon injection (Alley 2016). However, evaluating how the PETM compares to anthropogenic emissions requires accurate estimates of the mass and rate of carbon release during the PETM, as well as the strength of feedback processes responsible for terminating the event. Numerous sources and mechanisms have been proposed for carbon release during the PETM,
including methane clathrate dissociation (Dickens et al 1995, Zeebe et al 2009), organic carbon oxidation (Cui et al 2011, Bowen 2013), comet impact (Kent et al 2003, Schaller et al 2016), and North Atlantic volcanism (Svensen et al 2004, Storey et al 2007, Frieling et al 2016). Each of these mechanisms is associated with a feasible δ13C and mass of carbon and duration of release. However, due to the limits of chronologic tools that can be applied in deep time, the actual rate of the onset is not yet sufficiently well constrained to test all mechanisms.

Several modeling studies have assessed scenarios for carbon release and sequestration during the PETM. Zeebe et al (2009) and Panchuk et al (2008) used records of sedimentary CaCO3 reduction during the acidification phase to estimate the carbon release mass, whereas Gutjahr et al (2017) used single-site boron isotopes and δ13C to constrain scenarios of carbon emissions and sequestration in an Earth system model. Each of these studies presents one or two scenarios that most closely conform to a single dataset, without simultaneously considering constraints imposed by different types of data (e.g. carbonate chemistry proxies alongside global CaCO3 records), or exploring the range of carbon release scenarios allowed by the uncertainty in proxy reconstructions. Furthermore, recent geochemical and sedimentological evidence from novel records of the PETM have improved constraints on the response of seawater carbonate chemistry and carbonate burial patterns during the PETM, which allow the re-evaluation and refinement of scenarios of the event using carbon cycle modeling.

The most direct evidence of ocean acidification comes from recent studies utilizing the boron concentration and isotopes in planktic foraminifera (Penman et al 2014, Babila et al 2016, Gutjahr et al 2017, Babila et al 2018). At ODP Sites 1209, 689, and 690 (Penman et al 2014, Babila et al 2018) and at sites along the New Jersey margin (Babila et al 2016), the B/Ca proxy, which herein is treated as a qualitative proxy for acidification (Allen et al 2011, Penman et al 2014, Uchikawa et al 2015, Haynes et al 2017, Uchikawa et al 2017), shows a rapid ∼30%–40% decrease at the event onset, followed by a plateau of low values and finally a recovery to near pre-event levels in step with the carbon isotope excursion (CIE, figure 2). This decrease is consistent with a rapid (similar to the CIE onset rate), global, and sustained (similar to the CIE body duration) acidification of the surface ocean. At ODP Sites 1209, 865, 401, and 1263, a record of the boron isotopic composition (δ11B, a direct proxy for seawater pH) of surface-dwelling planktic foraminifers corroborates the acidification suggested by B/Ca records (Penman et al 2014, Gutjahr et al 2017, Babila et al 2018), and allows for its quantification. Due to the differing sensitivity of δ11B at different pH, the estimate for ΔpH across the PETM is a function of assumed initial pH, but for a reasonable assumption of pre-event (Paleocene) pH, the ~1% decrease in planktic δ11B across the P-E boundary represents acidification of approximately 0.3 pH units (Penman et al 2014, Babila et al 2018). This falls within the higher end of the range of simulated ΔpH assuming various carbon inputs (Panchuk et al 2008, Zeebe et al 2009, Ridgwell and Schmidt 2010).

Additional evidence for the response of ocean carbonate chemistry during the PETM is the decrease in wt% CaCO3 in sediment cores globally (Zachos et al 2005, Zeebe and Zachos 2007), a consequence of rapid shoaling of the CCD as the injection of CO2 into the oceans decreases pH and carbonate saturation state in tandem (Hönisch et al 2012). These records (Zachos et al 2005) also show how the CCD gradually recovered as seafloor carbonate dissolution and

![Figure 1. Map of all sites providing data for carbonate chemistry constraints placed on PETM simulations with Eocene geography by Colorado Plateau Geosystems (http://cpgeosystems.com/index.html).](http://cpgeosystems.com/index.html)
negative feedbacks restored ocean carbonate saturation. Numerical and conceptual models of the long-term carbon cycle predict that these negative feedbacks should have caused a period of carbonate oversaturation (relative to pre-event levels) during the recovery, wherein the build-up of alkalinity in the ocean would have caused an ‘overshoot’ of the CCD (Dickens et al 1997, Zeebe and Zachos 2013). Elevated carbonate burial during this period of oversaturation represents the long-term removal of not only the external carbon input, but also the carbonate dissolved during the initial acidification phase, the suppression of calcification during that phase (Luo et al 2016), and most importantly, the elevated delivery of alkalinity to the oceans by accelerated terrestrial chemical weathering. Evidence for enhanced weathering during the PETM comes from sedimentary records of Osmium isotopes (Ravizza et al 2001, Wieczorek et al 2013, Dickson et al 2015) and a pulse of silica burial in the North Atlantic (Penman 2016). The first direct evidence of a subsequent CCD overshoot was recently recovered in the North Atlantic at IODP Site U1403. This abyssal (paleo-water depth = 4400 m) site features a transition from Paleocene carbonate-barren clay to Eocene sediments containing 10%–40% carbonate (Norris et al 2014) starting in the early stages of the recovery interval of the CIE (Penman et al 2016). The approximate timing of the CCD overshoot at Site U1403 correlates well with existing records of elevated wt% CaCO3 elsewhere (figure 3) (Zachos et al 2005, Kelly et al 2010, Murphy et al 2010). The depth, timing and magnitude of the carbonate overshoot provides additional key observations on the evolution of the CCD during the PETM and can thus be used in models to constrain carbon fluxes.

This study aims to estimate carbon fluxes utilizing the latest observations on changes in ocean carbonate chemistry during the PETM. To this end, we use a carbon cycle model to determine a range of scenarios for carbon release and sequestration that are consistent

![Figure 2. Bulk carbonate δ13C (Colosimo et al 2005, McCarren et al 2008, Kelly et al 2012), planktic foraminifer δ11B (Penman et al 2014), and planktic foraminifer B/Ca from all sites versus time. Red symbols are surface-dwellers, blue symbols are thermocline dwellers. M.vel = Morozovella velascoensis, A.sol = Acaranina soldadoensis, A.p5c = Acaranina praepentaexamera, Sub = genus Subbotinae. For B/Ca, open symbols are Southern Ocean (Sites 689 and 690), closed symbols are North Pacific (Site 1209). Age models were generated for all sites by correlating the fine fraction or bulk carbonate δ13C to that of Rohl et al (2007), and in the case of Sites 689 and 690 used the tie points of Kelly et al (2012). Error bars on δ11B represent 2 standard errors of repeat measurements. Error bars on B/Ca represent two standard deviations of repeat measurements of an in-house foraminiferal carbonate standard (7%).]
with these new constraints on the magnitude of acidification and the overshoot of the CCD.

**LOSCAR modeling of the PETM onset**

In order to establish a range of scenarios which are consistent with the above constraints on the evolution of the carbon cycle during the PETM, we performed two sets of experiments using LOSCAR (long-term ocean sediment CArbon reservoir), a numerically efficient box model of the exogenic carbon cycle that calculates fluxes of carbon between atmosphere, oceans, and sediments on timescales of decades to millions of years (Zeebe 2012). The Paleogene configuration contains surface, intermediate, and deep-water reservoirs for all modern oceans and a Tethys basin, plus a high-latitude surface reservoir where the majority of deep-water ventilation occurs. Modeled interactions between oceans and sediments include bioturbation and realistic calculations of CaCO₃ dissolution and carbonate compensation, which are crucial for modeling the evolution of the CCD. Loscar also includes a parameterization of the weathering response (which consumes atmospheric CO₂, while delivering alkalinity and dissolved carbon to the oceans) to elevated atmospheric pCO₂. Two sets of experiments were performed, the first aiming to constrain the PETM onset, and then a second to simulate the body and recovery from the event.

To determine which combinations of initial conditions and carbon release scenarios are consistent with the magnitude of initial ocean acidification and constraints on the global CCD shoal, we performed a suite of LOSCAR experiments in which input parameters were varied systematically. These input parameters include the mass, location, and duration of carbon release, pre-event pCO₂, the strength of the weathering feedback, and varied ocean circulation response, and are detailed in table 1. In contrast to previous modeling efforts (Panchuk et al 2008, Zeebe et al 2009, Cui et al 2011, Gutjahr et al 2017), for the present experiment we ignore the δ¹³C of carbon released, relying on carbonate chemistry constraints with the expectation that δ¹³C could be altered for any carbon emission scheme post-hoc to match the CIE. This first suite of experiments only considers the magnitude of the PETM onset; the body and recovery of the event are modeled in later sections. All possible combinations of the above parameters were run (table 1), totaling 18 000 different model permutations. All model runs that featured differences in initial conditions were run to stable equilibrium over 10 million years before initiating the PETM perturbation experiments. This subtly changed some of the initial conditions, such as CCD depth, which affects the initial buffering capacity of the deep-sea sedimentary CaCO₃ reservoir. Global temperature increase (which effects carbonate chemistry equilibrium and solubility constants, among others) was parameterized with a simple (fast) climate sensitivity of 3.0 °C per doubling of pCO₂.

For each PETM onset run, limits of acceptable ΔpH were calculated from the Site 1209 boron isotope data as a function of initial surface pH using the ‘population statistics’ method of Penman et al (2014) (table 2), which calculates ΔpH and associated uncertainty for each assumed initial pH from uncertainty-weighted populations of pre-PETM and peak-PETM Site 1290 δ¹¹B data. δ¹¹B data from other sites globally indicate similar ΔpH (Penman et al 2014,
Paci as well as a switch from the Southern Ocean as the sole source of deep-water formation, to reduced direct injection into the deep Atlantic, and the remainder being released into the atmosphere.

We assume a linear rate of release recognizing that fluxes could have been nonlinear, especially if feedbacks were involved.

Estimates of pre-event (Paleogene) atmospheric pCO2 vary considerably (Pagani et al 2005, Beerling and Royer 2011, Anagnostou et al 2016) and represent a source of uncertainty in PETM scenarios constrained by boron isotope data, owing to the changing sensitivity of δ13B at different initial pH (and thus initial pCO2). 500 ppm can be considered an extreme lower limit, as the absence of large Antarctic ice sheets in the Late Paleocene is thought to be inconsistent with pCO2 levels lower than ~700 ppm (Pollard and DeConto 2005). While it is of much greater importance on longer timescales, the sensitivity of silicate and carbonate weathering flux to elevated pCO2 can have a significant impact on ocean acidification and carbonate preservation even during the shorter timescale (10^5 year) PETM onset. The silicate and carbonate weathering feedbacks are parameterized in LOSCAR as Fw = Fw_eq (p[C02]/p[C02]eq)^x where Fw_eq and [C02]eq are equilibrium weathering flux and atmospheric pCO2 at which volcanic carbon emissions are perfectly balanced by silicate weathering and carbonate burial (Zeebe 2012). Exponents Nw and Nc, are free parameters in the model that set the strength of the silicate and carbonate weathering feedbacks. (default Nw = 0.2, Nc = 0.4). The PETM onset was modeled at default, double (Nw = 0.4, Nc = 0.8), and half (Nw = 0.1, Nc = 0.2) the default weathering exponents.

An interesting feature of the carbonate dissolution response during the PETM is the large apparent difference in initial CCD shoaling between ocean basins. The Atlantic experienced the largest CCO2 shoaling, constrained by a depth transect at Walvis Ridge to >2 km (Zachos et al 2005), in contrast to the Pacific, where depth transects suggest a CCO2 shoal of ~500 m or less (Colosimo et al 2005, Zeebe and Zachos 2007, Zeebe et al 2009, Sluijs et al 2012). In order to reproduce this pattern, Zeebe et al (2009) included a 75% slowdown of circulation as well as a switch from the Southern Ocean as the sole source of deep-water formation, to reduced direct injection into the deep Atlantic, and the remainder being released into the atmosphere.

### Table 1. Initial conditions, feedback parameters, and carbon release scenarios varied in the PETM onset experiment suite.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values</th>
<th># Of permutations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass of carbon input (GtC)⁴</td>
<td>1000–10 000 by increments of 1000</td>
<td>15</td>
</tr>
<tr>
<td>Duration of carbon input (kyr)⁴</td>
<td>1000–10 000 by increments of 1000</td>
<td>10</td>
</tr>
<tr>
<td>Equilibrium (pre-event) pCO2 (ppm)⁵</td>
<td>500, 750, 1000, 1250, 1500</td>
<td>5</td>
</tr>
<tr>
<td>Weathering feedback (% of LOSCAR default)⁵</td>
<td>50%, 100%, 200%</td>
<td>3</td>
</tr>
<tr>
<td>Circulation change of Zeebe et al (2009)⁵</td>
<td>On or off</td>
<td>2</td>
</tr>
<tr>
<td>Deep Atlantic carbon injection⁵</td>
<td>0%, 25%, 50%, 100%</td>
<td>4</td>
</tr>
</tbody>
</table>

| Total | 18 000 runs |

⁴ Past estimates of the mass of carbon released during the PETM onset range from 1200–10 000 gigatons of carbon (GtC) (Dickens et al 1997, Panchuk et al 2008, Zeebe et al 2009, Cai et al 2011). While we do not attempt to use δ13C as a constraint on the PETM onset, we note that this range of carbon mass would, using mass balance calculations of the CIE magnitude, encompass the range of methane clathrate, thermogenic methane, organic carbon, and volcanic input δ13C values (McInerney and Wing 2011).

⁵ The duration of carbon release brackets most estimates of carbon release (Zeebe et al 2014, Turner and Ridgwell 2016, Zeebe et al 2016). Here, we assume a linear rate of release recognizing that fluxes could have been nonlinear, especially if feedbacks were involved.

### Table 2. Constraints on surface Pacific acidification from boron isotopes (Penman et al 2014) used to constrain LOSCAR simulations of the PETM onset. Each set of constraints is tailored to an initial surface Pacific pH in LOSCAR equilibrated to specific pCO2.

<table>
<thead>
<tr>
<th>Initial pCO2 (ppm)</th>
<th>Initial surface pH</th>
<th>Minimum ΔpH</th>
<th>Maximum ΔpH</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>7.83</td>
<td>0.18</td>
<td>0.33</td>
</tr>
<tr>
<td>750</td>
<td>7.74</td>
<td>0.21</td>
<td>0.39</td>
</tr>
<tr>
<td>1000</td>
<td>7.67</td>
<td>0.23</td>
<td>0.46</td>
</tr>
<tr>
<td>1250</td>
<td>7.61</td>
<td>0.24</td>
<td>0.53</td>
</tr>
<tr>
<td>1500</td>
<td>7.56</td>
<td>0.26</td>
<td>0.61</td>
</tr>
</tbody>
</table>

### Results of PETM onset experiment

363 combinations of input parameters (~2% of total runs, appendix A is available online at stacks.iop.org/ERL/13/105008/mmedia) resulted in runs that satisfied δ13B and basin-specific CCO2 shoal constraints on the PETM onset. An example plot of ΔpH for one set of initial conditions is shown in figure 4. For most (but not all) sets of initial conditions, some combinations of carbon mass and duration were found that satisfied the PETM onset constraints. However, in order to satisfy basin-specific CCO2 shoal constraints, all successful PETM onset runs required either deep Atlantic injection, the circulation switch of Zeebe et al (2009), or both. The mass of carbon inputs in successful PETM onset scenarios ranged from 2000 (which, in order to achieve a CIE of −3.5‰, would require a source δ13C lower than −55‰, e.g. methane) to 7000 GtC (which would require a source δ13C ∼ −25‰, e.g. organic carbon), and all timescales of input

Gutjahr et al 2017, Babila et al 2018) during the PETM onset. Runs were deemed consistent if the Pacific surface pH decline during the event onset fell within those run-specific limits, and if the initial CCO2 shoaling (minimum CCO2 subtracted from pre-event CCO2) exceeded 2 km in the Atlantic and was restricted to less than 500 m in the Pacific, in accordance with existing records of the CCO2 (see table 1 caption) (Colosimo et al 2005, Zachos et al 2005, Zeebe and Zachos 2007, Sluijs et al 2012).
considered here (1000–10 000 years) generated conformable PETM onset simulations when combined with specific initial conditions and carbon inputs.

All successful PETM onset simulations featured a decline in seawater carbonate saturation state ($\Omega$), reaching minimum values shortly after the cessation of carbon injection. Minimum low-latitude surface $\Omega$ is shown in figure 5, and ranges from 1.4–2.2 for aragonite, and from 3.1–4.7 for calcite. The lack of surface under-saturated conditions ($\Omega < 1$) in any successful PETM onset simulations is consistent with the general lack of extinctions among pelagic surface calcifiers.
Table 3. LOSCAR parameters for three simulations (low, intermediate, and high carbon release) of the full PETM including body and recovery. Carbon leak refers to carbon released to the atmosphere over 70 kyr following the initial carbon pulse, and carbon removal refers to carbon removed from the atmosphere over the subsequent 50 kyr.

<table>
<thead>
<tr>
<th>Simulation</th>
<th>Equilibrium (initial) pCO₂ (ppm)</th>
<th>Initial carbon pulse (GtC)</th>
<th>Pulse duration (years)</th>
<th>% Deep Atlantic injection</th>
<th>Circulation switch?</th>
<th>Weathering feedback strength</th>
<th>Carbon leak (GtC)</th>
<th>Carbon removal (GtC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Small release</td>
<td>500</td>
<td>2000</td>
<td>1000</td>
<td>50</td>
<td>Yes</td>
<td>100%</td>
<td>6100</td>
<td>4500</td>
</tr>
<tr>
<td>Medium release</td>
<td>750</td>
<td>3300</td>
<td>5000</td>
<td>0</td>
<td>Yes</td>
<td>75%</td>
<td>3800</td>
<td>3800</td>
</tr>
<tr>
<td>Large release</td>
<td>1500</td>
<td>7000</td>
<td>10 000</td>
<td>25</td>
<td>Yes</td>
<td>200%</td>
<td>14 700</td>
<td>4200</td>
</tr>
</tbody>
</table>
This suggests that at least in the case of the PETM, marine calcifiers were able to cope with reductions (over thousands of years) in $\Omega$ in the above range through geographic migration, adaptation, and evolution. The magnitude and rate of $\Omega$ reduction in successful PETM onset simulations, however, stands in stark contrast to future simulations of anthropogenic ocean acidification, which is currently occurring much faster than the PETM onset and is projected to reach a more severe $\Omega$ minimum in coming centuries (Caldeira and Wicket 2003, Cui et al 2011, Zeebe and Zachos 2013).

Comparing the range of $pCO_2$ increase (maximum $pCO_2$ versus initial $pCO_2$) in successful scenarios of the PETM onset with existing estimates of the global temperature increase during the PETM onset (Dunkley-Jones et al 2013) can be used to constrain climate sensitivity (expressed herein as the temperature increase in response to a doubling of $pCO_2$, or S2x) on 103-year timescales during the PETM onset. Due to the wide range (500–1500 ppm) in initial atmospheric $pCO_2$ in successful runs, the absolute $pCO_2$ increase is highly variable (from a minimum increase of $\sim$350 ppm in runs started from an initial $pCO_2$ of 500 ppm to a maximum increase of $\sim$1700 ppm in runs started at 1500 ppm). However, the $pCO_2$ increase expressed as the number of doublings of initial $pCO_2$ is much more similar among successful runs, limited to the range of 0.8–1.5 doublings of $pCO_2$. Combined with 4°C–5°C of global temperature increase during the PETM (e.g. Dunkley-Jones et al 2013), this range in $pCO_2$ increase implies 103-year climate sensitivities of 2.7°C–6.2°C per doubling of $pCO_2$. This range overlaps with the high end of climate sensitivities considered by the IPCC (Parry et al 2007) for anthropogenic warming (1.5°C–4.5°C per doubling of $pCO_2$).

**Full PETM scenarios**

The above suite of experiments only considers carbonate chemistry constraints on the onset of the PETM (the first 1000–10 000 years). However, the event lasted at least an additional 100 000 years (Rohl et al 2007, Murphy et al 2010) and observations of carbonate chemistry during the remainder of the CIE and the recovery interval can be used to constrain an emissions trajectory and recovery for a full PETM scenario using LOSCAR. Three sets of observations argue for a sustained ‘leak’ of carbon after the initial large carbon release: the prolonged plateau of minimum $\delta^{13}C$ (the ‘body’ of the CIE) in most records (Zeebe et al 2009), the sustained acidifications in records of planktic foraminifer $\delta^{11}B$ and B/Ca globally (Babilia et al 2018), both of which would otherwise begin to recover immediately following emissions cessation, and the delayed CCD overshoot at Site U1403 (Penman et al 2016), which would occur shortly (within a few tens of thousands of years) after the cessation of carbon emissions in the absence of a sustained leak.

For modeling the body and recovery of the PETM, LOSCAR was modified from the standard Paleogene setup (Zeebe et al 2009, Zeebe 2012) with the seafloor bathymetry and sediments more finely subdivided to 100 m water depth bins (from the default 500 m resolution) so that CCD evolution could be modeled at a finer scale (see methods of Henehan et al 2016). Three scenarios of the PETM onset were selected representing small, intermediate, and large carbon releases (table 3) that all satisfied the carbonate chemistry constraints on the onset of the event. Following this initial carbon release, we introduced a sustained ‘leak’ of carbon lasting 70 kyr (the approximate duration of the CIE body, Rohl et al 2007). The mass of the leak was iteratively adjusted in order to achieve a plateau of near-constant, decreased pH in accordance with the shape of $\delta^{11}B$ and B/Ca records.

A key feature of the PETM that reflects the process of carbon sequestration is the rate of the recovery. After the body of the CIE, $\delta^{13}C$ recovers within approximately 50 kyr, which is thought to be too rapid to be explained by silicate weathering alone (Bowen and Zachos 2010). The $\delta^{11}B$ and B/Ca records of ocean acidification (figure 2) also recover within a similar time frame, far more quickly than some carbon cycle models of the PETM (e.g. Zeebe et al 2009) which rely on silicate weathering alone as the long-term carbon sequestration process. These two corroborating lines of evidence suggest that some process for removing $^{13}C$-depleted carbon (i.e. organic) from the exogenic carbon cycle (e.g. Bowen and Zachos 2010, Bowen 2013) must have operated during the PETM recovery. In order to replicate the rapidity of the pH (and $\delta^{13}C$) recovery in our full PETM scenarios, carbon removal from the atmosphere was introduced to those same three simulations of the PETM onset and body. The length of carbon removal was set as the duration of the $\delta^{13}C$ recovery in Rohl et al (2007) (an additional 50 000 years after the end of the body of the CIE) and the $\delta^{13}C$ of carbon removed was set at −25‰, consistent with organic carbon burial. The amount of carbon removed was iteratively adjusted to obtain a pH recovery consistent with the Site 1209 $\delta^{13}B$ record (Penman et al 2014).

Sustaining acidified conditions for 70 kyr requires a continuous input (leak) of carbon in all full PETM scenarios, but the total mass of leaked carbon required varies considerably depending on the mass of the initial C release during the onset of the event. In the case of the low initial C release scenario (figure 6, a spike of 2000 GtC in 1000 years), an additional 6100 GtC is needed to sustain surface acidification in the full PETM scenario, an amount that far surpasses the initial release. This is a consequence of the brief input duration (1000 years) which is shorter than a full ocean mixing time. The small carbon injection...
(2000 GtC) is enough to depress surface ocean pH in accordance with $\delta^{11}$B estimates at $t = 1000$ years, however on longer timescales this carbon is mixed into the deep ocean, so large additional emissions are needed to keep the surface acidified. A large, sustained leak would seem to be required of any PETM scenario that invoked a carbon release shorter than the ocean mixing time. Invoking 6100 GtC as a leak following a 2000 GtC pulse is problematic: 6100 GtC is larger than the entire modern terrestrial biosphere including soil.
carbon (~2700 GtC, Wang et al. 2010). Furthermore, the carbon isotopic composition of the larger leak would have to be significantly more $^{13}$C-enriched than the initial release in order to reproduce the shape of the CIE, which features a rapid onset (a result of the carbon pulse) followed by ~70 kyr minimum. This would require an initial pulse of highly $^{13}$C-depleted carbon (e.g. methane), followed by a more $^{13}$C-heavy leak. While this may be supplied by repeated volcanic events (Frieling et al. 2016), it is difficult to imagine volcanism acting as a feedback or response to an initial trigger, so invoking that sequence of C release would rely on very fortuitous timing.

At the other extreme, in the case of the high C release scenario (figure 7, 7000 GtC over 10,000 years), an additional 14,700 GtC are required over 60,000 years to sustain acidification in the full PETM scenario. The main reason for this very large leak is that this simulation (and indeed, all PETM onset simulations that can accommodate such a large initial release without violating CCD constrains) is run with double LOSCAR’s default weathering feedback strength, which works to expedite pH recovery relative to scenarios run at default weathering strength. Hence, more carbon is needed to keep pH depressed (as constrained by the boron records) despite a greater weathering flux. A side effect of this massive carbon leak combined with rapid weathering is the complete decoupling of pH and $\Omega$, which recovers far more quickly and results in a CCD overshoot that occurs too soon (in conflict with the overshoot documented at Site 1403) and is too large, covering the entire seafloor to a depth of 6.5 km, the deepest sediment level in LOSCAR. This stands in conflict with records of the PETM from the deep sea, for example Site 1211 which remains carbonate barren (hence below the CCD) throughout the event (Colosimo et al. 2005).

In the intermediate C release scenario (figure 8, 3300 GtC over 5000 years, which is longer than the ocean mixing time), a leak of an additional 3800 GtC over 65,000 years is required to sustain acidification. The resulting CCD curves fall within constraints throughout the event, and a CCD overshoot in the Atlantic occurs ~75,000 years after the CIE onset, in line with the record at Site 1403.

After the PETM body, all three of the pulse + leak (without C removal) scenarios feature a recovery in surface pH that is far more gradual and prolonged than indicated by the $\delta^{13}$B-based pH record. In order to match the rapidity of the pH recovery, removal of organic carbon ($^\delta^{13}$C = ~25%) from the atmosphere over ~50 kyr was required. In the case of the low C release scenario (figure 6), 4500 GtC were removed, while 3800 and 4200 GtC were removed in the intermediate (figure 8) and high (figure 7) release scenarios, respectively. In all cases, removal of carbon acts to temporarily deepen the CCD, aiding the CCD overshoot during the PETM recovery.

The intermediate carbon release full PETM scenario most closely conforms to all constraints on carbonate chemistry over the PETM. In order to generate a CIE of ~3.5‰, the intermediate carbon release scenario requires a carbon input of ~58‰, which could be interpreted as a mixture of organic carbon and methane. Interestingly, in this scenario (and all conformable scenarios that feature sustained acidification) at least half the total carbon release occurs after the initial onset, suggesting a significant slow positive feedback between warming and carbon release. Both methane (Dickens et al. 1995, Zeebe 2013) and terrestrial organic carbon (Bowen 2013) have been proposed as potential long-term feedbacks capable of releasing carbon at similar rates to the leak in the intermediate release scenario (~0.1 GtC yr$^{-1}$) over tens of thousands of years. Given that much of the carbon released during the PETM was the result of a gradual flux, it is possible that the flux was generated by volcanism (Frieling et al. 2016), or was part of a positive feedback (s) to a modest initial warming, either the result of some small trigger (such as volcanism, Svensen et al. 2004) or simply the crossing of a temperature threshold during the warming trend across the Late Paleocene—Early Eocene (Lunt et al. 2011). Identifying the exact source of these feedbacks will prove a challenging but necessary endeavor as they may be important components of the Earth System on 10$^3$–10$^5$ year time-scales following current anthropogenic carbon release.

Revised criteria for the PETM onset

The inconsistencies of the low and high C release full PETM scenarios with the sustained acidification and rapid recovery of the PETM can be used to further constrain the range of realistic scenarios in the PETM onset experiment. We can now exclude runs that feature greater than default weathering strength (for example the high C release full PETM scenario) on the basis of the rapidity of CCD recovery/overshoot that conflicts with constraints including the timing of the CCD overshoot at Site U1403. Additionally, we exclude runs starting from an initial pCO$_2$ of 500 ppm, which conflicts with the lack of Antarctic ice sheets during the Paleogene and the theoretical ~700 ppm threshold for their initiation (DeConto and Pollard 2003). Once those runs are excluded, only 43 simulations of the PETM onset are considered successful (referred to as revised PETM onset), and span a much narrower range of input and output parameters (figure 5). Only runs starting from an initial pCO$_2$ of 750 or 1000 ppm are consistent with the revised requirements, and require an initial carbon release (not including ‘leak’ carbon) of 3000 or 4000 GtC, although the input duration of the initial C release during the PETM onset still spans 2000–10,000 years. All of the successful revised PETM onset runs require
the ocean circulation switch of Zeebe et al 2009, with variable deep Atlantic injection (from 0%–100%). Minimum surface Pacific Ω in the successful revised PETM onset runs ranges from 1.6–1.9 for aragonite and from 3.5–4.1 for calcite, far less severe than predicted for future anthropogenic acidification (figure 9) and occurring far more slowly. The pCO$_2$ increase in successful revised PETM onset runs ranges from 0.8–1.1 doublings of pCO$_2$, which, when combined with estimates of 4°C–5°C of global temperature increase during the PETM (Dunkley-Jones et al 2013), is consistent with a 10$^3$ year climate sensitivity of 3.6°C–6.2°C per doubling of pCO$_2$ during the PETM onset, which overlaps only with the higher end of climate sensitivities considered by the IPCC (Parry et al 2007) (1.5°C–4.5°C per doubling of pCO$_2$).

While the intermediate C release scenario is consistent with all available constraints on carbonate chemistry over the PETM, the assumptions made about pre-PETM initial conditions in the intermediate release scenario represent a source of uncertainty. Further constraining several free parameters in the model would help to improve confidence in a consistent PETM scenario. Initial (Paleocene) pCO$_2$ is not precisely known (Beerling and Royer 2011), and the wide range of possible values introduces considerable uncertainty on the magnitude of ocean acidification used to constrain PETM scenarios. Progress is being made (Anagnostou et al 2016), but additional, concordant estimates of paleo-CO$_2$ for the Late Paleocene would greatly improve quantitative interpretation of δ$^{13}$B records of the event and improve confidence in PETM simulations. We use the age model of Rohl et al (2007) for full PETM scenarios, however, alternative age models (e.g. Murphy et al 2010) are available that suggest a longer duration of the CIE body, and a faster recovery. Full PETM scenarios conforming to such an age model would require additional carbon released during the ‘leak’ and more depleted carbon removed at a faster rate during the recovery. The strength of the weathering feedback is also an area of uncertainty that greatly affects the range of possible PETM simulations. The simple parameterization of weathering in LOSCAR as a function of pCO$_2$ is unlikely to completely represent the complex interaction between pCO$_2$, continental temperatures, global hydrology, and soil chemistry that determine the rates of silicate and carbonate weathering. Further constraining PETM scenarios requires a more complete mechanistic
understanding of the global response of chemical weathering rates to $p\text{CO}_2$/temperature increase and/or additional observations to quantify silicate weathering change over the PETM (e.g. Ravizza et al 2001, Penman 2016).

**Comparison to anthropogenic carbon emissions**

New constraints on the evolution of the carbon cycle during the PETM have quantitatively refined reconstructions of this ancient global warming event, allowing a re-evaluation of its utility as an analog for contemporary anthropogenic emissions. The onset of the PETM involved the release of a mass of carbon similar to that projected for ‘business as usual’ anthropogenic fossil fuel emissions (Parry et al 2007), but distributed over a duration an order of magnitude longer (figure 9). This slower rate allowed for $\text{CO}_2$ to be mixed into the deep ocean as it was released, instead of remaining concentrated in the atmosphere and surface ocean, as is anticipated to occur on the short term in response to comparatively more rapid and short-lived anthropogenic emissions. This spared Earth’s surface from extremely high temperatures resulting from a short-lived peak in $p\text{CO}_2$, and spared the surface ocean from a rapid and severe decline in $pH$ and $\Omega$ on similarly short timescales (Zeebe and Zachos 2013). Intriguingly, the recovery of the PETM was delayed for tens of thousands of years by the sustained release of additional carbon. It is as yet unclear if this leak of carbon was supplied by a positive feedback to initial warming, such as oxidizing terrestrial organic carbon (Bowen 2013) or destabilizing seafloor methane hydrates (Dickens et al 1995, Zeebe 2013) that might be important players in the carbon cycle’s response to anthropogenic emissions, or from an external carbon source unique to the PETM, such as sustained volcanism (Frieling et al 2016). Furthermore, when the PETM recovery did begin, it proceeded far more quickly than expected as a result of the silicate weathering feedback alone. Identifying the causes and effects of the carbon fluxes operating during the body and recovery of the PETM may be key to anticipating the future of the carbon cycle over the next tens to hundreds of thousands of years.

![Figure 9. Comparison of our optimal PETM simulation with the LOSCAR anthropogenic simulation of Zeebe and Zachos (2013) featuring the release of 5000 GtC over 500 years.](image-url)
Acknowledgments

We thank Richard Zeebe for supplying code and assistance with the LOSCAR model. This work was supported by the Richard Foster Flint postdoctoral fellowship to DEP, and by NSF grant OCE-1220615 to JCZ.

ORCID iDs

Donald E Penman @ https://orcid.org/0000-0003-4191-0505

References

Alley R B 2016 A heated mirror for future climate Science 352 151–2
Babila T, Penman D, Hönisch B, Kelly D, Bralower T, Rosenthal Y and Zachos J 2018 Capturing the global signature of surface ocean acidiﬁcation during the Palaeocene-Eocene Thermal Maximum Phil. Trans. A 376 20170072
Babila T L, Rosenthal Y, Wright J D and Miller K G 2016 A continental shelf perspective of ocean acidiﬁcation and temperature evolution during the Palaeocene-Eocene Thermal Maximum Geology 44 275–8
Beierling D and Boyer D L 2011 Convergent Cenozoic CO2 history Nat. Geosci. 4 118–20
Bice K L and Marotzke J 2002 Could changing ocean circulation have destabilized methane hydrate at the Palaeocene-Eocene boundary?—art. no. 1018 Paleoceanography 17 1018
Bowen G J 2013 Up in smoke: a role for organic carbon feedbacks in termination of the Palaeocene-Eocene thermal maximum Phil. Trans. R. Soc. B 371 20150510
Lunt D J, Ridgwell A, Sliuija A, Zachos J, Hunter S and Haywood A 2011 A model for orbital pacing of methane hydrate destabilization during the Palaeogene Nat. Geosci. 4 775–8
Pagani M, Zachos J C, Freeman K H, Tipple B H and Bohaty S 2005 Marked decline in atmospheric carbon-dioxide concentrations during the Paleogene Science 309 600–3
Henehan M J, Hul PM, Penman D E, Rae J W and Schmidt D N 2016 Biogeochemical signiﬁcance of pelagic ecosystem function: an end-Cretaceous case study Phil. Trans. R. Soc. B 371 20150510
Lunt D J, Ridgwell A, Sliuija A, Zachos J, Hunter S and Haywood A 2011 A model for orbital pacing of methane hydrate destabilization during the Palaeogene Nat. Geosci. 4 775–8
Pagani M, Zachos J C, Freeman K H, Tipple B H and Bohaty S 2005 Marked decline in atmospheric carbon-dioxide concentrations during the Paleogene Science 309 600–3
Penman D E 2016 Silicate weathering and North Atlantic silica burial during the Paleocene–Eocene Thermal Maximum Geology 44 731–4
Penman D E, Honisch B, Zeebe R E, Thomas E and Zachos J C 2014 Rapid and sustained surface ocean acidification during the Paleocene–Eocene Thermal Maximum Paleoceanography 29 357–69
Pollard D and DeConto R M 2005 Hysteresis in Cenozoic Antarctic ice-sheet variations Glob. Planet. Change 45 9–21
Ridgwell A and Schmidt D N 2010 Past constraints on the vulnerability of marine calcifiers to massive carbon dioxide release Nat. Geosci. 3 196–200
Slujs A, Zachos J C and Zeebe R E 2012 Constraints on hyperthermals Nat. Geosci. 5 231
Zeebe R 2012 LOSCAR: long-term ocean–atmosphere–sediment carbon cycle reservoir model v2. 0.4 Geosci. Model Dev. 5 139–86
Zeebe R E 2013 What caused the long duration of the Paleocene–Eocene Thermal Maximum? Paleoceanography 28 440–52
Zeebe R E, Ridgwell A and Zachos J C 2016 Anthropogenic carbon release rate unprecedented during the past 66 million years Nat. Geosci. 9 325–9
Zeebe R E and Zachos J C 2007 Reversed deep-sea carbonate ion basin gradient during Paleocene–Eocene Thermal Maximum Paleoceanography and Paleoclimatology 22
Zeebe R E and Zachos J C 2013 Long-term legacy of massive carbon input to the Earth system: anthropocene versus Eocene Phil. Trans. R. Soc. A 371 20120006