Research

CrossMark
click for updates

Author for correspondence:
Richard E. Zeebe
e-mail: zeebe@soest.hawaii.edu

Long-term legacy of massive carbon input to the Earth system: Anthropocene versus Eocene

Richard E. Zeebe[1] and James C. Zachos[2]

[1]Department of Oceanography, School of Ocean and Earth Science and Technology, University of Hawaii at Manoa, Honolulu, HI, USA
[2]Earth and Planetary Sciences, University of California, Santa Cruz, CA, USA

Over the next few centuries, with unabated emissions of anthropogenic carbon dioxide (CO_2), a total of 5000 Pg C may enter the atmosphere, causing CO_2 concentrations to rise to approximately 2000 ppmv, global temperature to warm by more than 8°C and surface ocean pH to decline by approximately 0.7 units. A carbon release of this magnitude is unprecedented during the past 56 million years—and the outcome accordingly difficult to predict. In this regard, the geological record may provide foresight to how the Earth system will respond in the future. Here, we discuss the long-term legacy of massive carbon release into the Earth's surface reservoirs, comparing the Anthropocene with a past analogue, the Palaeocene–Eocene Thermal Maximum (PETM, approx. 56 Ma). We examine the natural processes and time scales of CO_2 neutralization that determine the atmospheric lifetime of CO_2 in response to carbon release. We compare the duration of carbon release during the Anthropocene versus PETM and the ensuing effects on ocean acidification and marine calcifying organisms. We also discuss the conundrum that the observed duration of the PETM appears to be much longer than predicted by models that use first-order assumptions. Finally, we comment on past and future mass extinctions and recovery times of biotic diversity.

1. Introduction

Since the beginning of the industrial era, anthropogenic emissions of carbon dioxide (CO_2) from fossil fuel

burning and, to a lesser extent, land-use change and cement manufacturing have increased the concentration of CO_2 in the Earth's atmosphere by approximately 40%. The combined fossil fuel and cement emissions reached a record high in 2010 of $9.1 \, Pg \, C \, yr^{-1}$ ($1 \, Pg = 10^{15} \, g$) [1], higher than predicted 20 years ago under business-as-usual scenarios for the year 2010 ($8.7 \, Pg \, C \, yr^{-1}$, IS92a scenario) [2]. The rapidly rising levels of CO_2 in the atmosphere are altering the radiative forcing of the Earth's climate, which, until recently, has been the sole focus of the scientific and public discussion. A second impact of anthropogenic CO_2 emissions is ocean acidification, which refers to the ongoing decline in ocean pH and the reduction in the ocean's carbonate mineral saturation state, with possible negative consequences for marine life [3–5]. Other geochemical and physical consequences of an increasingly acidic ocean include effects on metal speciation, reduced NH_3/NH_4^+ ratios (probably affecting ammonia oxidation rates), the marine source of atmospherically active trace gases and alteration of underwater sound absorption [6–9].

Projections of future CO_2 emissions and attendant modifications of climate and ocean chemistry have typically focused on the century time scale, most notably until the year 2100 [10]. However, from a geological perspective, the longer term consequences of the carbon released by human activities may be considered equally, if not more, important. For instance, on millennial time scales, total emissions of $5000 \, Pg \, C$ are projected to increase the Earth's global surface temperature by more than $8°C$ and drop surface ocean pH by approximately 0.7 units (figure 1). A carbon release of this rate and magnitude represents a massive perturbation to the Earth system, most probably unprecedented during the past 56 million years [12–14]. The climatic and geochemical recovery will take tens to hundreds of thousands of years well after emissions have ceased [15]. Biotic recovery in terms of diversity and ecosystem functioning may take millions of years [16]. However, owing to the complexity of the Earth system, particularly involving the contribution of physical and biogeochemical feedbacks, the precise details of the future response is difficult to predict. In this regard, the geological record may provide foresight to what the future will hold for the Earth's climate, ocean chemistry and ecosystems.

The closest analogue for a massive carbon release in the past is the Palaeocene–Eocene Thermal Maximum (PETM, approx. 56 Ma). This event is characterized by a transient global warming of $6°C$, with a relatively rapid onset and gradual recovery over $150 \, kyr$ [12,17–20]. The onset was accompanied by intense dissolution of carbonate sediments throughout the deep sea as well as an anomalous excursion in the ratio $^{13}C/^{12}C$ of the surficial carbon reservoir, i.e. ocean, atmosphere and biosphere [17,21]—phenomena which could have been generated only by a rapid and massive release of carbon, causing ocean acidification. Although the surface ocean appears to have remained oversaturated, communities of marine calcifiers, primarily coralgals, phyto- and zooplankton and benthic foraminifera, experienced changes in both diversity and abundances [22–28]. While many species ultimately survived, the community perturbations persisted for tens of thousands of years, recovering only as carbon levels abated and the planet cooled. Numerical models demonstrate that the scale of seafloor carbonate dissolution and $^{13}C/^{12}C$ excursion can be simulated only with the release of thousands of Pg C, and most of it in less than $5–10 \, kyr$ [29–31]. These simulations also show that the long tail of the atmospheric lifetime of this carbon should have exceeded $150 \, kyr$, a result that is consistent with the actual duration of the PETM and ocean acidification. However, using first-order assumptions, the models predict that the main phase of high pCO_2 and intense warming should have faded after a few ten thousand years (first-order assumptions signify a simple, single carbon input pulse over a few thousand years). In order to explain the prolonged warming over a time scale of hundred thousand years, additional assumptions are necessary such as continuous, prolonged carbon input over tens of thousands of years [32].

In this paper, we discuss the long-term legacy of massive carbon input to the Earth system, mainly focusing on the Anthropocene and the Early Eocene, and implications for the future. Our aim is not to constrain the PETM carbon input mass, which is discussed elsewhere [29–31,33–35], but to study the long-term legacy of massive carbon input. To this end, we
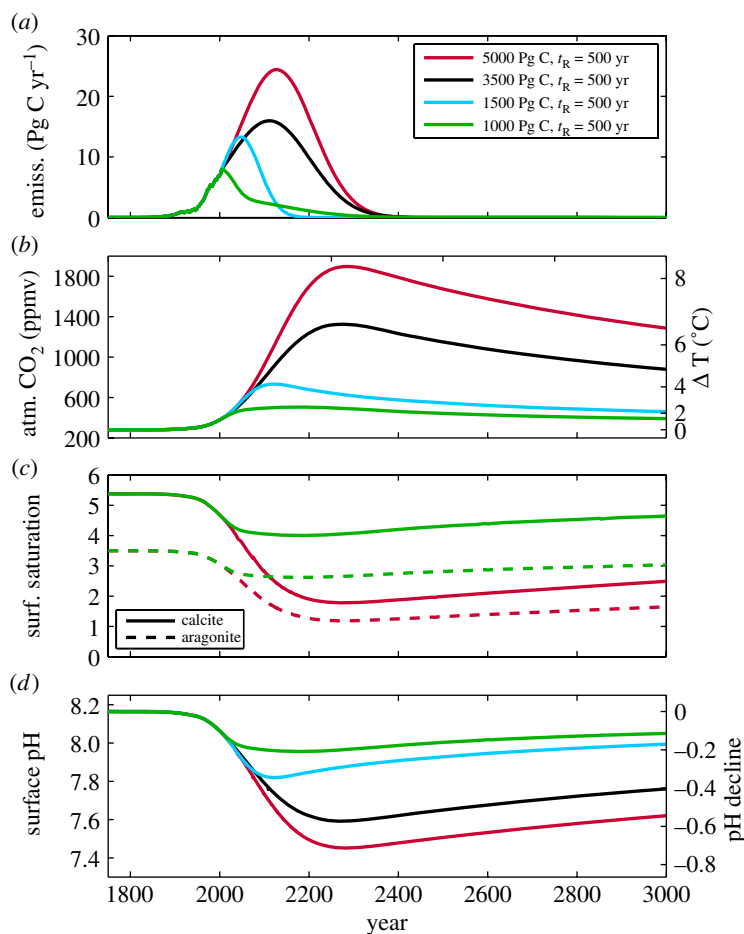
Figure 1. Consequences of anthropogenic carbon release for various CO_2 emission scenarios [4]; t_R = release time. Simulations were performed with the LOSCAR model [11]. (Online version in colour.)

focus on a limited number of carbon input scenarios [31] and employ the LOSCAR (Long-term Ocean–atmosphere–Sediment CArbon cycle Reservoir) model as a tool to illustrate various carbon cycle processes. The LOSCAR model is described in detail in the study of Zeebe [11].

2. Massive carbon release

The known total fossil fuel reserves (currently available for combustion) have been estimated at several thousands of Pg C. These figures do not include potential contributions from other fossil resources such as methane hydrates. For total carbon emissions of 3500 and 5000 Pg C over 500 years, the Earth's surface temperature would rise by more than 6°C and 8°C, respectively, during the next few centuries (figure 1). This estimate assumes a climate sensitivity of 3°C per doubling of CO_2, which includes only fast feedback processes [10]. However, over millennial time scales, additional, slower feedbacks could become active, which would exacerbate the warming [36–38]. The projected consequences for ocean chemistry are equally severe, with a decline in ocean pH by up to approximately 0.7 units (from approx. 8.2 to 7.5, a fivefold increase in acidity or H^+ concentration) and a two- to threefold reduction in the carbonate mineral saturation state (figure 1) [4]. To place this in a geological perspective, surface ocean pH has probably not been below approximately 8.1 during the past 2 Myr [39]. A range of simulations show that, in order to avoid large changes in the Earth's climate and ocean chemistry, drastic and immediate reductions

in CO_2 emissions would be necessary (figure 1). For instance, in order to limit the total carbon input to 1000 Pg C and stretch emissions over 500 years, global carbon emissions would need to be cut in half over the next 30 years, starting tomorrow.

Projections of future changes in ocean carbonate chemistry are relatively robust and largely model-independent on a time scale of a few centuries, mainly because the chemistry of CO_2 in seawater is well known and because changes in surface ocean carbonate chemistry closely track changes in atmospheric CO_2 [15,40,41]. However, the climatic and biotic response is far more difficult to forecast because of the complexity of the climate system, ecosystem dynamics and biogeochemical feedbacks [42]. One way to improve our predictions of the Earth-system response to massive and rapid carbon release is to look to the past. The PETM as an extreme and transient event that caused widespread environmental change is probably the best analogue for a massive carbon release in the geological past, for which a sufficient number of widely distributed sediment records are available [18–20,43]. One critical element for a comparison between the Anthropocene and the PETM is the time scale of carbon input. While it is clear that the carbon input during the PETM was rapid on geological time scales (a few thousand years), establishing the approximate rate of emissions has proved difficult using conventional stratigraphic methods [33,34].

Given the limitations of stratigraphy, numerical tools are required to provide additional constraints on the time scale of the PETM carbon release, for example by using carbon cycle models that include a sediment component [11,31]. Simulations of the carbon release with a single input of 3000 Pg C (source $\delta^{13}C = -50‰$) indicate that the release time was probably much shorter than 20 kyr, otherwise the shoaling of the calcite compensation depth (CCD) in the deep Atlantic would be too muted (figure 2). Observations across the Palaeocene–Eocene boundary (PEB) have shown that the CCD shoaled substantially in the Atlantic and by at least 2.0 km in the South Atlantic [13,44–46]. Hence the simulations suggest that the release time was approximately 6 kyr or less for an initial input of 3000 Pg C (figure 2). Note that the simulations assume a 40% carbon release directly into the deep Atlantic from the possible dissociation of methane hydrates [47]. If the carbon was injected entirely into the model's atmosphere, the Atlantic CCD shoaling would be less, calling for an even shorter release time [48]. Note also that the CCD shoaling in the Pacific was less pronounced than in the Atlantic [31,34,49]. At input rates over periods approaching approximately 1 kyr, the model predicts a large but short-lived total carbon isotope excursion (CIE) in the surface ocean of up to −6‰. However, this anomaly quickly returns to the long-lived CIE, which slowly decays from a peak value of about −3.5‰ at approximately 3 kyr after the PEB (figure 2). The reason for the short-lived $\delta^{13}C$ anomaly is that, on time scales shorter than approximately 1 kyr, the source carbon has not yet been mixed throughout the entire deep ocean, which leaves the atmosphere and surface ocean disproportionately depleted in ^{13}C (relative to the total exogenic carbon pool). So far, such an anomaly has not been found in sediment records [50], which would argue against a release time shorter than approximately 1 kyr. However, at this stage, it is not clear whether it is even possible to observe such an anomaly given the fidelity of even the highest resolution marine/terrestrial sediment records.

All deep-sea carbonate PEB sections are condensed to varying degrees as a consequence of the acidification/carbonate dissolution pulse. A variety of conventional and unconventional strategies have been applied to estimate the duration of the condensed intervals in pelagic sections including orbital stratigraphy and relative abundances of extraterrestrial ^3He, a constant flux proxy (figure 3) [51–53]. While the overall duration of the excursion and recovery have been well constrained, both approaches lack the precision to unambiguously constrain the duration of the onset in these condensed sequences to ±10 kyr. Alternatively, carbon isotope data for populations of individual shells from closely spaced samples across the boundary throughout the ocean yield clear bimodal distributions of shells recording pre-excursion and excursion carbon isotope values, but with no transitional values, suggestive of an abrupt shift in surface water $\delta^{13}C$ [22,54], though this also could be an artefact of dissolution. Expanded shallow marine, siliciclastic sections, on the other hand, lack the needed stratigraphic control to constrain rapid changes in sediment accumulation, and thus yield conflicting results for the initial onset of the CIE, with estimates ranging from just a few thousand years to as long as 20 kyr [19,33,50,55]. In sum, the
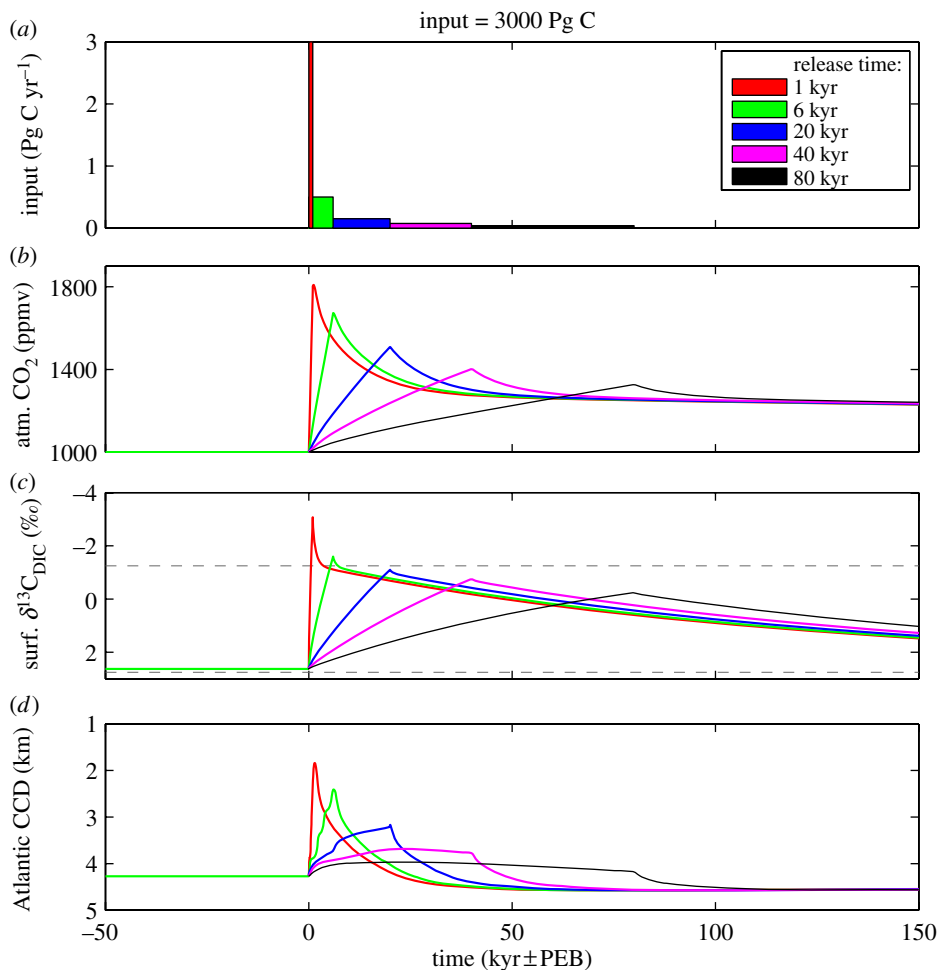
Figure 2. Effect of releasing 3000 Pg C over various time intervals during the PETM [11,31]. The source carbon has a $\delta^{13}C$ value of $-50‰$; 40% of the carbon was injected into the deep Atlantic. Note that the Pacific CCD shoaling was much less pronounced than in the Atlantic [31]. (Online version in colour.)

rate of carbon release is still insufficiently constrained to eliminate the possibility of a relatively fast release, of the order of a few thousand years, or for a more gradual release, interrupted by one or more rapid pulses.

Carbon cycle models that include a weathering feedback predict an 'overshoot' of the CCD in the aftermath of the carbon release. That is, a few ten thousand years after the carbon input has stopped, the position of the CCD is deeper than its position before the event and remains suppressed on a time scale of 100 kyr or more (figure 2d). Note that, while figure 2d shows examples for the Atlantic CCD, the model-predicted CCD overshoot is global [11,31]. The cause for the CCD overshoot can be traced back to the weathering feedback. Immediately after the carbon input has ceased, atmospheric pCO_2 is still elevated over the initial pCO_2 (figure 2b), which causes enhanced weathering of carbonate and silicate rocks on the continents. The enhanced weathering produces an influx of calcium and carbonate ions to the ocean that exceeds the removal of these ions as $CaCO_3$ because the burial is reduced at that point owing to the diminished carbonate mineral saturation state of the ocean. As a result, the excess weathering flux subsequently begins to raise the ocean's saturation state and deepens the CCD until a quasi-steady state of riverine flux and burial has been established. The quasi-steady state on a
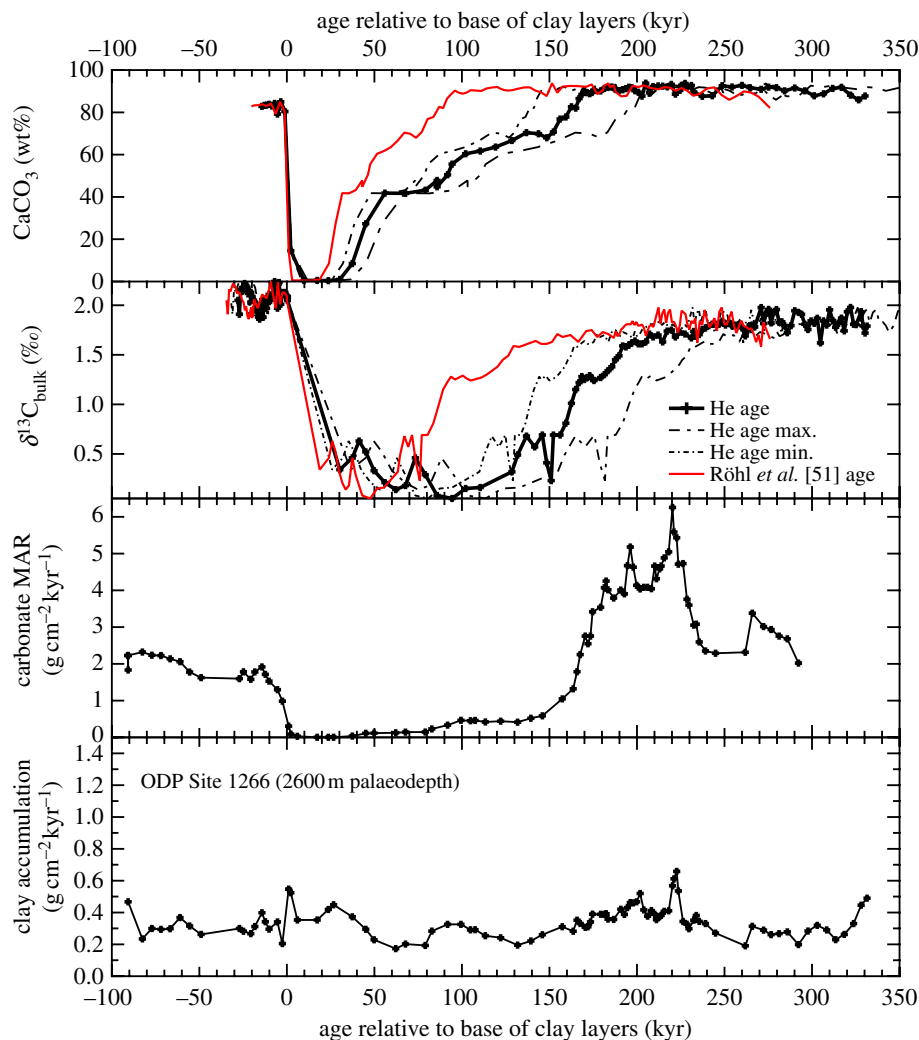
Figure 3. Two estimates of the duration of the CIE and CaCO$_3$ dissolution event at Ocean Drilling Program (ODP) Site 1266, Walvis Ridge, in the South Atlantic [13]. One estimate is based on orbital cycle stratigraphy [51], the other on extraterrestrial ^{3}He$_{ET}$ concentrations [52]. The latter assigns a greater duration to the dissolution interval and a shorter duration to the recovery interval. The lower two panels show the changes in carbonate and non-soluble fractions as measured by Murphy *et al.* [52] using just the ^{3}He$_{ET}$ age constraints. We note that an undetermined portion of the clay layer (0% CaCO$_3$) represents Upper Palaeocene material deposited prior to the PETM/CIE and thus adds (10–30 kyr) to the total duration of the event. (Online version in colour.)

hundred thousand year time scale must be maintained at a deeper CCD than initially (because of enhanced influx and burial) until atmospheric pCO$_2$ and weathering fluxes return to their initial steady-state values on a million year time scale. This process slowly removes the excess carbon from the system via silicate weathering.

In general, the model-predicted oversaturation and CCD overshoot are in agreement with observations [13,49,52,53,56,57]. The observations include an unusual transient pulse (20–40 kyr) in carbonate accumulation rates during the recovery phase, roughly 100 kyr after peak acidification (figure 3) [52,53] as well as enhanced preservation of plankton shells (figure 4; phase II) [57]. These observations, recorded in all ocean basins and at all depths, indicate that over much of the ocean the entire water column was highly oversaturated. The highly oversaturated surface waters might have contributed to blooms of coccolithophores dominated by just a few species
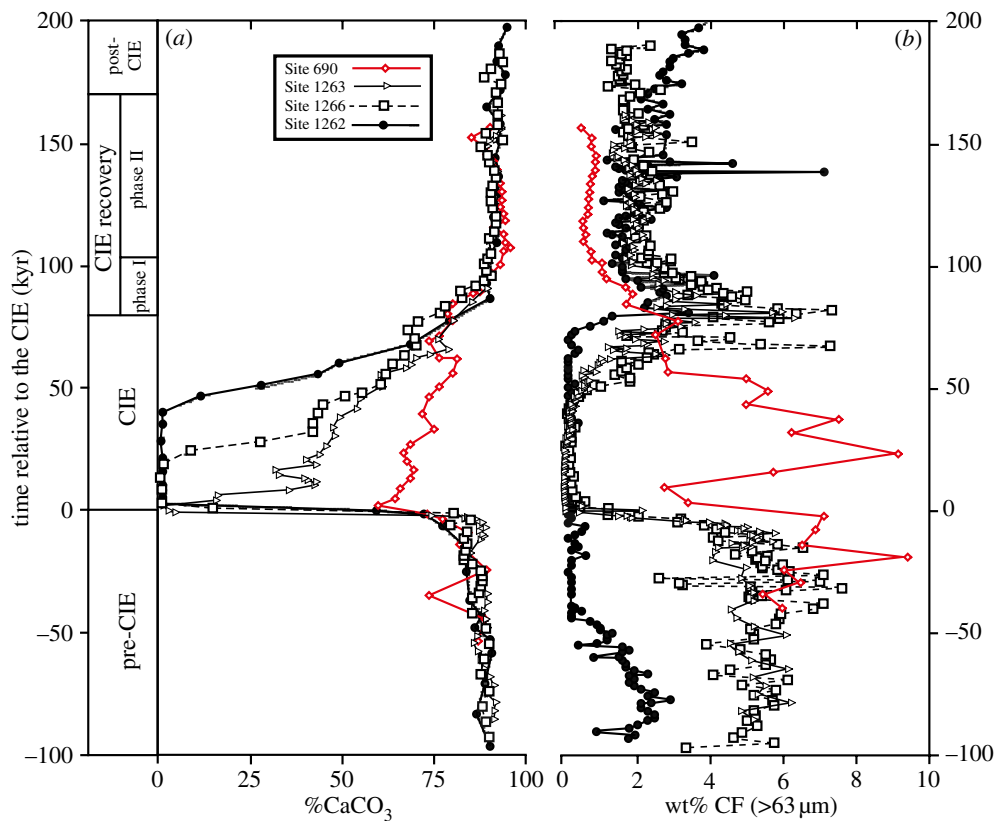
Figure 4. The pelagic sediment evidence for ocean acidification during the PETM. (*a*) Per cent calcite (%CaCO$_3$) showing the dissolution horizon and (*b*) weight-per cent coarse fraction (wt% CF) records for three sections from Walvis Ridge (Sites 1262, 1263 and 1266) and one from the Weddell Sea (Site 690) [57]. The age model is based on cycle (orbital) stratigraphy [51]. The CF primarily comprises planktonic foraminifera shells, which are highly susceptible to solution, and thus wt% CF represents a qualitative indicator of deep-sea saturation state. The acidification phase is represented in the lower most part of the CIE by the minima in both %CaCO$_3$ and %CF. The period of oversaturation is represented by the relatively uniform %CaCO$_3$ and CF values in phase II of the recovery, as well as by the overall low %CF which is a consequence of enhanced production and flux of coccoliths which are predominantly in the less than 30 μm fraction, thus diluting the more than 63 μm fraction. (Online version in colour.)

documented at a number of locations [58,59]. Unfortunately, attempts to locate deep-sea sections that were positioned just below the CCD prior to the PETM, and thus might have recorded the transient overshoot, have yet to be successful.

The magnitude of the CCD overshoot at $t \gtrsim 100$ kyr is predominantly a function of the total carbon input and largely independent of the release time (figure 2*d*). Hence, one might ask whether the overshoot could provide an additional, independent constraint on the total carbon release. In other words, if observations were to establish the CCD suppression, could one simply use a carbon cycle model to tease out the carbon input? Unfortunately, the predicted magnitude of the overshoot in carbon cycle models depends—among other variables—on the strength of the weathering feedback. The weathering feedback strength in models is usually set by choosing numbers for the weathering feedback parameters. These parameters have large uncertainties, which currently preclude establishing a unique relationship between overshoot and carbon input. For example, nearly identical CCD overshoots can be obtained with the same carbon cycle model using two different sets of values for the carbon input/weathering parameters that are all within the range of uncertainties [60].

3. Ocean acidification

The term ocean acidification commonly refers to the ongoing decrease in ocean pH owing to the ocean's uptake of anthropogenic CO_2. Over the period from 1750 to 2000, the oceans have absorbed approximately one-third of the CO_2 emitted by humans; this absorption has already caused a decrease in surface ocean pH by approximately 0.1 units from approximately 8.2 to 8.1 [61]. In a more general sense, ocean acidification may also refer to a decrease in ocean pH owing to other causes and to time scales that are not limited to the present or near future. However, the phrase ocean 'acidification event' should be used in the context of the Earth's history to describe an episode that involved geologically rapid changes of ocean carbonate chemistry on time scales of less than 10 000 years [62,63]. For instance, the decline in surface ocean pH and $CaCO_3$ saturation state (Ω) is coupled on these time scales in response to carbon input. By contrast, on long time scales (greater than 10 000 years), the saturation state of the ocean is generally well regulated by the requirement that $CaCO_3$ sources (weathering) and sinks (shallow- and deep-water $CaCO_3$ burial) must balance [64,65].

The present acidification of the oceans due to anthropogenic CO_2 emissions is expected to have negative consequences for a variety of marine organisms [3–5]. For example, a decline in carbonate saturation state will affect stability and production rates of $CaCO_3$ minerals, which constitute the building blocks of coral reefs and the shells and skeletons of other marine calcifying groups. Laboratory and mesocosm studies indicate that a decrease of 0.2–0.3 units in seawater pH inhibits or slows calcification in many marine organisms, including corals, foraminifera and some calcareous plankton. Note that a drop of 0.3 pH units corresponds to a doubling of the hydrogen ion concentration ($pH = -\log([H^+])$). Large increases in seawater acidity will potentially reduce calcification rates in coral reefs such that erosion will outweigh accretion, thereby compromising the structural integrity of reefs with detrimental impacts on reef communities as well as shore protection. Most of the effects on marine life described earlier are a result of the decline in surface ocean pH and saturation state occurring over a relatively short period of time (figure 1). Rapidly increasing CO_2 levels over a few hundred years because of fossil fuel burning cannot be stabilized by natural feedbacks such as dissolution of deep-sea carbonates or weathering of terrestrial carbonate and silicate rocks. These natural feedbacks operate on time scales of tens to hundreds of thousands of years and are too slow to mitigate ocean acidification on time scales of decades to centuries. But could natural feedbacks have mitigated ocean acidification during the PETM?

For the PETM, a number of carbon input scenarios have been proposed with masses ranging from 1100 to more than 10 000 Pg C over durations of a few thousand to tens of thousands of years [30,31,33,47]. However, initial estimates with very low carbon input mass may have underestimated the magnitude of the CIE and hence the total carbon input [47]. The high-end scenarios with very large carbon input mass require certain assumptions about the CCD before the event and/or predict deep-sea carbonate dissolution patterns during the event that seem difficult to reconcile with the sediment record [31,34,35,43]. Moreover, the mechanism (i.e. source) for such a large and rapid carbon emission is problematic. The scenario that we favour requires an initial carbon pulse of about 3000 Pg C over approximately 6 kyr in order to be consistent with the timing and magnitude of stable carbon isotope records and deep-sea dissolution patterns [31]. We have compared this PETM scenario with a business-as-usual scenario of fossil fuel emissions of 5000 Pg C over approximately 500 years (figure 5). Our results show that if the proposed PETM scenario roughly resembles the actual conditions during the onset of the event, then the effects on ocean chemistry, including surface ocean saturation state, were less severe during the PETM than expected for the future [65,66]. As shown by Zeebe *et al.* [4], not only the magnitude but also the time scale of the carbon input is critical for its effect on ocean carbonate chemistry. The time scale of the anthropogenic carbon input is so short that the natural capacity of the surface reservoirs to absorb carbon is overwhelmed (figure 1). As a result of a 5000 Pg C input over approximately 500 years, the surface ocean saturation state of calcite (Ω_c) would drop from about 5.4 to less than 2 within a few hundred years. By
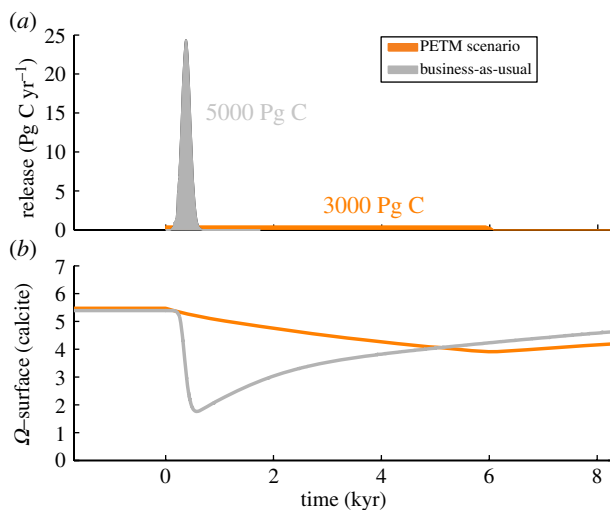
Figure 5. Comparison of the effects of anthropogenic business-as-usual emissions (total of 5000 Pg C over 500 years) and PETM carbon release (3000 Pg C over 6 kyr) on the surface ocean saturation state of calcite. (Online version in colour.)

contrast, the PETM scenario suggests a corresponding decline of Ω_c from 5.5 to only about 4 within a few thousand years. Note, however, that the PETM scenario may be subject to revision, depending on the outcome of future studies that will help to better constrain the time scale of the carbon input.

The premise that the PETM carbon input had only a moderate long-term impact on the surface ocean saturation state is consistent with the findings on nannoplankton origination and extinction during the PETM, which indicate that the perturbation of the surface water saturation state across the PETM was not detrimental to the long-term survival of most species of calcareous nannoplankton taxa [67,68]. Still, transient anomalies in coccolithophore diversity and abundances have been documented globally at the onset of the event and have been attributed to factors such as reduced fertility and warming, while the contribution of acidification remains unclear [23,28,58,59,67–70]. Similarly, planktonic foraminifer communities at low and high latitudes show reductions in diversity, invasions of warmer water or excursion taxa, but no obvious evidence of severe undersaturation [22,71]. One shallow-water carbonate record from a Pacific Ocean guyot shows no major evidence for a permanent carbonate production crisis after the PETM, indicating that the effects of any changes in temperatures or surface ocean pH may have been relatively short-lived or relatively minor [72]. For calcifiers residing deeper in the ocean, the impact of the PETM was much more severe, for example, with a major extinction event of benthic foraminifera, affecting 30–50% of species globally [25]. It is not clear, however, whether the benthic extinction was caused by changes in oxygenation, bottom water temperatures, carbonate undersaturation as a result of the carbon input, and/or other factors [25,65]. Finally, a growing body of evidence suggests that coastal coral reef and ostracode communities experienced a significant reduction in diversity at the end of the Palaeocene [27,73], though the exact role of acidification has yet to be firmly established. In sum, it appears that the direct effects of ocean acidification on marine planktonic calcifiers during the PETM may have been limited because of a relatively 'slow' carbon input rate (slow on human time scales, rapid on geological time scales). However, conclusions are premature at this stage as the number of studies addressing acidification effects on pelagic calcifiers during the PETM is still very limited. The impacts on coastal marine calcifiers, on the other hand, might have been fairly significant. Yet, additional studies are also desirable in this area for a more comprehensive analysis of ocean acidification effects on marine organisms during the PETM.

4. Long-term legacy of carbon release

The lifetime of fossil fuel CO_2 in the atmosphere has been inadequately addressed by many studies and reports, including the Intergovernmental Panel on Climate Change [74]. The fundamental difference between CO_2 and other greenhouse gases such as methane is that the decrease in atmospheric CO_2 over time does not follow a simple decay pattern of a single exponential—even after several millennia, a substantial fraction of the CO_2 remains in the atmosphere [11,15]. Fossil fuel neutralization involves various processes that operate on different time scales. The steps include ocean uptake, mixing with surface waters and reaction with dissolved carbonate ions (10–10^2 years), transport and mixing throughout the deep ocean (10^2–10^3 years), reaction of CO_2 with deep-sea carbonate sediments (10^2–10^4 years) and long-term neutralization via weathering of carbonate and silicate minerals on the continents (10^4–10^6 years). For example, for a rapid pulse of 1000 and 5000 Pg C injected into the atmosphere, the airborne fraction as calculated by various models is still approximately 20% and 50%, respectively, after 1000 years, and approximately 15% and 20%, respectively, after 10 000 years [15]. Very similar results have been obtained with the LOSCAR model used in this study, where we use the LOSCAR model as a tool to illustrate carbon cycle processes; for a detailed model description, see [11]. For anthropogenic emissions of 5000 Pg C stretched over 500 years (rather than a pulse; see figure 1), the LOSCAR model predicts a maximum pCO_2 of approximately 1900 μatm, which declines to approximately 600 μatm after 10 000 years ($t = 0$ here refers to the onset of industrialization; see figure 6). Given a pre-industrial initial pCO_2 of 280 μatm, the airborne fraction is hence 20% after 10 000 years, in agreement with the suite of models tested by Archer *et al.* [15]. After 50 kyr, atmospheric CO_2 has dropped below approximately 500 μatm (airborne fraction less than 14%). This number is somewhat sensitive to the choice of parameter values used in the weathering parametrization [75]. However, the LOSCAR model's standard configuration uses a relatively weak weathering feedback. A stronger weathering feedback would produce a smaller airborne fraction after 50 kyr. In summary, state-of-the-art carbon cycle models predict that the long tail of the atmospheric lifetime of fossil fuel CO_2 is tens to hundreds of thousands of years. However, the airborne fraction of the initial carbon input should drop substantially over a period of 10–20 kyr.

On the contrary, PETM records indicate little if any decline in, for instance, $\delta^{13}C$ values after 50 kyr (figure 3). Similar durations of the PETM main phase can be inferred from $\delta^{18}O$ records (indicating temperature) and surface ocean carbonate chemistry proxies [76]. The inferred main phase duration of greater than 50 kyr is also independent of the age model applied (figure 3). One age model is based on orbital cycle stratigraphy [51], the other on extraterrestrial $^3He_{ET}$ concentrations [52]. An undetermined portion of the clay layer represents Upper Palaeocene material deposited prior to the PETM/CIE and thus adds to the total duration of the event (10–30 kyr). Nevertheless, the two age models agree that the duration of the PETM main phase lasted for at least 50 kyr, a duration that is also consistent with observations from the most expanded terrestrial sequences [77,78].

Based on first-order assumptions of a single carbon input over several thousand years, carbon cycle models predict that the main phase of high pCO_2 and intense warming should have faded after a few ten thousand years (compare 6 kyr scenario in figure 2). This behaviour is consistent with the results of the fossil fuel experiments, but inconsistent with the PETM reconstructions. Hence, additional assumptions are required to explain the observed greater than 50 kyr duration of the PETM main phase. For example, we have proposed a PETM scenario that assumes an additional, continuous carbon input of approximately 1500 Pg C over 70 kyr with a $\delta^{13}C$ value of -50‰ (figure 6) [31,32]. While the total amount of the additional carbon 'bleeding' is significant, the annual rate of approximately 0.02 Pg C yr^{-1} is modest. For comparison, natural long-term weathering fluxes are of the order of 0.2 Pg C yr^{-1}; fossil fuel carbon emissions in 2010 were 9.1 Pg C yr^{-1} [1]. Possible causes for the prolonged carbon input could include additional slow dissociation of clathrates in response to continued warming of subsurface sediments [32] and/or terrestrial carbon feedbacks that release carbon under intense greenhouse conditions
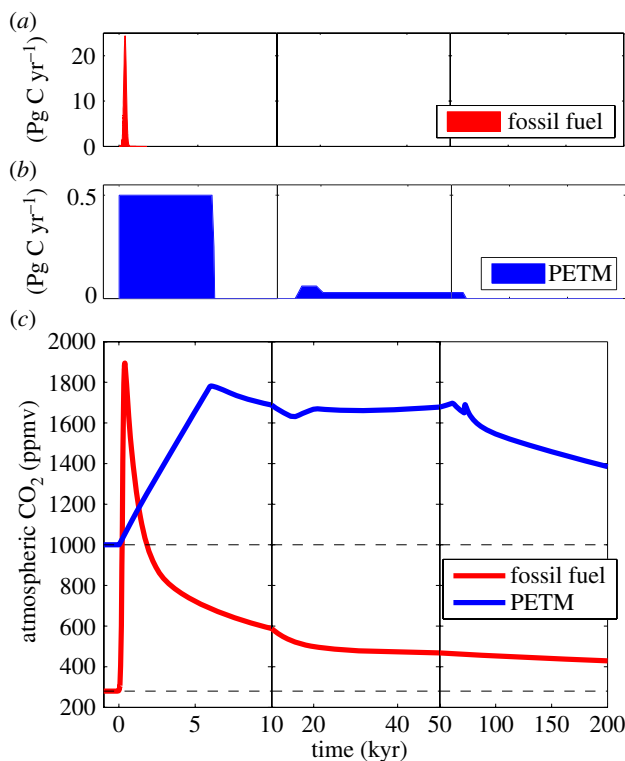
Figure 6. Long-term legacy of massive carbon input to the Earth system: Anthropocene versus PETM. (*a*) Fossil fuel emissions: total of 5000 Pg C over 500 years. (*b*) PETM carbon release: 3000 Pg C over 6 kyr plus approximately 1500 Pg over more than 50 kyr. Note different *y*-axis scales in (*a*,*b*). (*c*) Simulated evolution of atmospheric CO$_2$ in response to the carbon input using the LOSCAR model [11,31]. (Online version in colour.)

(i.e. shrinking of soil organic carbon reservoirs). As of yet, most of these feedbacks are not well understood. It seems imperative to identify and thoroughly understand these feedbacks as similar processes could lead to unpleasant surprises in the future [38].

5. Biotic recovery

The fossil record indicates that recovery of biotic diversity after mass extinctions generally takes several million years. For example, biotic diversity after major extinction events throughout the Phanerozoic required of the order of 5 Myr to rebound [16,79–82]. These events include the Late Ordovician approximately 450 Ma, Late Devonian approximately 370 Ma, End-Permian approximately 250 Ma, End-Triassic approximately 200 Ma and End-Cretaceous approximately 65 Ma, which have traditionally been labelled the 'big five' extinctions. However, more recent studies point out that perhaps only three events qualify as true global mass extinctions, among them the End-Permian and End-Cretaceous [16,81]. It took 10–15 Myr after the End-Permian for coral reefs to recover and approximately 2 Myr after the Cretaceous–Tertiary (K-T) boundary for corals to leave a trace in the fossil record [82,83]. Pre-existing levels of coral diversity were established only about 10 Myr after the K-T boundary. Geochemical evidence such as surface-to-deep gradients in δ^{13}C suggests that marine export production was severely suppressed after the K-T event for approximately 0.5 Myr, most probably because of the extinction of grazers [84,85]. Yet, there is little evidence that the K-T impact led to a sterile ocean devoid of life, commonly termed 'strangelove ocean' in the literature [64,86].

While the PEB marks a major extinction event of benthic foraminifera, affecting 30–50% of species globally, and the decline of coralgal reefs [25,27,73], most species of calcareous

nannoplankton and zooplankton taxa appear to have survived the PEB (see discussion above). Also, terrestrial species experienced only minor extinction [87]. However, the PETM triggered major reorganization and dispersal of animals, particularly in mammals [21,88,89], which also experienced a reduction in mean body size, probably in response to warming or less nutritious vegetation [90]. Plants experienced a major, but temporary, reorganization and drop in diversity related to changes in climate, particularly precipitation [91,92]. In essence, the impacts on biota were largely transient in nature on geological time scales, but long on human time scales.

As discussed earlier, parallels exist between the Anthropocene and the PETM in terms of carbon input and climate change. Does this also imply similar impacts in terms of species extinction and recovery? We argue that the Anthropocene will more likely resemble the End-Permian and End-Cretaceous catastrophes, rather than the PETM. First, the present extinction rate of the Anthropocene is more than 100 species per million species per year, while the fossil record indicates background extinction rates of marine life and mammals of 0.1–1 and 0.2–0.5 species per million species per year, respectively [93]. In other words, the current rate of species extinction is already 100–1000 times higher than would be considered natural. The causes for the current extinctions are diverse, including factors such as changes in land use and fresh water, pollution, exploitation of natural resources, etc. Second, with respect to ocean acidification and impacts on marine calcifiers, the anthropogenic carbon input rate is most probably greater than during the PETM, causing a more severe decline in ocean pH and saturation state (figure 5). In addition, changes in ocean chemistry and sea surface temperature will be imposed on ecosystems that are already affected by other environmental factors. Analysis of the marine fossil record suggests that, if the Anthropocene mass extinction rivals the K-T or End-Permian disasters, recovery will take tens of millions of years [16]. At this point, there are obviously large uncertainties regarding the progression of the rate of extinction and origination, dispersal and success of species in the future. However, if the current trend of species extinction continues, the geological record tells us that humans will have a major and long-lasting impact on the evolution of species on this planet for millions of years to come.

6. Summary and conclusions

We have discussed the long-term legacy of massive carbon release into the Earth's surface reservoirs, focusing on the Anthropocene and the PETM. The comparison of the rate of carbon release suggests that the ensuing effects on ocean acidification and marine calcifying organisms will probably be more severe in the future than during the PETM. However, firm conclusions are difficult to draw at this stage because (i) current research shows mixed responses to acidification in some calcifying taxa and (ii) the number of studies addressing acidification effects on pelagic calcifiers during the PETM is still very limited. The observed duration of the PETM appears to be much longer than predicted by models using first-order assumptions, which poses a conundrum. One explanation involves prolonged, additional carbon release, for instance from marine gas hydrate systems [32].

In this regard, additional observational constraints on the CCD before, during and after the PETM main phase are required in the South Pacific, Indian and North Atlantic Ocean. To be of more practical use, these observational constraints should be placed within a robust chronostratigraphic framework that includes, if possible, the long-term background variability (on orbital time scales) immediately preceding and following the PETM. Ultimately, such a framework will help to constrain the carbon release during the PETM. One important task for the modelling community is to focus on simulating carbonate sediment accumulation profiles across the PEB, including carbon isotopes and other sediment/porewater tracers (e.g. calcium, boron). Among other things, this will help to account for the effects of dissolution and sediment mixing on carbon isotope profiles. It is also important to recognize that the PETM is part of a series of hyperthermals superimposed on a long-term warming trend from the Late Palaeocene to the Early Eocene Climatic Optimum. Throughout this interval, carbon isotope ratios gradually drop by about 2‰, while deep-sea carbonate records indicate a long-term deepening of the CCD.

Reconciling the character and origin of the multi-million year trend in both the climate system and carbon cycle will aid with setting the baseline state (boundary conditions) for the hyperthermals in models, and thus in identifying potential triggers and feedbacks.

In terms of past and future mass extinctions and recovery times of biotic diversity, we have argued that the Anthropocene will more likely resemble the End-Permian and End-Cretaceous disasters, rather than the PETM. If civilization is to avoid such a fate, carbon emission rates must reverse within the next few decades in order to keep total emissions below a certain limit. Note that, while the short-term effects of massive carbon release are modulated by the release time, the long-term legacy is primarily determined by the total integrated emissions. Yet, if the current trend in carbon emissions continues, humans will—given sufficient fossil fuel reserves—release several thousand Pg of carbon, with severe consequences for climate, ocean chemistry, biota, etc., as discussed above. This underlines the urgency for immediate action on global carbon emission reductions and sequestration.

References

1. Peters GP, Marland G, Le Quéré C, Boden T, Canadell JG, Raupach MR. 2012 Rapid growth in CO_2 emissions after the 2008–2009 global financial crisis. *Nat. Clim. Change* **2**, 2–4. (doi:10.1038/nclimate1332)
2. Pepper WJ, Leggett J, Swart R, Wasson J, Edmonds J, Mintzer I. 1992 Emissions scenarios for the IPCC. An update: assumptions, methodology, and results. Support document for ch. A3. In *Climate Change 1992: Supplementary Report to the IPCC Scientific Assessment* (eds JT Houghton, BA Callandar, SK Varney), pp. 69–96. Cambridge, UK: Cambridge University Press.
3. Raven J, Caldeira K, Elderfield HO, Hoegh-Guldberg PL, Riebesell U, Shepherd J, Turley C, Watson A. 2005 *Ocean acidification due to increasing atmospheric carbon dioxide*, p. 60. London, UK: The Royal Society.
4. Zeebe RE, Zachos JC, Caldeira K, Tyrrell T. 2008 Oceans: carbon emissions and acidification (in perspectives). *Science* **321**, 51–52. (doi:10.1126/science.1159124)
5. Gattuso J-P, Hansson L. 2011 Ocean acidification: history and background. In *Ocean acidification* (eds J-P Gattuso, L Hansson), pp. 1–20. Oxford, UK: Oxford University Press.
6. Millero FJ, Woosley R, DiTrolio B, Waters J. 2009 Effect of ocean acidification on the speciation of metals in seawater. *Oceanography* **22**, 72–85. (doi:10.5670/oceanog.2009.98)
7. Beman JM *et al.* 2011 Global declines in oceanic nitrification rates as a consequence of ocean acidification. *Proc. Natl Acad. Sci. USA* **108**, 208–213. (doi:10.1073/pnas.1011053108)
8. Hopkins F, Nightingale P, Liss P. 2011 Effects of ocean acidification on the marine source of atmospherically active trace gases. In *Ocean acidification* (eds J-P Gattuso, L Hansson), pp. 210–229. Oxford, UK: Oxford University Press.
9. Ilyina T, Zeebe RE, Brewer PG. 2010 Future ocean increasingly transparent to low-frequency sound owing to carbon dioxide emissions. *Nat. Geosci.* **3**, 18–22. (doi:10.1038/ngeo719)
10. IPCC. 2007 Intergovernmental Panel on Climate Change. In *Climate Change 2007: The Physical Science Basis* (ed. S Solomon), p. 996. Cambridge, UK: Cambridge University Press.
11. Zeebe RE. 2012 LOSCAR: Long-term Ocean-atmosphere-Sediment CArbon cycle Reservoir model v2.0.4. *Geosci. Model Dev.* **5**, 149–166. (doi:10.5194/gmd-5-149-2012)
12. Zachos JC, Pagani M, Sloan L, Thomas E, Billups K. 2001 Trends, rhythms, and aberrations in global climate 65 Ma to present. *Science* **292**, 686–693. (doi:10.1126/science.1059412)
13. Zachos JC *et al.* 2005 Rapid acidification of the ocean during the Paleocene-Eocene Thermal Maximum. *Science* **308**, 1611–1615. (doi:10.1126/science.1109004)
14. Zeebe RE. 2012 History of seawater carbonate chemistry, atmospheric CO_2, and ocean acidification. *Annu. Rev. Earth Planet. Sci.* **40**, 141–165. (doi:10.1146/annurev-earth-042711-105521)

15. Archer D *et al.* 2009 Atmospheric lifetime of fossil fuel carbon dioxide. *Annu. Rev. Earth Planet. Sci.* **37**, 117–134. (doi:10.1146/annurev.earth.031208.100206)

16. Alroy J. 2008 Dynamics of origination and extinction in the marine fossil record. *Proc. Natl Acad. Sci. USA* **105**, 11 536–11 542. (doi:10.1073/pnas.0802597105)

17. Kennett JP, Stott LD. 1991 Abrupt deep-sea warming, palaeoceanographic changes and benthic extinctions at the end of the Palaeocene. *Nature* **353**, 225–229. (doi:10.1038/353225a0)

18. Zachos JC, Wara MW, Bohaty SM, Delaney ML, Rose-Petrizzo M, Brill A, Bralower TJ, Premoli-Silva I. 2003 A transient rise in tropical sea surface temperature during the Paleocene-Eocene Thermal Maximum. *Science* **302**, 1551–1554. (doi:10.1126/science.1090110)

19. Zachos JC, Schouten S, Bohaty S, Sluijs A, Brinkhuis H, Gibbs S, Bralower T, Quattlebaum T. 2006 Extreme warming of mid-latitude coastal ocean during the Paleocene-Eocene Thermal Maximum: inferences from TEX_{86} and isotope data. *Geology* **34**, 737–740. (doi:10.1130/G22522.1)

20. Sluijs A *et al.* 2006 Subtropical Arctic Ocean temperatures during the Palaeocene/Eocene Thermal Maximum. *Nature* **441**, 610–613. (doi:10.1038/nature04668)

21. Koch PL, Zachos JC, Gingerich PD. 1992 Correlation between isotope records in marine and continental carbon reservoirs near the Palaeocene/Eocene boundary. *Nature* **358**, 319–322. (doi:10.1038/358319a0)

22. Kelly DC, Bralower TJ, Zachos JC, Premoli Silva I, Thomas E. 1996 Rapid diversification of planktonic foraminifera in the tropical Pacific (ODP Site 865) during the late Paleocene Thermal Maximum. *Geology* **24**, 423–426. (doi:10.1130/0091-7613(1996)024<0423:RDOPFI>2.3.CO;2)

23. Tremolada F, Bralower TJ. 2004 Nannofossil assemblage fluctuations during the Paleocene-Eocene Thermal Maximum at Site 213 (Indian Ocean) and 401 (North Atlantic Ocean): paleoceanographic implications. *Mar. Micropaleontol.* **36**, 107–116. (doi:10.1016/j.marmicro.2004.04.002)

24. Takeda K, Kaiho K. 2007 Faunal turnovers in central Pacific benthic foraminifera during the Paleocene-Eocene Thermal Maximum. *Palaeogeogr. Palaeoclim. Palaeoecol.* **251**, 175–197. (doi:10.1016/j.palaeo.2007.02.026)

25. Thomas E. 2007 Cenozoic mass extinctions in the deep sea: what disturbs the largest habitat on Earth? In *Large ecosystem perturbations: causes and consequences* (eds S Monechi, R Coccioni, MR Rampino), pp. 1–23. The Geological Society of America Special Paper 424. Boulder, CO: The Geological Society of America.

26. Raffi I, De Benardi B. 2008 Response of calcareous nannofossils to the Paleocene-Eocene Thermal Maximum: observations on composition, preservation and calcification in sediments from ODP Site 1263 (Walvis Ridge-SW Atlantic). *Mar. Micropal.* **69**, 119–138. (doi:10.1016/j.marmicro.2008.07.002)

27. Scheibner C, Speijer RP. 2008 Late Paleocene Early Eocene Tethyan carbonate platform evolution: a response to long- and short-term paleoclimatic change. *Earth Sci. Rev.* **90**, 71–102. (doi:10.1016/j.earscirev.2008.07.002)

28. Bown P, Pearson P. 2009 Calcareous plankton evolution and the Paleocene/Eocene Thermal Maximum event: new evidence from Tanzania. *Mar. Micropaleontol.* **71**, 60–70. (doi:10.1016/j.marmicro.2009.01.005)

29. Dickens GR, Castillo MM, Walker JCG. 1997 A blast of gas in the latest Paleocene; simulating first-order effects of massive dissociation of oceanic methane hydrate. *Geology* **25**, 259–262. (doi:10.1130/0091-7613(1997)025<0259:ABOGIT>2.3.CO;2)

30. Panchuk K, Ridgwell A, Kump LR. 2008 Sedimentary response to Paleocene-Eocene Thermal Maximum carbon release: a model-data comparison. *Geology* **36**, 315–318. (doi:10.1130/G24474A.1)

31. Zeebe RE, Zachos JC, Dickens GR. 2009 Carbon dioxide forcing alone insufficient to explain Palaeocene-Eocene Thermal Maximum warming. *Nat. Geosci.* **2**, 576–580. (doi:10.1038/ngeo578)

32. Zeebe RE. 2013 What caused the long duration of the Paleocene-Eocene Thermal Maximum? *Paleoceanography* **28**. (doi:10.1002/palo.20039)

33. Cui Y, Kump LR, Ridgwell AJ, Charles AJ, Junium CK, Diefendorf AF, Freeman KH, Urban NM, Harding IC. 2011 Slow release of fossil carbon during the Palaeocene-Eocene Thermal Maximum. *Nat. Geosci.* **4**, 481–485. (doi:10.1038/ngeo1179)

34. Sluijs A, Zachos JC, Zeebe RE. 2012 Constraints on hyperthermals. (Comment on 'Slow release of fossil carbon during the Palaeocene-Eocene Thermal Maximum' by Cui *et al.*, 2011 *Nature Geoscience*.) *Nat. Geosci.* **5**, 231. (doi:10.1038/ngeo1423)

35. Cui Y, Kump LR, Ridgwell AJ, Charles AJ, Junium CK, Diefendorf AF, Freeman KH, Urban NM, Harding IC. 2012 Constraints on hyperthermals. (Reply to comment on 'Slow release of fossil carbon during the Palaeocene-Eocene Thermal Maximum' by Cui *et al.*, 2011 *Nature Geoscience*.) *Nat. Geosci.* **5**, 231–232. (doi:10.1038/ngeo1424)

36. Lunt DJ, Haywood AM, Schmidt GA, Salzmann U, Valdes PJ, Dowsett HJ. 2010 Earth system sensitivity inferred from Pliocene modelling and data. *Nat. Geosci.* **3**, 60–64. (doi:10.1038/ngeo706)

37. Zeebe RE. 2011 Where are you heading Earth? (Commentary). *Nat. Geosci.* **4**, 416–417. (doi:10.1038/ngeo1196)

38. Zeebe RE. 2013 Time-dependent climate sensitivity and the legacy of anthropogenic greenhouse gas emissions. *Proc. Natl Acad. Sci. USA* **110**. (doi:10.1073/pnas.1222843110)

39. Hönisch B, Hemming NG, Archer D, Siddall M, McManus JF. 2009 Atmospheric carbon dioxide concentration across the mid-Pleistocene transition. *Science* **324**, 1551–1554. (doi:10.1126/science.1171477)

40. Zeebe RE, Wolf-Gladrow DA. 2001 *CO_2 in seawater: equilibrium, kinetics, isotopes*, p. 346. Amsterdam, The Netherlands: Elsevier Oceanography Series.

41. Tyrrell T, Shepherd JG, Castle S. 2007 The long-term legacy of fossil fuels. *Tellus B* **59**, 664–672. (doi:10.1111/j.1600-0889.2007.00290.x)

42. Friedlingstein P *et al.* 2006 Climate carbon cycle feedback analysis: results from the C4MIP model intercomparison. *J. Clim.* **19**, 3337–3353. (doi:10.1175/JCLI3800.1)

43. Dickens GR. 2011 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. *Clim. Past* **7**, 831–846. (doi:10.5194/cp-7-831-2011)

44. Schmitz B, Asaro F, Molina E, Monechi S, von Salis K, Speijer RP. 1997 High-resolution iridium, δ^{13}C, δ^{18}O, foraminifera and nannofossil profiles across the latest Paleocene benthic extinction event at Zumaya, Spain. *Palaeogeogr. Palaeoclim. Palaeoecol.* **133**, 49–68. (doi:10.1016/S0031-0182(97)00024-2)

45. Bralower TJ, Thomas DJ, Zachos JC, Hirschmann MM, Röhl U, Sigurdsson H, Thomas E, Whitney DL. 1997 High-resolution records of the late Paleocene Thermal Maximum and circum-Caribbean volcanism: is there a causal link? *Geology* **25**, 963–966. (doi:10.1130/0091-7613(1997)025<0963:HRROTL>2.3.CO;2)

46. Zeebe RE, Zachos JC. 2007 Reversed deep-sea carbonate ion basin-gradient during Paleocene-Eocene Thermal Maximum. *Paleoceanography* **22**, PA3201. (doi:10.1029/2006PA001395)

47. Dickens GR, O'Neil JR, Rea DK, Owen RM. 1995 Dissociation of oceanic methane hydrate as a cause of the carbon isotope excursion at the end of the Paleocene. *Paleoceanography* **10**, 965–971. (doi:10.1029/95PA02087)

48. Dickens GR. 2000 Methane oxidation during the late Palaeocene Thermal Maximum. *Bull. Soc. Geol. France* **171**, 37–49.

49. Leon-Rodriguez L, Dickens GR. 2010 Constraints on ocean acidification associated with rapid and massive carbon injections: the early Paleogene record at ocean drilling program site 1215, equatorial Pacific Ocean. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **298**, 409–420. (doi:10.1016/j.palaeo.2010.10.029)

50. Zachos JC, Bohaty SM, John CM, McCarren H, Kelly DC, Nielsen T. 2007 The Paleocene–Eocene carbon isotope excursion: constraints from individual shell planktonic foraminifer records. *Phil. Trans. R. Soc. A* **365**, 1829–1842. (doi:10.1098/rsta.2007.2045)

51. Röhl U, Westerhold T, Bralower TJ, Zachos JC. 2007 On the duration of the Paleocene-Eocene Thermal Maximum (PETM). *Geochem. Geophys. Geosyst.* **8**, Q12002. (doi:10.1029/2007GC001784)

52. Murphy BH, Farley KA, Zachos JC. 2010 An extraterrestrial ^{3}He-based timescale for the Paleocene-Eocene Thermal Maximum (PETM) from Walvis Ridge, IODP Site 1266. *Geochim. Cosmochim. Acta* **74**, 5098–5108. (doi:10.1016/j.gca.2010.03.039)

53. Farley KA, Eltgroth SF. 2003 An alternative age model for the Paleocene-Eocene Thermal Maximum using extraterrestrial ^{3}He. *Earth Planet. Sci. Lett.* **208**, 135–148. (doi:10.1016/S0012-821X(03)00017-7)

54. Thomas DJ, Zachos JC, Bralower TJ, Thomas E, Bohaty S. 2002 Warming the fuel for the fire: evidence for the thermal dissociation of methane hydrate during the Paleocene-Eocene Thermal Maximum. *Geology* **30**, 1067–1070. (doi:10.1130/0091-7613(2002)030<1067: WTFFTF>2.0.CO;2)

55. John CM, Bohaty SM, Zachos JC, Sluijs A, Gibbs S, Brinkhuis H, Bralower TJ. 2008 North American continental margin records of the Paleocene-Eocene Thermal Maximum: implications for global carbon and hydrological cycling. *Paleoceanography* **23**, PA2217. (doi:10.1029/2007PA001465)

56. Kelly DC, Zachos JC, Bralower TJ, Schellenberg SA. 2005 Enhanced terrestrial weathering/runoff and surface-ocean carbonate production during the recovery stages of the Paleocene-Eocene Thermal Maximum. *Paleoceanography* **20**, PA4023. (doi:10.1029/2005PA001163)

57. Kelly DC, Nielsen TMJ, McCarren HK, Zachos JC, Röhl U. 2010 Spatiotemporal patterns of carbonate sedimentation in the South Atlantic: implications for carbon cycling during the Paleocene-Eocene Thermal Maximum. *Paleogeogr. Palaeoclim. Palaeocol.* **293**, 30–40. (doi:10.1016/j.palaeo.2010.04.027)

58. Bralower TJ. 2002 Evidence for surface water oligotrophy during the late Paleocene Thermal Maximum: nannofossil assemblage data from Ocean Drilling Program Site 690, Maud Rise, Weddell Sea. *Paleoceanography* **17**, 13. (doi:10.1029/2001PA000662)

59. Raffi I, Backman J, Zachos JC, Sluijs A. 2009 The response of calcareous nannofossil assemblages to the Paleocene Eocene Thermal Maximum at the Walvis Ridge in the South Atlantic. *Mar. Micropaleontol.* **70**, 201–212. (doi:10.1016/j.marmicro.2008.12.005)

60. Zeebe RE, Komar N. 2010 Constraints on transient pCO_2 variations based on oceanic calcium, CCD, and terrestrial weathering. *Geochim. Cosmochim. Acta Suppl.* **74**, A1197.

61. Caldeira K, Wickett ME. 2003 Anthropogenic carbon and ocean pH. *Nature* **425**, 365. (doi:10.1038/425365a)

62. Zeebe RE, Ridgwell A. 2011 Past changes of ocean carbonate chemistry. In *Ocean acidification* (eds J-P Gattuso, L Hansson), pp. 21–40. Oxford, UK: Oxford University Press.

63. Hönisch B *et al.* 2012 The geological record of ocean acidification. *Science* **335**, 1058–1063. (doi:10.1126/science.1208277)

64. Zeebe RE, Westbroek P. 2003 A simple model for the $CaCO_3$ saturation state of the ocean: the 'Strangelove', the 'Neritan', and the 'Cretan' Ocean. *Geochem. Geophys. Geosyst.* **4**, 1104. (doi:10.1029/2003GC000538)

65. Ridgwell A, Schmidt D. 2010 Past constraints on the vulnerability of marine calcifiers to massive carbon dioxide release. *Nat. Geosci.* **3**, 196–200. (doi:10.1038/ngeo755)

66. Zeebe RE, Zachos JC. 2007 Ocean acidification in the early Eocene and Anthropocene. *EOS Trans. AGU* **88**, Fall Meet. Suppl., Abstract OS14A–04.

67. Gibbs SJ, Bown PR, Sessa JA, Bralower T, Wilson P. 2006 Nannoplankton extinction and origination across the Paleocene-Eocene Thermal Maximum. *Science* **314**, 1770–1773. (doi:10.1126/science.1133902)

68. Gibbs SJ, Stoll HM, Bown PR, Bralower TJ. 2010 Ocean acidification and surface water carbonate production across the Paleocene-Eocene Thermal Maximum. *Earth Planet. Sci. Lett.* **295**, 583–592. (doi:10.1016/j.epsl.2010.04.044)

69. Jiang S, Wise SW. 2006 Surface-water chemistry and fertility variations in the tropical Atlantic across the Paleocene/Eocene Thermal Maximum as evidenced by calcareous nannoplankton from ODP Leg 207, Hole 1259B. *Rev. Micropaleontol.* **49**, 227–244. (doi:10.1016/j.revmic.2006.10.002)

70. Mutterlose J, Linnert C, Norris R. 2007 Calcareous nannofossils from the Paleocene-Eocene Thermal Maximum of the equatorial Atlantic (ODP Site 1260B): evidence for tropical warming. *Mar. Micropaleontol.* **65**, 13–31. (doi:10.1016/j.marmicro.2007.05.004)

71. Kaiho K, Takeda K, Petrizzo MR, Zachos JC. 2006 Anomalous shifts in tropical Pacific planktonic and benthic foraminiferal test size during the Paleocene-Eocene Thermal Maximum. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **237**, 456–464. (doi:10.1016/j.palaeo.2005.12.017)

72. Robinson SA. 2011 Shallow-water carbonate record of the Paleocene-Eocene Thermal Maximum from a Pacific Ocean guyot. *Geology* **39**, 51–54. (doi:10.1130/G31422.1)

73. Kiessling W, Simpson C. 2010 On the potential for ocean acidification to be a general cause of ancient reef crises. *Global Change Biol.* **16**, 56–67. (doi:10.1111/j.1365–2486.2010.02204.x)

74. IPCC. 2001 Intergovernmental Panel on Climate Change. In *Climate Change 2001: the scientific basis* (ed. JT Houghton), p. 881. Cambridge, UK: Cambridge University Press.

75. Uchikawa J, Zeebe RE. 2008 Influence of terrestial weathering on ocean acidification and the next glacial inception. *Geophys. Res. Lett.* **35**, L23608. (doi:10.1029/2008GL035963)

76. Penman DE, Zachos JC, Zeebe RE, Hönisch B, Bohaty S. 2011 B/Ca of planktic foraminifera documents elevated pCO$_2$ and ocean acidification during the Paleocene-Eocene Thermal Maximum. *AGU Fall Meet.* **2011**, PP21E-07.

77. Bowen GJ, Koch PL, Gingerich PD, Norris RD, Bains S, Corfield RM. 2001 Refined isotope stratigraphy across the continental Paleocene–Eocene boundary on Polecat Bench in the Northern Bighorn Basin. In *Paleocene–Eocene stratigraphy and biotic change in the Bighorn and Clarks Fork Basins*, vol. 33 (ed. PD Gingerich), pp. 73–88. University of Michigan Papers on Paleontology. Ann Arbor, MI: University of Michigan.

78. Giusberti L, Domenico R, Agnini C, Backman J, Fornaciari E, Tateo F, Oddone M. 2007 Mode and tempo of the Paleocene–Eocene Thermal Maximum in an expanded section from the Venetian pre-Alps. *Bulletin* **119**, 391–412.

79. Erwin DH. 2001 Lessons from the past: biotic recoveries from mass extinctions. *Proc. Natl Acad. Sci. USA* **98**, 5399–5403. (doi:10.1073/pnas.091092698)

80. Myers N, Knoll AH. 2001 The biotic crisis and the future of evolution. *Proc. Natl Acad. Sci. USA* **98**, 5389–5392. (doi:10.1073/pnas.091092498)

81. Bambach RK, Knoll AH, Wang SC. 2004 Origination, extinction, and mass depletions of marine diversity. *Paleobiology* **30**, 522–542. (doi:10.1666/0094-8373(2004)030<0522:OEAMDO>2.0.CO;2)

82. Caldeira K. 2007 What corals are dying to tell us about CO$_2$ and ocean acidification. *Oceanography* **20**, 188–195. (doi:10.5670/oceanog.2007.69)

83. Stanley GD. 2003 The evolution of modern corals and their early history. *Earth Sci. Rev.* **60**, 195–225. (doi:10.1016/S0012-8252(02)00104-6)

84. Zachos JC, Arthur MA, Dean WE. 1989 Geochemical evidence for suppression of pelagic marine productivity at the Cretaceous/Tertiary boundary. *Nature* **337**, 61–64. (doi:10.1038/337061a0)

85. D'Hondt S, Donaghay P, Zachos JC, Luttenberg D, Lindinger M. 1998 Organic carbon fluxes and ecological recovery from the Cretaceous-Tertiary mass extinction. *Science* **282**, 276–279. (doi:10.1126/science.282.5387.276)

86. Hsü KJ, McKenzie JA. 1985 A 'Strangelove' ocean in the earliest Tertiary. In *The carbon cycle and atmospheric CO$_2$: natural variations Archean to present* (ed. WS Broecker), pp. 487–492. Geophysical Monograph Series, vol. 32. Washington, DC: American Geophysical Union.

87. McInerney FA, Wing SL. 2011 The Paleocene-Eocene Thermal Maximum: a perturbation of carbon cycle, climate, and biosphere with implications for the future. *Annu. Rev. Earth Planet. Sci.* **39**, 489–516. (doi:10.1146/annurev-earth-040610-133431)

88. Alroy J, Koch PL, Zachos JC. 2000 Global climate change and North American mammalian evolution. In *Deep time: paleobiology's perspective* (eds DH Erwin, SL Wing), pp. 259–288. Paleobiology, vol. 26. Chicago, IL: University of Chicago.

89. Bowen GJ, Clyde WC, Koch PL, Ting S, Alroy J, Tsubamoto T, Wang Y, Wang Y. 2002 Mammalian dispersal at the Paleocene/Eocene boundary. *Science* **295**, 2062–2065. (doi:10.1126/science.1068700)

90. Gingerich PD. 2006 Environment and evolution through the Paleocene–Eocene Thermal Maximum. *Trends Ecol. Evol.* **21**, 246–253. (doi:10.1016/j.tree.2006.03.006)

91. Harrington GJ, Jaramillo CA. 2007 Paratropical floral extinction in the Late Palaeocene-Early Eocene. *J. Geol. Soc.* **164**, 323–332. (doi:10.1144/0016-76492006-027)

92. Wing SL, Harrington GJ, Smith FA, Bloch JI, Boyer DM, Freeman KH. 2005 Transient floral change and rapid global warming at the Paleocene–Eocene boundary. *Science* **310**, 993–996. (doi:10.1126/science.1116913)

93. Rockström J *et al.* 2009 A safe operating space for humanity. Nature **461**, 472–475. (doi:10.1038/461472a)