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

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

[1]School of Ocean and Earth Science and Technology, Department of Oceanography, University of Hawaii at Manoa, Honolulu HI, USA. zeebe@soest.hawaii.edu

[2]Earth and Planetary Sciences, University of California, Santa Cruz CA, USA. jzachos@ucsc.edu

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Abstract. Over the next few centuries, with unabated emissions of anthropogenic carbon dioxide (CO_2), a total of 5,000 Pg C may enter the atmosphere, causing CO_2 concentrations to rise to ~2,000 ppmv, global temperature to warm by more than 8°C, and surface ocean pH to decline by ~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 geologic 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 Earth's surface reservoirs, comparing the Anthropocene with a past analog, the Paleocene-Eocene Thermal Maximum (PETM, ~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 vs. 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 Earth's atmosphere by ~40%. The combined fossil-fuel and cement emissions reached a record high in 2010 of 9.1 Pg C y^{-1} (1 Pg = 10^{15} g) (Peters et al., 2012), higher than predicted twenty years ago under Business-as-Usual scenarios for the year 2010 (8.7 Pg C y^{-1}, IS92a scenario) (Pepper et al., 1992). The rapidly rising levels of CO_2 in the atmosphere are altering the radiative forcing of 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 of the ocean's carbonate mineral saturation state, with possible negative consequences for marine life (Raven et al., 2005; Zeebe et al., 2008; Gattuso & Hansson, 2011). Other geochemical and physical consequences of an increasingly acidic ocean include effects on metal speciation, reduced NH_3/NH_4^+-ratios (likely affecting ammonia oxidation rates), the marine source of atmospherically active trace gases, and alteration of underwater sound absorption (Millero et al., 2009; Beman et al., 2011; Hopkins et al., 2011; Ilyina et al., 2010).

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 (IPCC, 2007). 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 5,000 Pg C are projected to increase Earth's global surface temperature by >8°C and drop surface ocean pH by ~0.7 units (Fig. 1). A carbon release of this rate and magnitude represents a massive perturbation to the Earth system, most likely unprecedented during the past 56 million years (Zachos et al., 2001; Zachos et al., 2005; Zeebe, 2012a). The climatic and geochemical recovery will take tens to hundreds of thousands of years well after emissions have ceased (Archer et al., 2009). Biotic recovery in terms of diversity and ecosystem functioning may take millions of years (Alroy, 2008). However, due to the complexity of the Earth system, particularly involving the contribution of physical and biogeochemical feedbacks, the precise details of the future response are difficult to predict. In this regard, the geologic record may provide foresight to what the future will hold for Earth's climate, ocean chemistry, and ecosystems.

The closest analog for a massive carbon release in the past is the Paleocene-Eocene Thermal Maximum (PETM, ~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 (Kennett & Stott, 1991; Zachos et al., 2001; Zachos et al., 2003; Zachos et al., 2006; Sluijs et al., 2006). 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, biosphere (Kennett & Stott, 1991; Koch et al., 1992) — phenomena which could

only have been generated 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 (Kelly et al., 1996; Tremolada & Bralower, 2004; Takeda & Kaiho, 2007; Thomas, 2007; Raffi & De Benardi, 2008; Scheibner & Speijer, 2008; Bown & Pearson, 2009). 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 only be simulated with the release of thousands of Pg C, and most of it in less than 5 to10 kyr (Dickens et al., 1997; Panchuk et al., 2008; Zeebe et al., 2009). 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.

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 (Dickens et al., 1997; Panchuk et al., 2008; Zeebe et al., 2009; Cui et al., 2011; Sluijs et al., 2012; Cui et al., 2012), but to study the long-term legacy of massive carbon input. To this end, we focus on a limited number of carbon input scenarios (Zeebe et al., 2009) and employ the LOSCAR model (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 (Zeebe, 2012b).

2 Massive carbon release

The known total fossil fuel reserves currently available for combustion have been estimated at several thousand Pg C. These figures do not include potential contributions from other fossil resources such as methane hydrates. For total carbon emissions of 3,500 and 5,000 Pg C over 500 years, Earth's surface temperature would rise by more than 6°C and 8°C during the next few centuries, respectively (Fig. 1). This estimate assumes a climate sensitivity of 3°C per doubling of CO_2, which only includes fast feedback processes (IPCC, 2007). However, over millennial time scales additional, slower feedbacks could become active, which would exacerbate the warming (Lunt et al., 2010; Zeebe, 2011). The projected consequences for ocean chemistry are equally severe, with a decline in ocean pH by up to ~0.7 units (from ~8.2 to ~7.5, a five-fold increase in acidity or H^+ concentration) and a two- to three-fold reduction of the carbonate mineral saturation state (Fig. 1) (Zeebe et al., 2008). To put this in a geological perspective,

surface-ocean pH has probably not been below ~8.1 during the past 2 million years (Hönisch et al., 2009). A range of simulations show that in order to avoid large changes in Earth's climate and ocean chemistry, drastic and immediate reductions in CO_2 emissions would be necessary (Fig. 1). For instance, in order to limit the total carbon input to 1,000 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 (Zeebe & Wolf-Gladrow, 2001; Tyrrell et al., 2007; Archer et al., 2009). 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 (Friedlingstein et al., 2006). 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 likely the best analog for a massive carbon release in the geologic past, for which a sufficient number of widely distributed sediment records are available (Zachos et al., 2003; Zachos et al., 2006; Sluijs et al., 2006; Dickens, 2011). 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 geologic timescales (a few thousand years), establishing the approximate rate of emissions has proved difficult using conventional stratigraphic methods (Cui et al., 2011; Sluijs et al., 2012).

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, e.g. (Zeebe et al., 2009; Zeebe, 2012b). Simulations of the carbon release with a single input of 3,000 Pg C (source $\delta^{13}C = -50‰$) indicate that the release time was likely much shorter than 20 kyr, otherwise the shoaling of the calcite compensation depth (CCD) in the deep Atlantic would be too muted (Fig. 2). Observations across the Paleocene-Eocene boundary (PEB) have shown that the CCD shoaled substantially in the Atlantic and by at least 2.0 km in the South Atlantic (Schmitz et al., 1997; Bralower et al., 1997; Zachos et al., 2005; Zeebe & Zachos, 2007b). Hence the simulations suggest that the release time was ~6 kyr or less for an initial input of 3,000 Pg C (Fig. 2). Note that the simulations assume a 40% carbon release directly into the deep Atlantic from the possible dissociation of methane hydrates (Dickens et al., 1995). 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 (Dickens, 2000). Note also that the CCD shoaling in the Pacific was less pronounced than in the Atlantic (Zeebe et al., 2009; Leon-Rodriguez & Dickens, 2010; Sluijs et al., 2012). At input rates over periods approaching ~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 ~3 kyr after the PEB (Fig. 2). The reason for the short-lived $\delta^{13}C$ anomaly is that on time scales shorter than ~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 (Zachos et al., 2007), which would argue against a release time shorter than ~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 P-E boundary 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 ^{3}He, a constant flux proxy (Fig. 3) (Röhl et al., 2007; Farley & Eltgroth, 2003; Murphy et al., 2010). 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 sampled 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 $\delta^{13}C$ (Kelly et al., 1996; Thomas et al., 2002), though this too could be an artifact 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 (Zachos et al., 2006; Zachos et al., 2007; John et al., 2008; Cui et al., 2011). In sum, the rate of carbon release is still insufficiently constrained to eliminate the possibility of a relatively fast release, on 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 (Fig. 2d). Note that while Fig. 2d shows examples for the Atlantic CCD, the model-predicted CCD overshoot is global (Zeebe et al., 2009; Zeebe, 2012b). 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 (Fig. 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 due 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 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 (Farley & Eltgroth, 2003; Zachos et al., 2005; Kelly et al., 2005; Kelly et al., 2010; Murphy et al., 2010; Leon-Rodriguez & Dickens, 2010). The observations include an unusual transient pulse (20-40 kyr) in carbonate accumulation rates during the recovery phase, roughly 100 ky after peak acidification (Fig. 3) (Farley & Eltgroth, 2003; Murphy et al., 2010) as well as enhanced preservation of plankton shells (Fig. 4; Phase II) (Kelly et al., 2010). These observations, recorded in all ocean basins and 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 documented at a number of locations (Bralower, 2002; Raffi et al., 2009). 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 $t > \sim 100$ kyr is predominantly a function of the total carbon input and largely independent of the release time (Fig. 2d). 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 precludes 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 (Zeebe & Komar, 2010).

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 of surface-ocean pH by ~0.1 units from ~8.2 to ~8.1 (Caldeira & Wickett, 2003). In a more general sense, ocean acidification may also refer to a decrease in ocean pH due to other causes and to timescales that are not limited to the present or near future. However, the phrase ocean "acidification event" should be used in the context of Earth's history to describe an episode that involved geologically rapid changes of ocean carbonate chemistry on timescales less than 10,000 years (Zeebe & Ridgwell, 2011; Hönisch et al., 2012). 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. In contrast, on long timescales (>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 (Zeebe & Westbroek, 2003; Ridgwell & Schmidt, 2010).

The present acidification of the oceans due to anthropogenic CO_2 emissions is expected to have negative consequences for a variety of marine organisms (Raven et al., 2005; Zeebe et al., 2008; Gattuso & Hansson, 2011). For example, a decline in carbonate saturation state will affect stability and production rates of $CaCO_3$ minerals, which comprise 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 to 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 above are a result of the decline in surface ocean pH and saturation state occurring over a relatively short period of time (Fig. 1). Rapidly increasing CO_2 levels over a few hundred years due to 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 1,100 to >10,000 Pg C over durations of a few thousand to tens of thousands of years (Dickens et al., 1995; Panchuk et al., 2008; Zeebe et al., 2009; Cui et al., 2011). However, initial estimates with very low carbon input mass may have underestimated the magnitude of the CIE and hence the total carbon input (Dickens et al., 1995). 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 (Zeebe et al., 2009; Dickens, 2011; Sluijs et al., 2012; Cui et al., 2012). Moreover, the mechanism (i.e., source) for such a large and rapid carbon emission is problematic. The scenario that we favor requires an initial carbon pulse of about 3,000 Pg C over ~6 kyr in order to be consistent with the timing and magnitude of stable carbon isotope records and deep-sea dissolution patterns (Zeebe et al., 2009). We have compared this PETM scenario to a Business-as-USual scenario of fossil fuel emissions of 5,000 Pg C over ~500 yr (Fig. 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 (Zeebe & Zachos, 2007a; Ridgwell & Schmidt, 2010). As shown by Zeebe et al. (2008), not only the magnitude but also the timescale of the carbon input is critical for its effect on ocean carbonate chemistry. The

timescale of the anthropogenic carbon input is so short that the natural capacity of the surface reservoirs to absorb carbon is overwhelmed (Fig. 1). As a result of a 5,000 Pg C input over ~500 yr, the surface ocean saturation state of calcite (Ω_c) would drop from about 5.4 to less than 2 within a few hundred years. In 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 timescale of the carbon input.

The premise that the PETM carbon input had only a moderate long-term impact on 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 (Gibbs et al., 2006; Gibbs et al., 2010). 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 (Bralower, 2002; Tremolada & Bralower, 2004; Jiang & Wise, 2006; Gibbs et al., 2006; Gibbs et al., 2010; Raffi et al., 2009; Mutterlose et al., 2007; Bown & Pearson, 2009). 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 (Kelly et al., 1996; Kaiho et al., 2006). 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 (Robinson, 2011). 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 to 50% of species globally (Thomas, 2007). 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 (Thomas, 2007; Ridgwell & Schmidt, 2010). 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 Paleocene (Scheibner & Speijer, 2008; Kiessling & Simpson, 2010), 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 timescales, rapid on geologic timescales). 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.

3 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 IPCC (IPCC, 2001). The fundamental difference between CO_2 and other greenhouse gases like methane, for instance, is that the decrease of 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 (Archer et al., 2009; Zeebe, 2012b). 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 ($10–10^2$ y), transport and mixing throughout the deep ocean ($10^2–10^3$ y), reaction of CO_2 with deep-sea carbonate sediments ($10^2–10^4$ y), and long-term neutralization via weathering of carbonate and silicate minerals on the continents ($10^4–10^6$ y). For example, for a rapid pulse of 1,000 and 5,000 Pg C injected into the atmosphere, the airborne fraction as calculated by various models is still ~20% and ~50% respectively after 1,000 years, and ~15% and ~20% respectively after 10,000 years (Archer et al., 2009). Very similar results have been obtained with the LOSCAR model used in the present study; LOSCAR = Long-term Ocean-atmosphere-Sediment CArbon cycle Reservoir model (Zeebe, 2012b). In this paper, we use LOSCAR as a tool to illustrate carbon-cycle processes; for a detailed model description, see (Zeebe, 2012b)**.** For anthropogenic emissions of 5,000 Pg C stretched over 500 years (rather than a pulse, see Fig. 1), LOSCAR predicts a maximum pCO_2 of ~1,900 μatm, which declines to ~600 μatm after 10,000 years ($t = 0$ here refers to the onset of industrialization, see Fig. 6). Given a preindustrial 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. (2009). After 50 kyr, atmospheric CO_2 has dropped below ~500 μatm (airborne fraction < 14%). This number is somewhat sensitive to the choice of parameter values used in the weathering parameterization (Uchikawa & Zeebe, 2008). However, LOSCAR'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 to 20 kyr.

On the contrary, PETM records indicate little if any decline in, for instance, $\delta^{13}C$ values after 50 kyr (Fig. 3). Similar durations of the PETM main phase can be inferred from $\delta^{18}O$ records (indicating temperature) and surface ocean carbonate chemistry proxies (Penman et al., 2011). The inferred main phase duration of > 50 kyr is also independent of the age model applied (Fig. 3). One age model is based on orbital cycle stratigraphy (Röhl et al., 2007), the other on extraterrestrial $^3He_{ET}$ concentrations (Murphy et al., 2010). An undetermined portion of the clay-layer represents upper Paleocene material deposited prior to the PETM/CIE and thus adds to the total duration of the event (10 to 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 (Bowen et al., 2001; Giusberti et al., 2007).

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 Fig. 2). This behavior 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 >50 kyr-duration of the PETM main phase. For example, we have proposed a PETM scenario that assumes an additional, continuous carbon input of ~1500 Pg C over 70 kyr with a $\delta^{13}C$ value of −50‰ (Fig. 6) (Zeebe et al., 2009). While the total amount of the additional carbon "bleeding" is significant, the annual rate of ~0.02 Pg C y^{-1} is modest. For comparison, natural long-term weathering fluxes are of order 0.2 Pg C y^{-1}; fossil fuel carbon emissions in 2010 were 9.1 Pg C y^{-1} (Peters et al., 2012). Possible causes for the prolonged carbon input could include additional slow dissociation of clathrates in response to continued warming of subsurface sediments and/or terrestrial carbon feedbacks that release carbon under intense greenhouse conditions (i.e. shrinking of soil organic carbon reservoirs). As of yet, these feedbacks are unknown. It seems imperative to identify and thoroughly understand these feedbacks as similar processes could lead to unpleasant surprises in the future.

4 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 on the order of 5 million years to rebound (Erwin, 2001; Myers & Knoll, 2001; Bambach et al., 2004; Caldeira, 2007; Alroy, 2008). These events include the Late Ordovician ~450 Ma, Late Devonian ~370 Ma, end-Permian ~250 Ma, end-Triassic ~200 Ma, and end-Cretaceous ~65 Ma, which have traditionally been labeled 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 (Bambach et al., 2004; Alroy, 2008). It took 10 to 15 myr after the end-Permian for coral reefs to recover and ~2 myr after the Cretaceous-Tertiary (K-T) boundary for corals to leave a trace in the fossil record (Stanley, 2003; Caldeira, 2007). Pre-existing levels of coral diversity were only established about 10 myr after the K-T boundary. Geochemical evidence such as surface-to-deep gradients in $\delta^{13}C$ suggests that marine export production was severely suppressed after the K-T event for ~0.5 myr, most likely due to the extinction of grazers (Zachos et al., 1989; D'Hondt et al., 1998). 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 (Hsü & McKenzie, 1985; Zeebe & Westbroek, 2003).

While the Paleocene-Eocene boundary (PEB) marks a major extinction event of benthic foraminifera, affecting 30 to 50% of species globally, and the decline of coralgal reefs (Thomas, 2007; Scheibner & Speijer, 2008; Kiessling & Simpson, 2010), most species of calcareous nannoplankton and zooplankton taxa appear to have survived the PEB (see discussion above).

Also, terrestrial species experienced only minor extinction (McInerney & Wing, 2011). However, the PETM triggered major reorganization and dispersal of animals, particularly in mammals (Koch et al., 1992; Alroy et al., 2000; Bowen et al., 2002), which also experienced a reduction in mean body size, likely in response to warming or less nutritious vegetation (Gingerich, 2006). Plants experienced a major, but temporary, reorganization and drop in diversity related to changes in climate, particularly precipitation (Harrington & Jaramillo, 2007; Wing et al., 2005). In essence, the impacts on biota were largely transient in nature on geologic times scales, but long on human timescales.

As discussed above, 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 >100 species per million species per year, while the fossil record indicates background extinction rates of marine life and mammals of 0.1 to 1 and 0.2 to 0.5 species per million species per year, respectively (Rockström et al., 2009). In other words, the current rate of species extinction is already 100 to 1,000 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 likely greater than during the PETM, causing a more severe decline in ocean pH and saturation state (Fig. 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 (Alroy, 2008). 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 geologic 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.

5 Summary and Conclusions

We have discussed the long-term legacy of massive carbon release into Earth's surface reservoirs, focusing on the Anthropocene and the Paleocene-Eocene Thermal Maximum (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 (a) current research shows mixed responses to acidification in some calcifying taxa and (b) 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 — the underlying mechanism, however, remains uncertain. 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 modeling community is to focus on simulating carbonate sediment accumulation profiles across the P/E boundary, including carbon isotopes and other sediment/porewater tracers (e.g. calcium, boron, etc.). 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 Paleocene 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.

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References

Alroy, J. (2008), 'Dynamics of origination and extinction in the marine fossil record', *Proc. Nat. Acad. Sci.* **105**, 11536–11542.

Alroy, J., Koch, P. L. & Zachos, J. C. (2000), Global climate change and North American mammalian evolution, *in* D. H. Erwin & S. L. Wing, eds, 'Deep time: Paleobiology's perspective', Paleobiology 26, pp. 259–288.

Archer, D., Eby, M., Brovkin, V., Ridgwell, A., Cao, L., Mikolajewicz, U., Caldeira, K., Matsumoto, K., Munhoven, G., Montenegro, A. & Tokos, K. (2009), 'Atmospheric lifetime of fossil fuel carbon dioxide', *Ann. Rev. Earth Planet. Sci.* **37**, 117–134.

Bambach, R. K., Knoll, A. H. & Wang, S. C. (2004), 'Origination, extinction, and mass depletions of marine diversity', *Paleobiology* **30**(4), 522–542.

Beman, J. M., Chow, C.-E., King, A. L., Feng, Y., Fuhrman, J. A., Andersson, A., Bates, N. R., Popp, B. N. & Hutchins, D. A. (2011), 'Global declines in oceanic nitrification rates as a consequence of ocean acidification', *Proc. Nat. Acad. Sci.* **108**, 208–213.

Bowen, G. J., Clyde, W. C., Koch, P. L., Ting, S., Alroy, J., Tsubamoto, T., Wang, Y. & Wang, Y. (2002), 'Mammalian Dispersal at the Paleocene/Eocene Boundary', *Science* **295**, 2062–2065.

Bowen, G. J., Koch, P. L., Gingerich, P. D., Norris, R. D., Bains, S. & Corfield, R. M. (2001), Refined isotope stratigraphy across the continental Paleocene-Eocene Boundary on Polecat Bench in the Northern Bighorn Basin, *in* Gingerich P. D., ed., 'Paleocene-Eocene stratigraphy and biotic change in the Bighorn and Clarks Fork Basins', University of Michigan Papers on Paleontology, 33, pp. 73–88.

Bown, P. & Pearson, P. (2009), 'Calcareous plankton evolution and the Paleocene/Eocene thermal maximum event: New evidence from Tanzania', *Mar. Micropaleontol.* **71**, 60–70.

Bralower, T. J. (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', *Paleoceanogr.* **17**, doi 10.1029/2001PA000662.

Bralower, T. J., Thomas, D. J., Zachos, J. C., Hirschmann, M. M., Röhl, U., Sigurdsson, H., Thomas, E. & Whitney, D. L. (1997), 'High-resolution records of the late Paleocene thermal maximum and circum-Caribbean volcanism: Is there a causal link?', *Geology* **25**, 963–966.

Caldeira, K. (2007), 'What corals are dying to tell us about CO_2 and ocean acidification', *Oceanography* **20(2)**, 188–195.

Caldeira, K. & Wickett, M. E. (2003), 'Anthropogenic carbon and ocean pH', *Nature* **425**, 365.

Cui, Y., Kump, L. R., Ridgwell, A. J., Charles, A. J., Junium, C. K., Diefendorf, A. F., Freeman, K. H., Urban, N. M. & Harding, I. C. (2011), 'Slow release of fossil carbon during the Palaeocene-Eocene Thermal Maximum', *Nature Geoscience* **4**, 481–485.

Cui, Y., Kump, L. R., Ridgwell, A. J., Charles, A. J., Junium, C. K., Diefendorf, A. F., Freeman, K. H., Urban, N. M. & Harding, I. C. (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', *Nature Geosci.* **5**, 231–232.

D'Hondt, S., Donaghay, P., Zachos, J. C., Luttenberg, D. & Lindinger, M. (1998), 'Organic Carbon Fluxes and Ecological Recovery from the Cretaceous-Tertiary Mass Extinction', *Science* **282**, 276.

Dickens, G. R. (2000), 'Methane oxidation during the late Palaeocene Thermal Maximum', *Bull. Soc. Geol. France* **171(1)**, 37–49.

Dickens, G. R. (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.

Dickens, G. R., Castillo, M. M. & Walker, J. C. G. (1997), 'A blast of gas in the latest Paleocene; simulating first-order effects of massive dissociation of oceanic methane hydrate', *Geology* **25**, 259–262.

Dickens, G. R., O'Neil, J. R., Rea, D. K. & Owen, R. M. (1995), 'Dissociation of oceanic methane hydrate as a cause of the carbon isotope excursion at the end of the Paleocene', *Paleoceanogr.* **10**, 965–971.

Erwin, D. H. (2001), 'Lessons from the past: Biotic recoveries from mass extinctions', *Proc. Nat. Acad. Sci.* **98**, 5399–5403.

Farley, K. A. & Eltgroth, S. F. (2003), 'An alternative age model for the Paleocene-Eocene thermal maximum using extraterrestrial ^{3}He', *Earth Planet Sci. Lett.* **208**, 135–148.

Friedlingstein, P., Cox, P., Betts, R., Bopp, L., von Bloh, W., Brovkin, V., Cadule, P., Doney, S., Eby, M., Fung, I., Bala, G., John, J., Jones, C., Joos, F., Kato, T., Kawamiya, M., Knorr, W., Lindsay, K., Matthews, H. D., Raddatz, T., Rayner, P., Reick, C., Roeckner, E., Schnitzler, K.-G., Schnur, R., Strassmann, K., Weaver, A. J., Yoshikawa, C. & Zeng, N. (2006), 'Climate Carbon Cycle Feedback Analysis: Results from the C4MIP Model Intercomparison', *J. Clim.* **19**, 3337–3353.

Gattuso, J.-P. & Hansson, L. (2011), Ocean acidification: history and background, *in* Gattuso, J.-P. and L. Hansson, ed., 'Ocean Acidification', Oxford University Press, pp. 1–20.

Gibbs, S. J., Bown, P. R., Sessa, J. A., Bralower, T. & Wilson, P. (2006), 'Nannoplankton extinction and origination across the Paleocene-Eocene Thermal Maximum', *Science* **314**, 1770–1773.

Gibbs, S. J., Stoll, H. M., Bown, P. R. & Bralower, T. J. (2010), 'Ocean acidification and surface water carbonate production across the Paleocene-Eocene thermal maximum', *Earth and Planetary Science Letters* **295**, 583–592.

Gingerich, P. D. (2006), 'Environment and evolution through the Paleocene-Eocene thermal maximum', *Trends Ecol. Evol.* **21**(5), 246–253.

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', **119**(3-4), 391–412.

Harrington, G. J. & Jaramillo, C. A. (2007), 'Paratropical floral extinction in the Late Palaeocene-Early Eocene', *J. Geol. Soc.* **164**, 323–332.

Hönisch, B., Hemming, N. G., Archer, D., Siddall, M. & McManus, J. F. (2009), 'Atmospheric carbon dioxide concentration across the mid-Pleistocene transition', *Science* **324**, 1551–1554, 10.1126/science.1171477.

Hönisch, B., Ridgwell, A., Schmidt, D. N., Thomas, E., Gibbs, S. J., Sluijs, A., Zeebe, R., Kump, L., Martindale, R. C., Greene, S. E., Kiessling, W., Ries, J., Zachos, J. C., Royer, D. L., Barker, S., Marchitto, T. M., Moyer, R., Pelejero, C., Ziveri, P., Foster, G. L. & Williams, B. (2012), 'The Geological Record of Ocean Acidification', *Science* **335**, 1058–1063.

Hopkins, F., Nightingale, P. & Liss, P. (2011), Effects of ocean acidification on the marine source of atmospherically active trace gases, *in* Gattuso, J.-P. and L. Hansson, ed., 'Ocean Acidification', Oxford University Press, pp. 210–229.

Hsü, K. J. & McKenzie, J. A. (1985), A 'Strangelove' ocean in the earliest Tertiary, *in* E. T. S. . W. S. Broecker, ed., 'The Carbon Cycle and Atmospheric CO2: Natural Variations Archean to Present', pp. 487–492.

Ilyina, T., Zeebe, R. E. & Brewer, P. G. (2010), 'Future ocean increasingly transparent to low-frequency sound owing to carbon dioxide emissions', *Nature Geosci.* **3**, 18–22, doi: 10.1038/ngeo719.

IPCC (2001), *Intergovernmental Panel on Climate Change, J. T. Houghton et al. (Eds.), Climate Change 2001: The Scientific Basis*, Cambridge University Press, Cambridge, pp. 881.

IPCC (2007), *Intergovernmental Panel on Climate Change, Solomon, S. et al. (Eds.). Climate Change 2007: The Physical Science Basis*, Cambridge University Press, Cambridge, pp. 996.

Jiang, S. & Wise, S. W. (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', *Revue de Micropaléontologie* **49**, 227–244.

John, C. M., Bohaty, S. M., Zachos, J. C., Sluijs, A., Gibbs, S., Brinkhuis, H. & Bralower, T. J. (2008), 'North American continental margin records of the Paleocene-Eocene thermal maximum: Implications for global carbon and hydrological cycling', *Paleoceanogr.* **23**, PA2217, doi:10.1029/2007PA001465.

Kaiho, K., Takeda, K., Petrizzo, M. R. & Zachos, J. C. (2006), 'Anomalous shifts in tropical Pacific planktonic and benthic foraminiferal test size during the Paleocene-Eocene Thermal Maximum', *Palaeogeogr., Palaeoclimatol., Palaeoecol.* **237(2-4)**, 456–464.

Kelly, D. C., Bralower, T. J., Zachos, J. C., 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.

Kelly, D. C., Nielsen, T. J., H., M., Zachos, J. C. & 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.

Kelly, D. C., Zachos, J. C., Bralower, T. J. & Schellenberg, S. A. (2005), 'Enhanced terrestrial weathering/runoff and surface-ocean carbonate production during the recovery stages of the Paleocene-Eocene Thermal Maximum', *Paleoceanogr.* **20**, PA4023 doi:10.1029/2005PA001163.

Kennett, J. P. & Stott, L. D. (1991), 'Abrupt deep-sea warming, palaeoceanographic changes and benthic extinctions at the end of the Palaeocene', *Nature* **353**, 225–229.

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

Koch, P. L., Zachos, J. C. & Gingerich, P. D. (1992), 'Correlation between isotope records in marine and continental carbon reservoirs near the Palaeocene/Eocene boundary', *Nature* **358**, 319–322.

Leon-Rodriguez, L. & Dickens, G. R. (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.

Lunt, D. J., Haywood, A. M., Schmidt, G. A., Salzmann, U., Valdes, P. J. & Dowsett, H. J. (2010), 'Earth system sensitivity inferred from Pliocene modelling and data', *Nature Geosci.* **3**, 60–64.

McInerney, F. A. & Wing, S. L. (2011), 'The Paleocene-Eocene Thermal Maximum: A Perturbation of Carbon Cycle, Climate, and Biosphere with Implications for the Future', *Ann. Rev. Earth Planet. Sci.* **39**(1), 489–516.

Millero, F. J., Woosley, R., DiTrolio, B. & Waters, J. (2009), 'Effect of ocean acidification on the speciation of metals in seawater', *Oceanogr.* **22(4)**, 72–85.

Murphy, B. H., Farley, K. A. & Zachos, J. C. (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.

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', *Marine Micropaleontology* **65**, 13–31.

Myers, N. & Knoll, A. H. (2001), 'The biotic crisis and the future of evolution', *Proc. Nat. Acad. Sci.* **98**, 5389–5392.

Panchuk, K., Ridgwell, A. & Kump, L. R. (2008), 'Sedimentary response to Paleocene-Eocene Thermal Maximum carbon release: A model-data comparison', *Geology* **36(4)**, 315–318, doi: 10.1130/G24474A.1.

Penman, D. E., Zachos, J. C., Zeebe, R. E., 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.

Pepper, W. J., 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 Chapter A3, *in* J. T. Houghton, B. A. Callandar, S. K. Varney, ed., 'Climate Change 1992: Supplementary Report to the IPCC Scientific Assessment', Cambridge University Press.

Peters, G. P., Marland, G., Le Quéré, C., Boden, T., Canadell, J. G. & Raupach, M. R. (2012), 'Rapid growth in CO_2 emissions after the 2008-2009 global financial crisis', *Nature Clim. Change* **2**, 2–4.

Raffi, I., Backman, J., Zachos, J. C. & 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**(3-4), 201–212.

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.

Raven, J., Caldeira, K., Elderfield, H., O. Hoegh-Guldberg, P. L., Riebesell, U., Shepherd, J., Turley, C. & Watson, A. (2005), *Ocean acidification due to increasing atmospheric carbon dioxide*, The Royal Society, Policy Document, pp. 60, London, UK.

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

Robinson, S. A. (2011), 'Shallow-water carbonate record of the Paleocene-Eocene Thermal Maximum from a Pacific Ocean guyot', *Geology* **39**(1), 51–54.

Rockström, J., Steffen, W., Noone, K., Persson, Å., Chapin, F. S., Lambin, E. F., Lenton, T. M., Scheffer, M., Folke, C., Schellnhuber, H. J., Nykvist, B., de Wit, C. A., Hughes, T., van der Leeuw, S., Rodhe, H., Sörlin, S., Snyder, P. K., Costanza, R., Svedin, U., Falkenmark, M., Karlberg, L., Corell, R. W., Fabry, V. J., Hansen, J., Walker, B., Liverman, D., Richardson, K., Crutzen, P. & Foley, J. A. (2009), 'A safe operating space for humanity', **461**, 472–475.

Röhl, U., Westerhold, T., Bralower, T. J. & Zachos, J. C. (2007), 'On the duration of the Paleocene-Eocene thermal maximum (PETM)', *Geochem. Geophys. Geosyst.* **8**, Q12002, doi:10.1029/2007GC001784.

Scheibner, C. & Speijer, R. P. (2008), 'Late Paleocene early Eocene Tethyan carbonate platform evolution A response to long- and short-term paleoclimatic change', *Earth Science Reviews* **90**, 71–102.

Schmitz, B., Asaro, F., Molina, E., Monechi, S., von Salis, K. & Speijer, R. P. (1997), 'High-resolution iridium, $\delta^{13}C$, $\delta^{18}O$, foraminifera and nannofossil profiles across the latest Paleocene benthic extinction event at Zumaya, Spain', *Palaeogeogr., Palaeoclim., Palaeoecol.* **133**, 49 – 68.

Sluijs, A., Schouten, S., Pagani, M., Woltering, M., Brinkhuis, H., Damsté, J. S. S., Dickens, G. R., Huber, M., Reichart, G.-J., Stein, R., Matthiessen, J., Lourens, L. J., Pedentchouk, N., Backman, J., Moran, K. & The Expedition 302 Scientists (2006), 'Subtropical Arctic Ocean temperatures during the Palaeocene/Eocene thermal maximum', *Nature* **441**, 610–613.

Sluijs, A., Zachos, J. C. & Zeebe, R. E. (2012), 'Constraints on hyperthermals. Comment on "Slow release of fossil carbon during the Palaeocene-Eocene Thermal Maximum", by Cui et al., 2011 Nature Geoscience', *Nature Geosci.* **5**, 231.

Stanley, G. D. (2003), 'The evolution of modern corals and their early history', *Earth Sci. Rev.* **60**, 195–225.

Takeda, K. & Kaiho, K. (2007), 'Faunal turnovers in central Pacific benthic foraminifera during the Paleocene-Eocene thermal maximum', *Palaeogeogr. Palaeoclim. Palaeoecol.* **251(2)**, 175 – 197.

Thomas, D. J., Zachos, J. C., Bralower, T. J., 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.

Thomas, E. (2007), Cenozoic mass extinctions in the deep sea: What disturbs the largest habitat on Earth?, *in* Monechi, S., R. Coccioni, and M. Rampino, ed., 'Large Ecosystem Perturbations: Causes and Consequences', The Geological Society of America Special Paper 424, pp. spe424–01.

Tremolada, F. & Bralower, T. J. (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.

Tyrrell, T., Shepherd, J. G. & Castle, S. (2007), 'The long-term legacy of fossil fuels', *Tellus B* **59**, 664–672.

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

Wing, S. L., Harrington, G. J., Smith, F. A., Bloch, J. I., Boyer, D. M. & Freeman, K. H. (2005), 'Transient floral change and rapid global warming at the Paleocene-Eocene boundary', *Science* **310**, 993–996.

Zachos, J. C., Arthur, M. A. & Dean, W. E. (1989), 'Geochemical evidence for suppression of pelagic marine productivity at the Cretaceous/Tertiary boundary', *Nature* **337**, 61–64.

Zachos, J. C., Bohaty, S. M., John, C. M., McCarren, H., Kelly, D. C. & Nielsen, T. (2007), 'The Paleocene-Eocene Carbon Isotope Excursion: Constraints from Individual Shell Planktonic Foraminifer Records', *Royal Society Phil. Trans. A* **365**, 1829–1842, doi:10.1098/rsta.2007.2045.

Zachos, J. C., Pagani, M., Sloan, L., Thomas, E. & Billups, K. (2001), 'Trends, rhythms, and aberrations in global climate 65 Ma to present', *Science* **292**, 686–693.

Zachos, J. C., Röhl, U., Schellenberg, S. A., Sluijs, A., Hodell, D. A., Kelly, D. C., Thomas, E., Nicolo, M., Raffi, I., Lourens, L. J., McCarren, H. & Kroon, D. (2005), 'Rapid acidification of the ocean during the Paleocene-Eocene Thermal Maximum', *Science* **308**, 1611–1615.

Zachos, J. C., 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.

Zachos, J. C., Wara, M. W., Bohaty, S. M., Delaney, M. L., Rose-Petrizzo, M., Brill, A., Bralower, T. J. & Premoli-Silva, I. (2003), 'A transient rise in tropical sea surface temperature during the Paleocene-Eocene Thermal Maximum', *Science* **302**, 1551–1554.

Zeebe, R. E. (2011), 'Where are you heading Earth? (Commentary)', *Nature Geosci.* **4**, 416–417.

Zeebe, R. E. (2012a), 'History of seawater carbonate chemistry, atmospheric CO_2, and ocean acidification', *Annu. Rev. Earth Planet. Sci* **40**, 141–165.

Zeebe, R. E. (2012b), 'LOSCAR: Long-term Ocean-atmosphere-Sediment CArbon cycle Reservoir Model v2.0.4', *Geosci. Model Dev.* **5**, 149–166.

Zeebe, R. E. & Komar, N. (2010), 'Constraints on transient pCO_2 variations based on oceanic calcium, CCD, and terrestrial weathering', *Geochim. Cosmochim. Acta Suppl.* **74(11)**, A1197.

Zeebe, R. E. & Ridgwell, A. (2011), Past changes of ocean carbonate chemistry, *in* Gattuso, J.-P. and L. Hansson, ed., 'Ocean Acidification', Oxford University Press, pp. 21–40.

Zeebe, R. E. & 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(12)**, 1104, doi:10.1029/2003GC000538.

Zeebe, R. E. & Wolf-Gladrow, D. A. (2001), *CO_2 in Seawater: Equilibrium, Kinetics, Isotopes*, Elsevier Oceanography Series, Amsterdam, pp. 346.

Zeebe, R. E. & Zachos, J. C. (2007*a*), 'Ocean acidification in the early Eocene and Anthropocene', *EOS Trans. AGU* **88(52)**, Fall Meet. Suppl., Abstract OS14A–04.

Zeebe, R. E. & Zachos, J. C. (2007*b*), 'Reversed deep-sea carbonate ion basin-gradient during Paleocene-Eocene Thermal Maximum', *Paleoceanogr.* **22**, PA3201, doi:10.1029/2006PA001395.

Zeebe, R. E., Zachos, J. C., Caldeira, K. & Tyrrell, T. (2008), 'Oceans: Carbon Emissions and Acidification (in Perspectives)', *Science* **321**, 51–52, doi:10.1126/science.1159124.

Zeebe, R. E., Zachos, J. C. & Dickens, G. R. (2009), 'Carbon dioxide forcing alone insufficient to explain Palaeocene-Eocene Thermal Maximum warming', *Nature Geosci.* **2**, 576–580, doi:10.1038/ngeo578.

Fig. 1 Consequences of anthropogenic carbon release for various CO_2 emission scenarios (Zeebe et al., 2008); t_R = release time. Simulations were performed with the LOSCAR model: Long-term Ocean-atmosphere-Sediment CArbon cycle Reservoir model (Zeebe, 2012b).

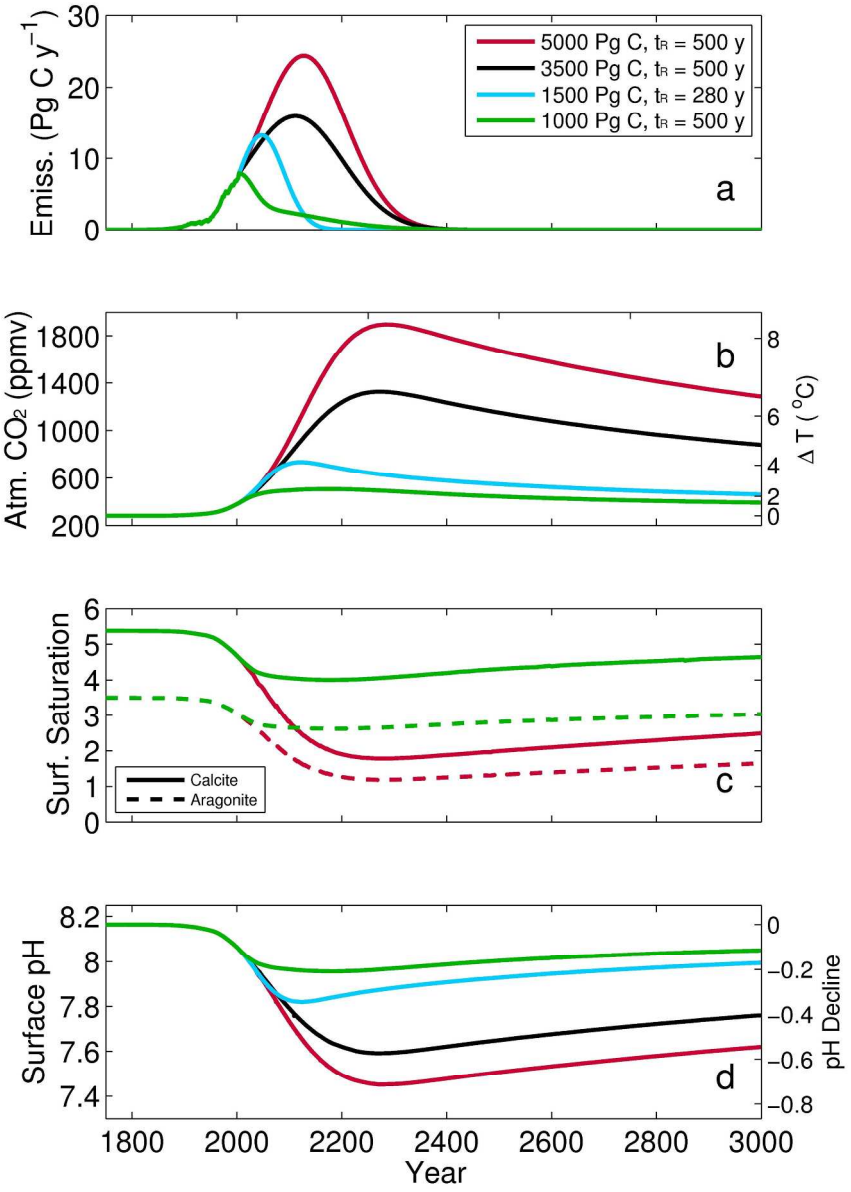
Fig. 2 Effect of releasing 3,000 Pg C over various time intervals during the PETM (Zeebe et al., 2009; Zeebe, 2012b). The source carbon has a $\delta^{13}C$ value of −50‰; 40% of the carbon was injected into the deep Atlantic. Note that the Pacific CCD shoaling was much less pronounced than in the Atlantic (Zeebe et al., 2009).

Fig. 3 Two estimates of the duration of the carbon isotope excursion and $CaCO_3$ dissolution event at ODP Site 1266, Walvis Ridge, in the South Atlantic (Zachos et al., 2005). One estimate is based on orbital cycle stratigraphy (Röhl et al., 2007), the other on extraterrestrial $^3He_{ET}$ concentrations (Murphy et al., 2010). 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 (2010) using just the $^3He_{ET}$ age constraints. We note that an undetermined portion of the clay-layer (0% $CaCO_3$) represents upper Paleocene material deposited prior to the PETM/CIE and thus adds (10 to 30 kyr) to the total duration of the event.

Fig. 4 The pelagic sediment evidence for ocean acidification during the PETM. (A) Percent calcite (%$CaCO_3$) showing the dissolution horizon, and (B) weight-percent coarse fraction (wt% CF) records for three sections from Walvis Ridge (Sites 1262, 1263, 1266) and one from the Weddell Sea (Site 690) (Kelly et al., 2010). The age model is based on cycle (orbital) stratigraphy (Röhl et al, 2007). The coarse fraction is comprised primarily of 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 <30 µm fraction, thus diluting the >63 µm fraction.

Fig. 5 Comparison of the effects of anthropogenic Business-as-USual emissions (total of 5,000 Pg C over 500 years) and PETM carbon release (3,000 Pg C over 6 kyr) on the surface ocean saturation state of calcite.

Fig. 6 Long-term legacy of massive carbon input to the Earth system: Anthropocene vs. PETM. (a) Fossil fuel emissions: total of 5,000 Pg C over 500 years. (b) PETM carbon release: 3,000 Pg C over 6 kyr plus ~1,500 Pg over >50 kyr. Note different y-axes scales in (a) and (b). (c) Simulated evolution of atmospheric CO_2 in response to the carbon input using the LOSCAR model (Zeebe et al., 2009; Zeebe, 2012b).



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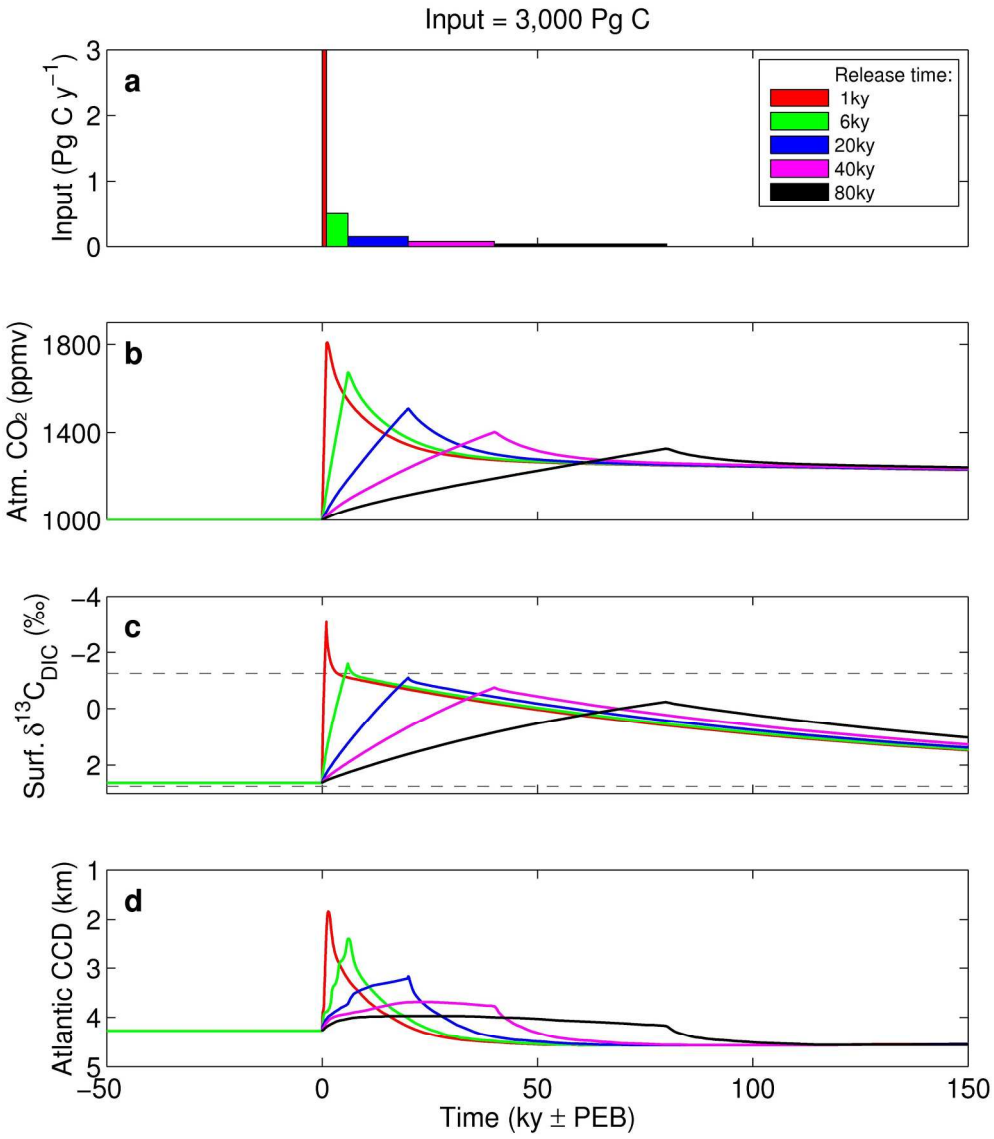

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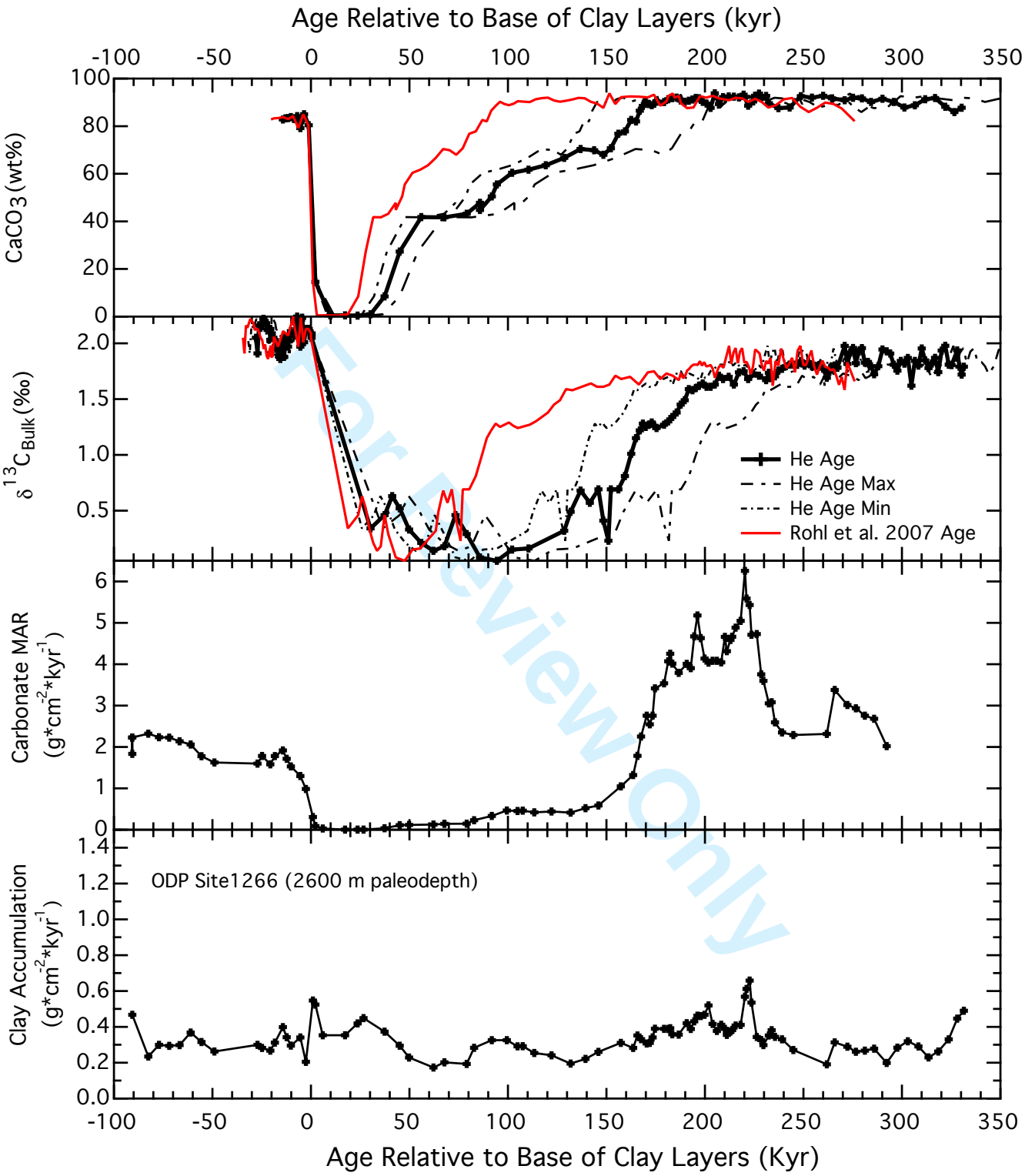


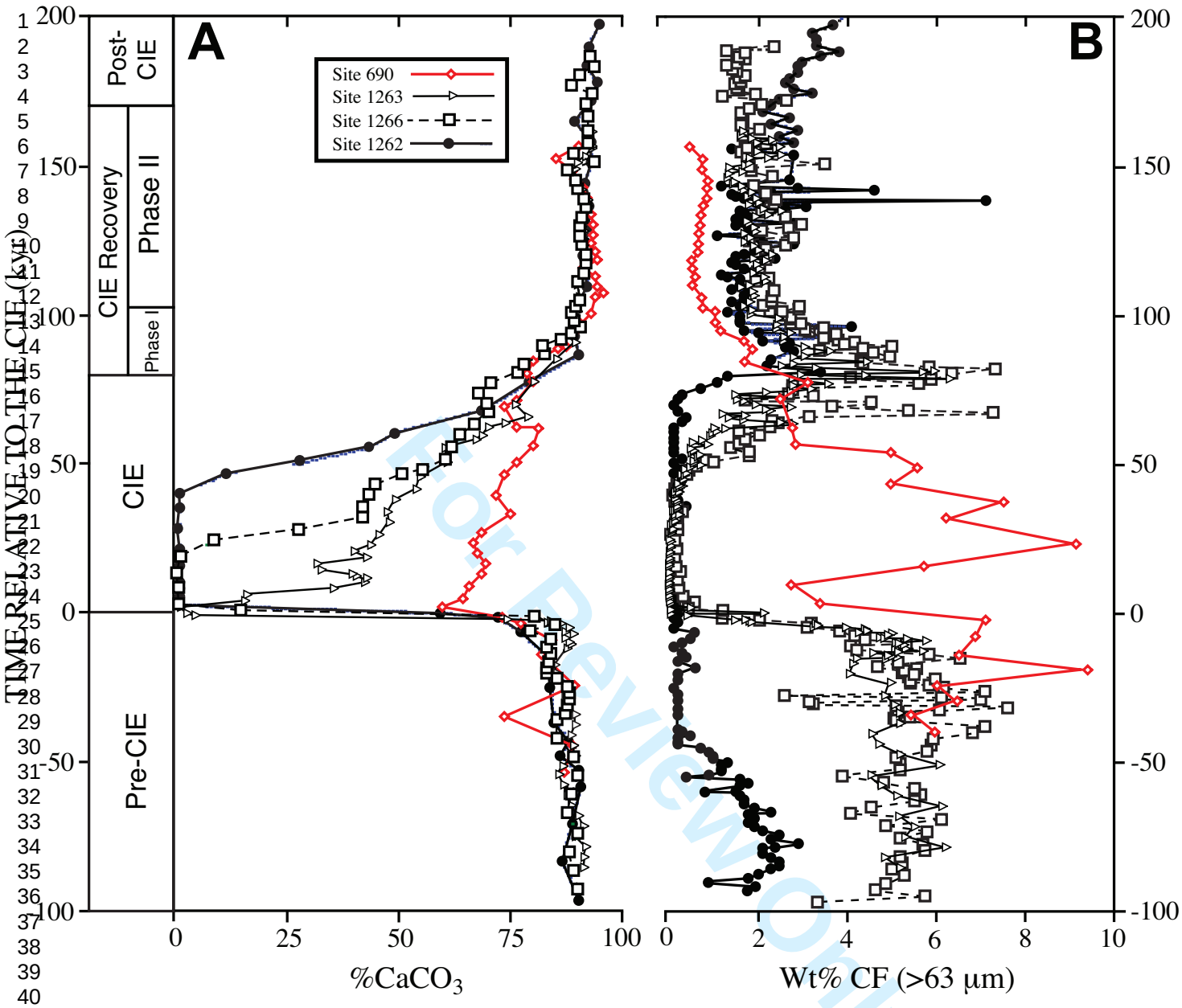
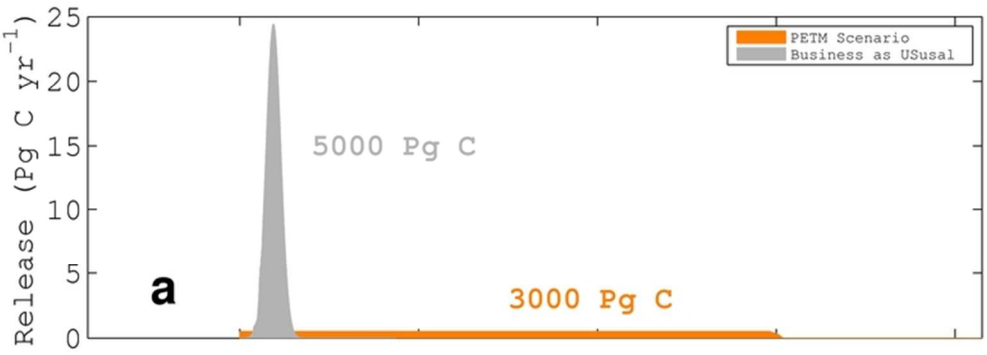


Figure 4.
Kelly et al.



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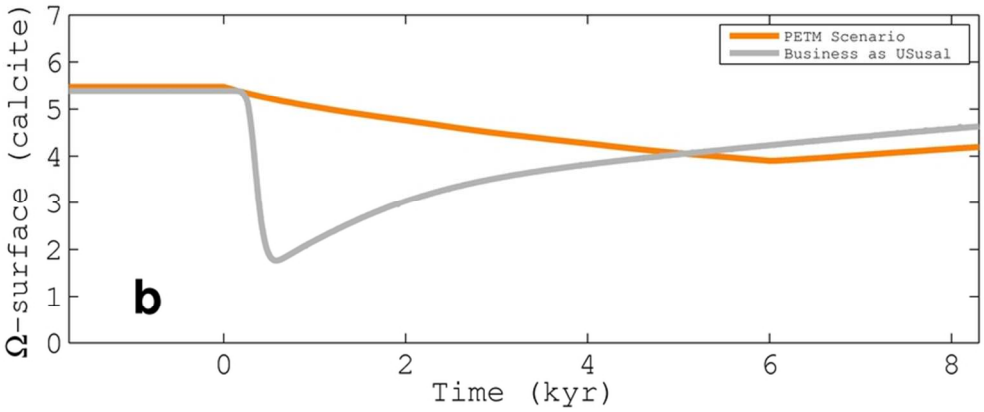

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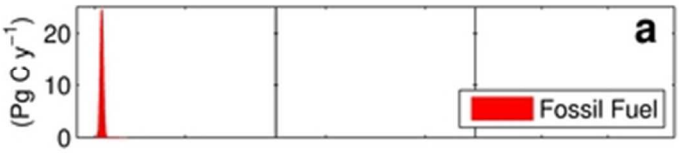

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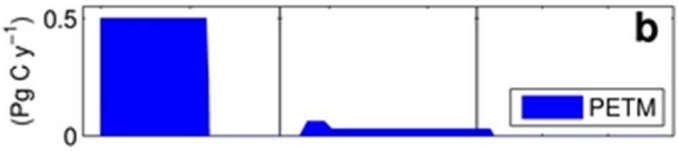

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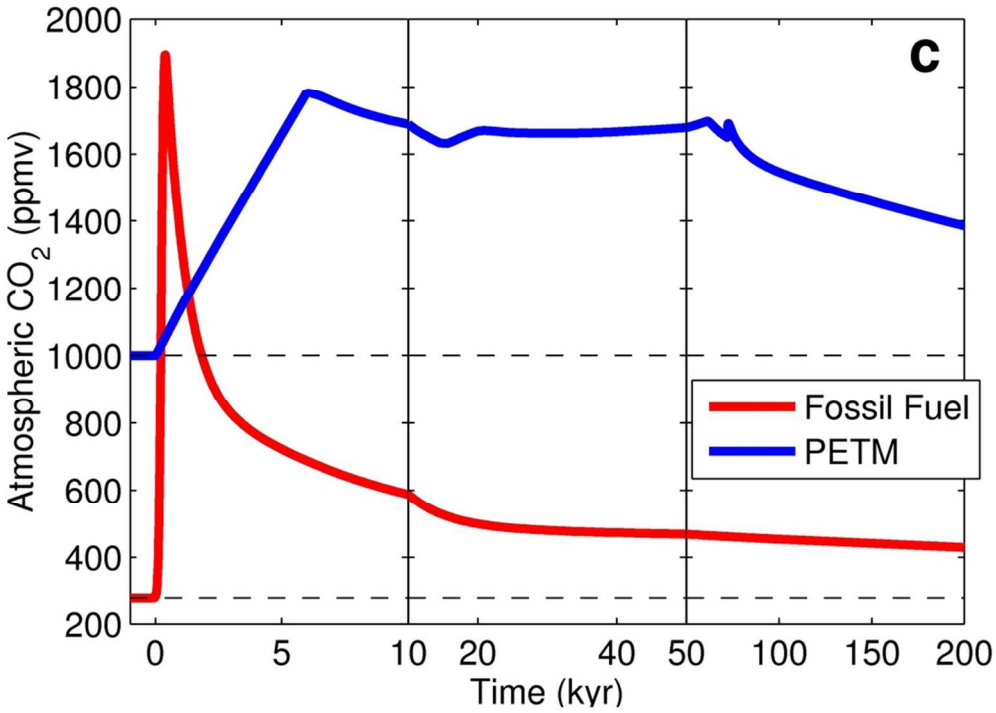

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