

BY LEE R. KUMP, TIMOTHY J. BRALOWER, AND ANDY RIDGWELL

OCEAN ACIDIFICATION IN DEEP TIME

Reconstruction of Alexander Island fossil forests, Antarctica, mid-Cretaceous (~ 100 million years ago). The reconstruction based on the work of J. Howe and J. Francis, University of Leeds, and work of the British Antarctic Survey. Artwork by R. Nicholls, <http://www.paleocreations.com>. The original painting is housed at the British Antarctic Survey, Cambridge, UK.

ABSTRACT. Is there precedence in Earth history for the rapid release of carbon dioxide (CO_2) by fossil fuel burning and its environmental consequences? Proxy evidence indicates that atmospheric CO_2 concentrations were higher during long warm intervals in the geologic past, and that these conditions did not prevent the precipitation and accumulation of calcium carbonate (CaCO_3) as limestone; accumulation of alkalinity brought to the ocean by rivers kept surface waters supersaturated. But these were steady states, not perturbations. More rapid additions of carbon dioxide during extreme events in Earth history, including the end-Permian mass extinction (251 million years ago) and the Paleocene-Eocene Thermal Maximum (PETM, 56 million years ago) may have driven surface waters to undersaturation, although the evidence supporting this assertion is weak. Nevertheless, observations and modeling clearly show that during the PETM the deep ocean, at least, became highly corrosive to CaCO_3 . These same models applied to modern fossil fuel release project a substantial decline in surface water saturation state in the next century. So, there may be no precedent in Earth history for the type of disruption we might expect from the phenomenally rapid rate of carbon addition associated with fossil fuel burning.

INTRODUCTION

As Roger Revelle and Hans Suess pointed out over 50 years ago, humanity is performing “the great geophysical experiment” by pumping vast quantities of carbon dioxide into the atmosphere (Revelle and Suess, 1957). One result of this experiment is an atmosphere that already contains more carbon dioxide than at any time in last 800,000 years of Earth history (as indicated from the analysis of bubbles trapped in Antarctic ice; Lüthi et al., 2008) and probably more than has occurred in several tens of millions of years (from various marine and terrestrial proxies; Royer, 2006). As summarized in detail by Feely et al.

(2009), the dissolution of excess CO₂ built up in the atmosphere in the ocean's surface waters is also lowering ambient pH in a phenomenon known as "ocean acidification" (Caldeira and Wickett, 2003). By 1994, the ocean had taken up approximately 50% of the CO₂ from fossil fuel burning and cement manufacture (Sabine et al., 2004), suppressing the pH of surface waters globally by an estimated ~ 0.1 pH units and equivalent to a ~ 30% increase in hydrogen ion (H⁺) concentration (Kleypas et al., 2006). Reconstructions suggest that ocean surface pH has not been this low for at least the last two million years (Hönisch et al., 2009). With continuing CO₂ emissions, ocean pH will decline further, potentially by another 0.7 pH units by the time fossil fuels are exhausted (Caldeira and Wickett, 2003; recent work of author Ridgwell and Daniela Schmidt, University of Bristol). Thus, there are no precedents in recent Earth history for what will be the immediate and direct consequences of the release of CO₂ into the atmosphere and its concurrent dissolution in the ocean's surface waters.

Both expanded observations and computer modeling, rooted in the improved process understanding of previous laboratory results and field studies, are essential for predicting the outcome of this great experiment and are the subject of other papers in this issue. But, laboratory experiments are necessarily limited in their spatial and temporal scales, while computer models must in effect be "told" the potential behaviors of the Earth system in response to massive CO₂ release before they can be used to predict anything meaningful. Currently, we have insufficient knowledge to predict confidently

the future impacts of ocean acidification on marine organisms and ecosystems.

The geologic record of ocean acidification can provide guidance as to the response of the global carbon cycle to an abrupt massive CO₂ release to the atmosphere, and how and at what rate pre-perturbation conditions are eventually restored. Studies of the geologic record may also provide valuable insights into potential biotic impacts and time scales of recovery. Such knowledge may prove particularly valuable in light of the often apparently conflicting predictions of the impact of acidification in previous laboratory manipulation experiments (summarized in Ridgwell et al., 2009). Furthermore, the large range of spatial and seasonal variability in environmental conditions for plankton in the ocean, in conjunction with the genetic diversity even with an assumed single "species," may impart an ability for species to adapt in the face of continuing ocean acidification, something that monocultures maintained in the laboratory and subjected to near instantaneous decreases in pH are unable to reflect. Evidence for the ability (or otherwise) of marine organisms to adapt to ocean acidification events may be extractable from the geologic record.

However, no interval of Earth's past is a perfect analog for today. We live in a glacial "ice house" era (Figure 1) that began 34 million years ago with the growth of ice sheets on Antarctica, and heightened with the spread of such conditions to the Northern Hemisphere during the Pliocene (since 2.7 million years ago). In contrast, most of the best-studied potential analogs for the future are events initiated during "hot house" (greenhouse) intervals of Earth history

(Figure 1)—times that exhibit little to no evidence for polar ice sheets and when atmospheric CO₂ was probably much higher. Moreover, because of continental drift and plate tectonics, the position of the continents; the elevation, orientation, and location of mountain belts; and thus the patterns of atmospheric and oceanic circulation were likely quite different from today. Add to that profound changes in global ocean chemistry and biota, and it becomes difficult to compare directly Earth's observed response to elevated CO₂ in the distant past with our projections of its response in the future (Goodwin et al., 2009; recent work of author Ridgwell and Daniela Schmidt, University of Bristol). Furthermore, in past warming events, inferred to have been driven by sharp increases in atmospheric CO₂ such as during the Cretaceous (146–66 million years ago) and Paleogene (66–23 million years ago), ocean acidification is only one of a host of potential environmental causes that must be considered in explaining the observed changes in the composition and diversity of the marine biota at the time. Finally, in interrogating the geologic record, temporal resolution is often compromised by intervals of nondeposition, physical mixing, bioturbation (the vertical mixing of sediments by the activity of benthic organisms), dissolution, and erosion, while accurate ages may be difficult to assign with absolute (radiometric) dates being few and far between. These variables create additional difficulties in drawing conclusions regarding cause and effect.

We proceed with these caveats in mind. First, we summarize the fundamental theoretical constraints imposed on the oceanic response to rapid CO₂

Lee R. Kump (*lkump@psu.edu*) is Professor of Geosciences, Pennsylvania State University, University Park, PA, USA. **Timothy J. Bralower** is Professor of Geosciences, Pennsylvania State University, University Park, PA, USA. **Andy Ridgwell** is Royal Society University Research Fellow, University of Bristol, Bristol, UK.

additions by the carbonate chemistry of the ocean, the adjustment of the alkalinity balance of the marine carbon cycle, and the response of the global carbon cycle to climate changes attendant upon variations in atmospheric CO₂ levels. We then march through Earth history, highlighting aspects of the record of global carbon cycle response to long-term

forcings and more abrupt perturbations with potential implications for calcification. Finally, we critically discuss the relevance of the geological record to the future and to what extent parallels can safely be drawn, especially if we continue to follow the massive total CO₂ release associated with “business as usual” fossil fuel burning trajectories.

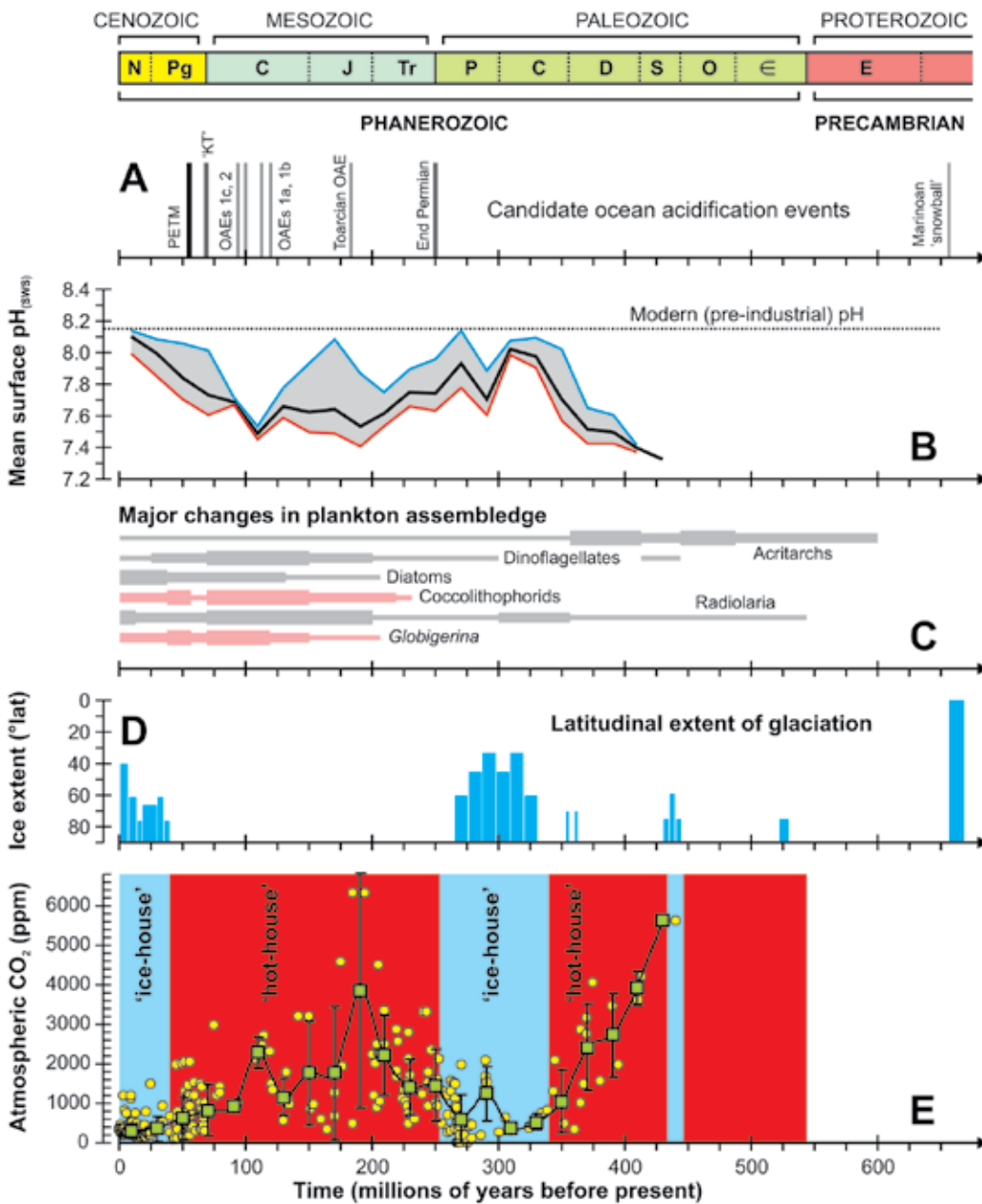


Figure 1. The geological context for ocean acidification. (A) Candidate ocean acidification events. (B) Model reconstruction of long-term changes in Phanerozoic mean ocean surface pH calculated at 20 million year intervals (Ridgwell, 2005). The solid black line represents the response of the global carbonate cycle to the mean paleo $p\text{CO}_2$ reconstruction, while the grey-filled envelope reflects the response to the uncertainty (one standard deviation) in paleo- $p\text{CO}_2$. The general trends are consistent with other modeling efforts and proxy data, as summarized in Arvidson et al. (2006). (C) Major changes in plankton assemblages (Martin, 1995). Calcifying taxa are highlighted in pink with noncalcifying taxa shown in grey. The rise during the early to mid Mesozoic of the importance of Globigerina is shown as broadly representative of the timing of changes in planktic foraminiferal taxa in general, although the evolution of the first foraminifera taxa occurred earlier in the mid Paleozoic (Martin, 1995). (D) Latitudinal extent of glaciation versus time (Crowley and Burke, 1998). (E) Phanerozoic evolution of atmospheric $p\text{CO}_2$ reconstructed from proxy records by Royer et al. (2004). Paleo- $p\text{CO}_2$ data have been binned into 20 million year intervals, with the mean and error (one standard deviation) for each interval shown as horizontal black dash and vertical grey bar, respectively. The geological periods from the end Precambrian to the end of the Phanerozoic are delineated at the top, running from Ediacran ('E'; 630 to 542 million years ago) at the far right through to Paleogene ('Pg') and Neogene ('N') on the left-hand side.

GLOBAL CARBON CYCLE RESPONSES TO OCEAN ACIDIFICATION

The ocean is a well-designed machine for maintaining a balance between the inputs of carbon associated with riverine and hydrothermal discharges and seafloor-weathering exchanges, and outputs through sedimentary burial

and seafloor weathering (Broecker and Peng, 1982; Delaney and Boyle, 1988). Of these, riverine input and sedimentary outputs dominate on the ca. 1 kyr to 100 kyr time scales relevant to ocean acidification events recorded in the geological record, and with carbon in inorganic forms dominating organic carbon (Figure 2a). There actually are

two balances involved in the long-term inorganic carbon cycle: one with dissolved inorganic carbon (DIC) and the other with alkalinity (ALK). DIC is defined as the sum of the concentrations of the inorganic carbon species, dissolved CO_2 , bicarbonate (HCO_3^-), and carbonate (CO_3^{2-}) ions:

$$\text{DIC} = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]. \quad (1)$$

(Carbonic acid, H_2CO_3 , is present in such minute concentrations in ambient seawater that it is ignored for all practical purposes.) ALK is the acid-neutralizing capacity of seawater and is formally defined as the difference between conservative cations (e.g., Na^+ , Ca^{2+}) and anions (e.g., Cl^- , SO_4^{2-}) in seawater (Zeebe and Wolf-Gladrow, 2001). This difference is plugged mainly by the buffers of the carbonate system, called carbonate alkalinity (cALK). Carbonate alkalinity is dependent on the charge of the species: singly charged anions can only react with one proton, whereas doubly charged anions can react with two:

$$\text{cALK} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]. \quad (2)$$

On long time scales (millions of years), both the DIC and ALK inputs and outputs must balance; otherwise, ocean chemistry, and atmospheric CO_2 content, would drift upwards or downwards inexorably (Berner and Caldeira, 1997). Negative, stabilizing feedbacks ensure that this balance is achieved.

For example, following a volcanic eruption that emitted large quantities of CO_2 into the atmosphere, the atmospheric CO_2 concentration would rise, and as it did, air-sea exchange of CO_2 would shift in favor of ocean uptake (Figure 2b). The ocean's DIC

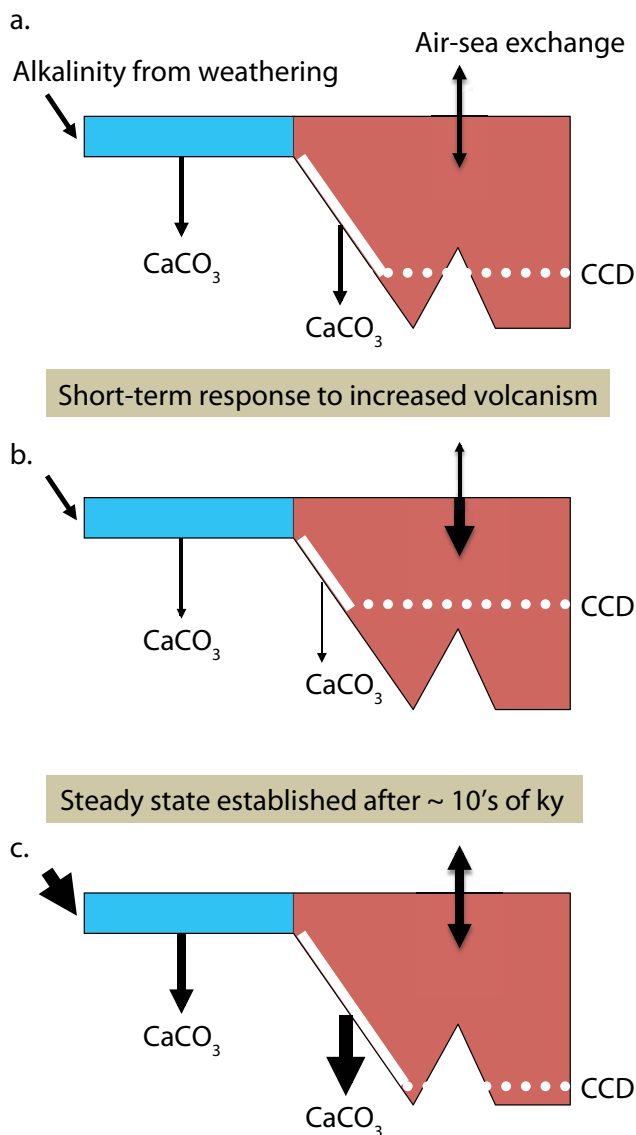
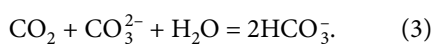


Figure 2. Schematic response of the global carbon cycle to CO_2 release and ocean acidification showing the alkalinity balance of the ocean and response to a step increase in volcanic CO_2 emission. (a) Initial steady state. (b) Short-term (millennial) response to increased volcanism. (c) Final steady state with sustained elevated rates of volcanism. CCD = calcite compensation depth.

concentration would increase, but its alkalinity would be unaffected (as CO_2 is uncharged). If we subtract Equation 1 from Equation 2 and ignore the small contribution from CO_2 , we see that the difference $\text{cALK} - \text{DIC} = [\text{CO}_3^{2-}]$ (Broecker and Peng, 1982). In other words, the mixing of volcanic CO_2 into the ocean, and hence increase in DIC but at constant ALK, causes a reduction in the carbonate ion concentration. The overall chemical reaction for this is



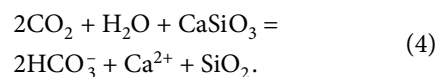
This reduction of carbonate ion concentration is important to calcifying organisms, because not only is it associated with a decrease in pH, it also reduces the saturation state of the ocean with respect to calcium carbonate (CaCO_3) minerals. The stability of CaCO_3 is proportional to the concentration (technically: activity) product of Ca^{2+} (spatially rather uniform and largely invariant on sub-million-year time scales) and CO_3^{2-} . The saturation state (Ω) is the relative deviation of ambient chemical conditions from thermodynamic equilibrium with the mineral phase ($\Omega = 1$) at any given temperature and pressure. The closer the saturation state to $\Omega = 1$, the lower the thermodynamic driving force for CaCO_3 precipitation, with carbonate chemistry manipulation experiments on corals indicating that this is translated into a reduction of calcification rates (e.g., Doney et al., 2009).

The solubility of calcium carbonate minerals is also dependent on pressure (depth), and in each ocean basin there is a saturation horizon below which CaCO_3 will start to dissolve. Deeper down, a point is reached at which the

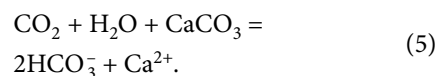
rate of CaCO_3 dissolution in sediments is sufficient to equal the rate of supply—the “calcite compensation depth” (CCD; Figure 2). At greater depths still, there is no preservation of CaCO_3 in the sediments. Adding CO_2 to the system and lowering the ocean saturation state means that the CCD shoals and less preservation and burial of CaCO_3 occur in deep-sea sediments globally. Not only may a CO_2 addition cause a transition from carbonate-rich sediments to clay, but an imbalance is induced between the rate of solutes supplied to the ocean by the weathering of rocks on land and (now reduced) sedimentation. Both main controls on carbonate mineral preservation—depth and the accumulation of (metabolic) CO_2 —can be seen in the distribution of CaCO_3 in the surface sediments of today’s ocean (Figure 3).

The rate of terrestrial weathering also can respond to CO_2 addition. Because CO_2 is a climatically active gas, an increase in its atmospheric concentration tends to increase the average temperature of the planet, and as a consequence of increased evaporation, global rainfall rates also increase. The combination of higher temperatures and more rainfall creates more favorable conditions for the weathering of rocks exposed on the land surface. The direct effect of increased CO_2 concentration in the rainwater (equilibrated with the atmosphere) in enhancing the weathering rate is rather small, because most soil environments have CO_2 concentrations that greatly exceed the atmospheric partial pressure, a result of root respiration and microbial breakdown. The weathering process involves reactions between calcium-silicate minerals (here simply represented by “ CaSiO_3 ”) and carbonic

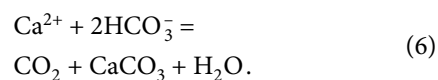
acid, H_2CO_3 (CO_2 dissolved in rainwater, H_2O); the CO_2 is neutralized, and bicarbonate is produced:



A similar reaction can be written for limestone weathering:



The key difference between the two reactions is that silicate weathering (Equation 4) requires two moles of atmospheric CO_2 in order to create two moles of bicarbonate (HCO_3^-), whereas in carbonate weathering (Equation 5), only one mole is required. In both cases, a single mole of carbonate will eventually be precipitated and buried, via



Hence, in (Equations 5 + 6), the CO_2 removed from the atmosphere is returned, whereas in (Equations 4 + 6), CO_2 is permanently consumed, and at a rate that must balance by the long-term average rate of CO_2 outgassing from the mantle (Berner and Caldeira, 1997), assuming no imbalance between the weathering and burial of organic carbon.

Rivers carry the dissolved products of the weathering reactions to the ocean. Thus, an increase in atmospheric CO_2 (from volcanism or some other cause) will increase the alkalinity input to the ocean (Figure 2c). Over time, this increase will reverse the initial shoaling of the CCD created by input of CO_2 from the atmosphere and ocean acidification, and then over-deepen the CCD sufficiently to create a new net burial rate of CaCO_3 (mineral-packaged alkalinity)

equal to the new, higher riverine input. At this point, steady state between inputs and outputs is re-established and initial surface saturation states are approximately restored or even exceeded. Following cessation of volcanic activity and thus excess CO_2 supply, the system would return to its original state over tens to hundreds of millennia as the remaining excess CO_2 in the atmosphere is gradually removed by higher rates of silicate weathering and CaCO_3 burial.

Based on this theory, we have predictable expectations for the rock record of pulsed additions of massive CO_2 to the ocean/atmosphere system and ocean acidification. On short time scales (millennia to tens of millennia), we expect to see the effects of ocean acidification dominating: dissolution of seafloor carbonates, and, perhaps,

reduction or even cessation of calcification in surface waters. Over tens of millennia, however, the resulting greenhouse climate promotes enhanced rock weathering and neutralization of the CO_2 and hence enhanced burial of CaCO_3 . As encapsulated into a computer model of the climate system and global carbon cycle (Ridgwell, 2007), operation of this cascade of processes predicts a distinctive sequence profile in composition in the rock record, as Figure 4 shows. For a more prolonged volcanic interval and hence sustained higher rate of CO_2 release, we would expect an acidification event followed by an approach to a new state with a deeper CCD and better carbonate preservation. In short, alkalinity builds up in the ocean until saturation state is sufficiently high to support a burial rate of CaCO_3 that

matches the (elevated) rate of alkalinity input from weathering. Somewhat counterintuitively, this higher saturation state is achieved under a high $p\text{CO}_2$ atmosphere and thus at a lower pH in the surface ocean than before the increase in volcanism. Next, we discuss evidence for the occurrence of ocean acidification events in Earth history, both prolonged and abrupt, as well as observations of any biotic response.

OCEAN ACIDIFICATION AND CALCIFICATION IN EARTH HISTORY

The Paradox of “Carbonate Factories” in a High CO_2 (Archean) World

Consider first the strongly elevated partial pressures of carbon dioxide, as high as 0.1 bar, invoked for Earth’s

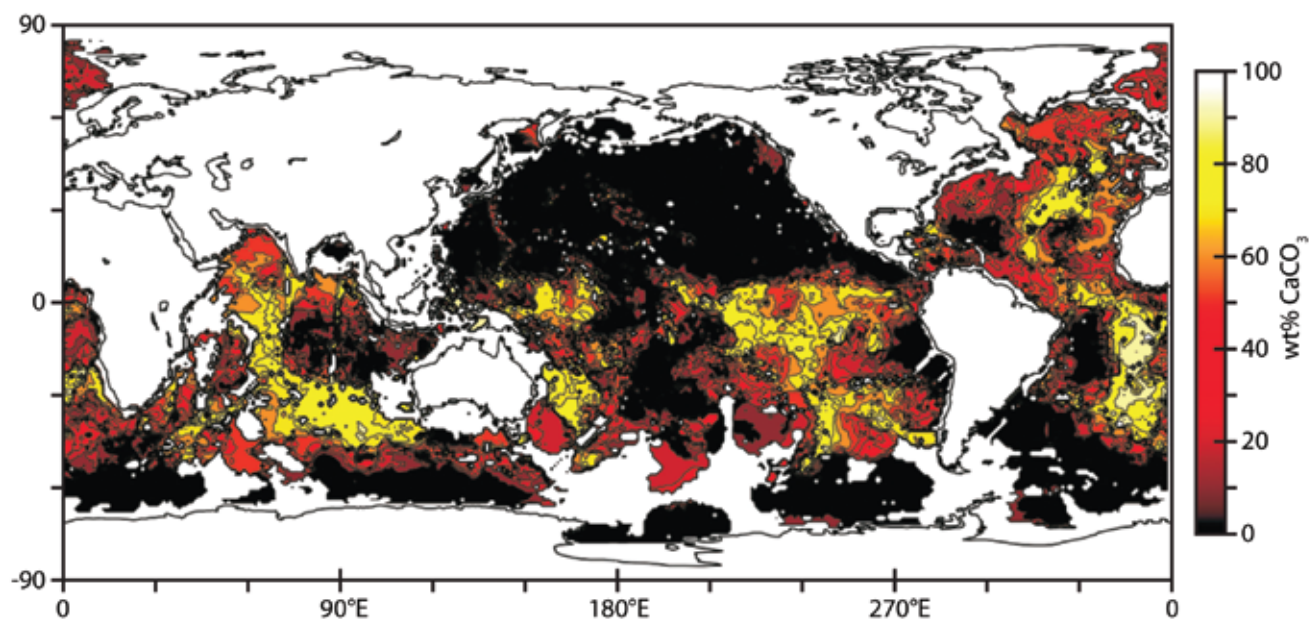


Figure 3. Carbonate burial in the deep sea. Distribution of the calcium carbonate (CaCO_3) content of the surface sediments of the deep sea. The apparent predominance of CaCO_3 accumulation taking place in the Atlantic and Indian oceans compared to much more sparse accumulation in the Pacific is primarily a consequence of the greater accumulation of metabolic CO_2 in deep Pacific waters, which drives a greater degree of undersaturation and shoals the depth of the calcite compensation depth, below which CaCO_3 is absent from the sediments. Topographic “highs” can be picked out as areas of higher wt% CaCO_3 compared to sediments elsewhere in the same basin at similar latitudes. Areas with no data coverage (parts of the Southern Ocean, and many of the continental margins) are left blank. Data from Archer (1996) and re-drawn after Ridgwell and Zeebe (2005)

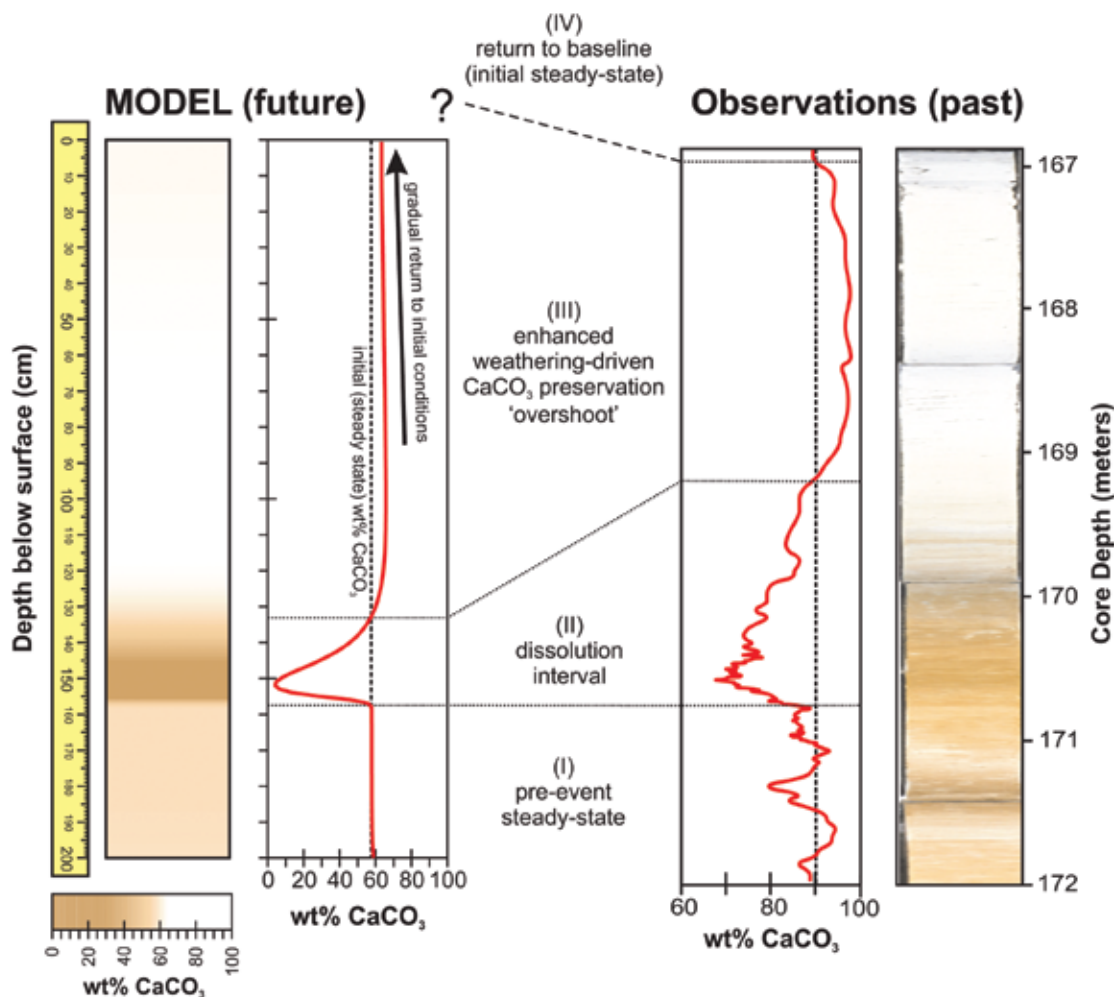


Figure 4. The (marine geological) signature of ocean acidification. The figure shows both model (left) and data (right) views of how massive CO₂ release and ensuing ocean acidification might be recorded in the geologic record. Highlighted are the intervals of: (I) initial relatively high CaCO₃ content (wt%) sediments, (II) CaCO₃ dissolution creating a much more clay-rich (and hence browner color) layer, (III) enhanced silicate weathering and alkalinity supply driving oversaturation and an overshoot in wt% CaCO₃, and (IV) eventual recovery to the initial state. The observations are from Ocean Drilling Program Site 690 in the Weddell Sea and span the Paleocene-Eocene Thermal Maximum (PETM) global warming and acidification event. The high-resolution CaCO₃ curve is from Farley and Eltgroth (2003) and the core picture from Kelly et al. (2005). The (future) model predictions

are made using the GENIE-1 Earth system model (e.g., Ridgwell, 2007; Ridgwell and Hargreaves, 2007) and assuming a total CO₂ release of 4500 on the time scale of (past and future) industrial consumption (400 years). The GENIE-1 model is configured as described in Ridgwell (2007) but with sediment bathymetry regridded to ×2 resolution (Ridgwell and Hargreaves, 2007). The model has been further extended as used here: modifying carbonate and silicate rock weathering rates as a function of global mean annual land surface air temperature following the pre-vascular plant weathering formulations of Berner (1994). This extension accounts for the ultimate CO₂ neutralization mechanism (silicate weathering) and allows capture of the carbonate burial “overshoot.” The predicted response to a pulse of CO₂ is thus: signs of dissolution followed by enhanced CaCO₃ deposition, and overcompensation that removes the added CO₂ (now as alkalinity). Note that on the 200 kyr time scale of the simulation, final recovery to the initial state has not yet been achieved, highlighting the exceptionally long-lived nature of the CO₂-acidification perturbation (Archer et al., 2009).

distant past to compensate for decreased solar irradiance in Earth’s early history (e.g., Kasting, 1988). A surface ocean equilibrated with such a CO₂-enriched atmosphere would be acidic, with a pH perhaps as low as 5.7 (Grotzinger and Kasting, 1993). One might think that these conditions would have precluded the formation of limestone. Yet, there are abundant limestones and dolostones (a rock composed of dolomite, a Ca, Mg carbonate mineral) of Archean age (older than 2.5 billion years; e.g., Grotzinger

and Kasting, 1993). These rocks include the remarkable stromatolites, likely to have been formed by calcification induced in bacterial mats, suggesting that there was no particular impediment to carbonate mineral deposition despite the very high CO₂ and low pH conditions on early Earth.

Similarly, although much of the Cretaceous is considered to be a “super-greenhouse” interval with high atmospheric CO₂ (Figure 1), at times perhaps as high as 2000 ppm (e.g., Royer, 2006),

this period is also characterized by the massive and widespread deposition of chalks (from which the Cretaceous takes its name). Proxy evidence and numerical modeling (summarized in Arvidson et al., 2006) indicate that ocean pH has risen over the last 100 million years; mean ocean surface pH was perhaps as much as 0.8 pH units lower than modern in the mid-Cretaceous, 100 million years ago (Figure 1; Ridgwell, 2005), lower even than in most future predictions (e.g., Caldeira and Wickett,

2003). Furthermore, it was during the Cretaceous (and the preceding Jurassic) that calcareous plankton diversified and proliferated (Figure 1). Hence, the key, but rather counterintuitive result, is that on long time scales, ocean pH and atmospheric CO₂ are decoupled from carbonate mineral saturation state, which is dictated primarily by weathering (in conjunction with the major cation [Ca²⁺, Mg²⁺] content of the ocean). Actually, saturation is not entirely decoupled geologically from pH and CO₂, as all things being equal, at high CO₂ (and a warmer climate), enhanced weathering requires higher carbonate burial and hence higher ocean saturation.

Thus, the presence of “carbonate factories” with widespread CaCO₃ production and burial is entirely consistent with a high CO₂, low pH world. In long-term quasi-steady-state conditions, there is also sufficient time for evolutionary innovation and adaptation by the biota to low pH conditions. Only in significant and geologically “rapid” departures from steady-state carbon cycling will both pH and saturation fall together, stressing calcifying marine organisms at a rate that may be beyond their ability to adapt and evolve. It is these transient events, in which ocean chemistry may have been perturbed in similar ways to the current “great geophysical experiment,” that we must look to for clues about future responses and biotic impacts.

Carbonate Chemistry Excursions During “Snowball Earth”

The response and recovery from a hypothesized supergreenhouse state following the global glaciations of the late Neoproterozoic (~ 1000–542 million

years ago) represents one of the most acute tests of feedbacks within the Earth system to restore equable environmental conditions. These “snowball Earth” episodes (Hoffman et al., 1998; Hoffman and Schrag, 2002) were multimillion-year glaciations with sea ice extending to the equator. This climate state is quite stable once achieved because of strong ice-albedo feedback; deglaciation presumably required the progressive buildup of CO₂ in the atmosphere to levels considerably higher than that before the glaciation, as high as a *p*CO₂ of 0.1 bar (350 × pre-industrial concentrations; Caldeira and Kasting, 1992) or more. This post-snowball supergreenhouse could be one of the first ocean acidification events in Earth history. Indeed, carbon cycle box models have estimated that ocean surface pH would have likely fallen to below 6.0 prior to the termination of a snowball state (Le Hir et al., 2008b).

However, calcifying organisms had yet to evolve by the late Neoproterozoic—corals did not arise on Earth until the Cambrian, for instance (e.g., Souraf and Savarese, 1995), while the first calcareous benthic foraminifera arose somewhat later, in the Devonian (e.g., Haq and Boersma, 1978). And only later still did calcifying plankton proliferate in the open ocean (e.g., see Figure 1). Furthermore, depending on assumptions regarding maximum glacial conditions and rates of weathering, if any, acidification might have built up only very slowly during an event lasting as long as 30 million years (Le Hir et al., 2008a), while other interpretations of the Neoproterozoic climate (e.g., Hyde et al., 2000) require neither extreme CO₂ buildup nor greatly increased acidification.

The ambiguity in the duration of, and pH of, the ocean during the Neoproterozoic glaciations, in conjunction with the absence of calcifying marine organisms, rules out snowball Earth as a potential analog for helping understand future marine ocean acidification impacts. Yet, assuming elevated CO₂ and hence enhanced greenhouse warming, the geological record following a snowball Earth should provide a window into the response of climate and global biogeochemical cycles to elevated atmospheric greenhouse gas concentrations and recovery of the Earth system through enhanced (silicate) rock weathering on land under higher temperatures and more intense precipitation. Indeed, the immediate aftermath of the glacial event is marked geologically by deposition of “cap” carbonates (Hoffman and Schrag, 2002), which represent the precipitation of a ubiquitous layer of carbonate directly overlying glacial deposits (or glaciated surface). Their very presence is consistent with a carbonate depositional “overshoot” in response to the removal of excess CO₂ from the atmosphere. Their exact thickness and geochemical (and isotopic) properties (e.g., Kasemann et al., 2005) may specifically tell us something about the controls on the rate of weathering and neutralization of added CO₂, albeit in the absence of plant vegetation on land. However, no consensus has emerged as to the causal mechanisms of cap carbonate formation or of the nature of atmospheric-oceanic conditions under which they were deposited, and some interpretations do not require increased weathering as the source of the precipitated alkalinity (Grotzinger and Knoll, 1995; Kennedy et al., 2001; Ridgwell et al., 2003).

Calcification Crisis During End-Permian Extinction

The latest Permian witnessed the largest mass extinction in Earth history, with as much as 95% of the marine animal species and a similarly high proportion of terrestrial plants and animals going extinct at ~ 251 million years ago (Erwin, 2006). Interestingly, heavily calcified organisms seem to have been preferentially hard hit (Knoll et al., 1996), including the existing major lineages of corals at the time, the Rugosa and Tabulata (Stanley, 2003). The Scleractinia appear abruptly in the succeeding Triassic interval, perhaps arising from “naked forms” of Anthozoa that survived the mass extinction (Stanley, 2003).

The search for the definitive cause(s) of this event continues, but a leading candidate for its trigger is the volcanic eruption of the gigantic Siberian Traps. Timing of this event is, to within analytical uncertainty, coincident with the extinction (Reichow et al., 2002). Moreover, the quantities of volatiles released are potentially unprecedented in Earth history. On its way to the surface, the magma penetrated coal and evaporite deposits that, when heated, released tremendous quantities of CO₂, SO₂, and methylated halogens (Svensen et al., 2008). Estimates of CO₂ release exceed 100,000 Gt (or nearly 30,000 GtC). Estimated average rates of CO₂ release range from 1–2 Gt CO₂ per year for ~ 50,000 years. This rate of release is a factor of 20 or so slower than modern fossil fuel burning, but was sustained for time scales considerably longer than the anticipated anthropogenic release. CO₂ could have been released in more intense pulses that had greater capacity

to disrupt climate and ocean chemistry (Svensen et al., 2008). Moreover, unlike today, the Permian ocean likely lacked a deep-sea CaCO₃ buffer system (Ridgwell, 2005) because planktonic carbonate-producing organisms hadn't yet evolved.

Evidence for considerable seafloor dissolution of CaCO₃ is just beginning to be collected (Payne et al., 2007). Pre-event shallow-marine carbonate deposits in South China, Turkey, and Japan exhibit features that are strongly suggestive of submarine dissolution. However, the interpretation is controversial (Wignall et al., 2009; Payne et al., 2009), with the fundamental issue being whether the dissolution features observed occurred during subaerial exposure (i.e., during weathering) or while submerged, in response to ocean acidification. A broader search for dissolution features and diagnostic criteria is underway. Interestingly, this tentatively identified acidification event was followed by an extended period of inorganic (ooids) and/or microbial carbonate production (e.g., Pruss and Bottjer, 2004), perhaps indicating that surface waters became highly supersaturated. We argue above that this response to a rapid addition of CO₂ to the ocean/atmosphere system is expected.

The Early Aptian Oceanic Anoxic Event

The early Aptian Oceanic Anoxic Event (OAE1a, ~ 120 million years ago; Figure 1) was an interval of dramatic change in climate and ocean circulation. The event was characterized by the occurrence of organic-carbon-rich sediments on a global basis along with evidence for warming and dramatic

change in nanoplankton (largely coccolithophorid) assemblages (Erba, 1994; Bralower et al., 1994). The generally accepted trigger for these changes is the eruption of the Ontong Java Plateau in the western Pacific over a few million years or less (Larson, 1991)—one of the largest “large igneous province” eruptions in Earth history. This eruption likely led to a major increase in atmospheric pCO₂ (Larson, 1991) and therefore had the potential to cause ocean acidification. The event initiated long-term shoaling of the CCD by over 2 km (e.g., Thierstein, 1979).

The OAE1a interval corresponds to wholesale changes in nanoplankton communities, including the demise of one of the most dominant groups in the Early Cretaceous, the nanoconids. The heavily calcified nanoconids occurred in rock-forming abundances, and their near disappearance is one of the most significant events in the 220 million year record of the nanoplankton. The demise of the nanoconids led to a dramatic decrease in nanoplankton carbonate production (Erba and Tremolada, 2004). The surviving nanoconid species were much more rare than those that dominated before OAE1a and were less heavily calcified. Moreover, with the exception of the relatively rare nanofossil taxa *Rucinolithus terebrodentarius* and *Assipetra infracretacea*, which were heavily calcified, the OAE1a interval was marked by a substantial increase in less-heavily calcified taxa (Erba, 1994; Bralower et al., 1994). Were these changes in response to surface ocean acidification?

Weissert and Erba (2004) and Erba (2004) interpreted the substantial changes in nanoplankton assemblages

in the OAE1a interval to be the result of increased $p\text{CO}_2$. These authors followed the conclusion of Paasche (1962) that calcification among nanoplankton is a strategy to maintain CO_2 levels inside the cell in order to sustain photosynthesis, and speculated that during intervals of increased $p\text{CO}_2$, calcification was less vital for nanoplankton to thrive. Even though the experimental basis for this assertion is controversial (e.g., Iglesias-Rodriguez et al., 2008), the pronounced change in the calcification of nanoplankton that accompanied the substantial increase in $p\text{CO}_2$ during OAE1a makes the interpretation highly plausible.

Paleocene-Eocene Thermal Maximum

The Paleocene-Eocene Thermal Maximum (PETM; 55.8 million years ago) was a short-lived (~ 200,000 years) global warming event. Temperatures increased by 5–9°C from equator to pole, and the Atlantic CCD shoaled to less than 2000 m (Zachos et al., 2005). A distinctive drop in the ratio of ^{13}C to ^{12}C in the ocean (as recorded in carbonate and organic-carbon-rich sediments) indicates that this event was caused by an abrupt release of thousands of gigatons of carbon from a fossil reservoir consisting of sedimentary organic carbon or seafloor methane clathrate, organic materials typically strongly depleted in ^{13}C (Dickens et al., 1995; Panchuk et al., 2008; Zeebe et al., 2009).

The PETM was marked by the largest deep-sea mass extinction among calcareous benthic foraminifera in the last 93 million years (e.g., Thomas, 1998), perhaps a response to deep-water acidification, but perhaps also a response

to basinal anoxia and/or increased temperatures and hence metabolic rates (Thomas, 2007). Other marine groups fared better, although shallow-water tropical carbonate platforms were transformed from coral-algal reefs to large-foraminifera-dominated platforms. Whether this was a response to acidification or warming has yet to be established (Scheibner and Speijer, 2008), although one accompanies the other in CO_2 -induced global warming events.

The PETM also involves dramatic changes among the calcareous plankton. A multitude of studies has focused on unraveling the significance of the truly spectacular plankton fossil record that accompanies this ancient global warming event (e.g., Kelly et al., 1996, 1998; Bralower, 2002). As the PETM is considered the best ancient analog to modern global warming, studies of the calcareous nanoplankton during the event offer vital clues to the potential

response of modern nanoplankton to ocean acidification, although other obvious environmental forcings must be taken into account; these include abrupt warming and the associated change in the thermal structure as well as the availability of nutrients, all thought to be the predominant causes of nanoplankton assemblage changes (Figure 5; Bralower, 2002; Gibbs et al., 2006a,b).

Detecting the potential impact of surface water acidification on calcareous plankton has thus proven to be difficult. In all but the very shallowest sites, effects of dissolution on the seafloor mask the record of plankton assemblage change. This dissolution has erased the record of assemblage change at the onset of the PETM, and, in the deeper sites, nanoplankton are absent for much of the early part of the event (Raffi et al., 2005; Raffi and De Benardi, 2008). Seafloor dissolution has also overprinted potential changes in fossil preservation that

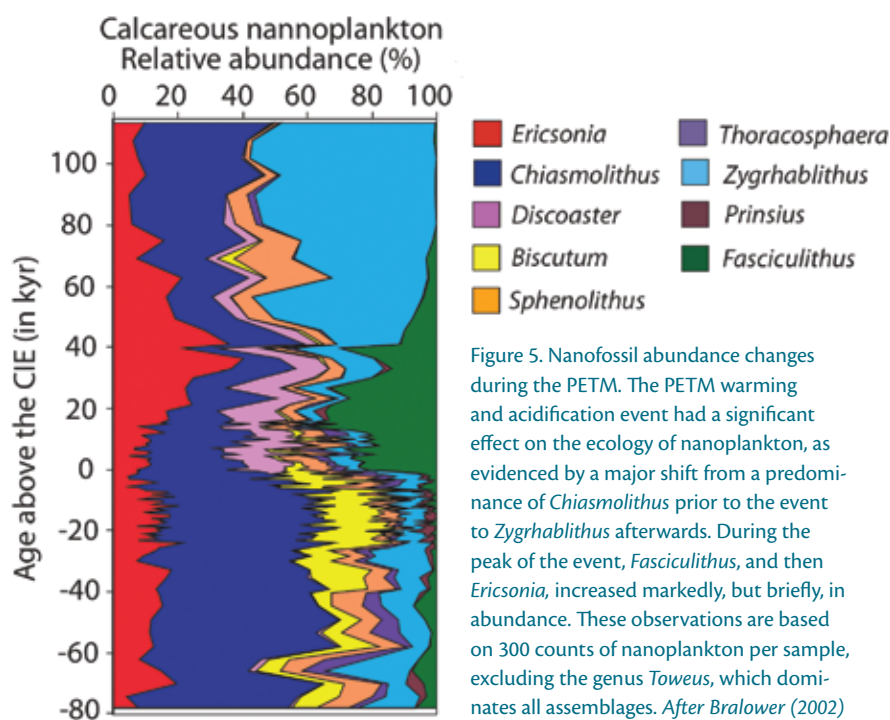


Figure 5. Nanofossil abundance changes during the PETM. The PETM warming and acidification event had a significant effect on the ecology of nanoplankton, as evidenced by a major shift from a predominance of *Chiasmolithus* prior to the event to *Zygrhablithus* afterwards. During the peak of the event, *Fasciculithus*, and then *Ericsonia*, increased markedly, but briefly, in abundance. These observations are based on 300 counts of nanoplankton per sample, excluding the genus *Toweus*, which dominates all assemblages. After Bralower (2002)

occurred at the sea surface.

The PETM is associated with the appearance of transient nanoplankton taxa characterized by heavily calcified forms of *Rhombaster* spp., *Discoaster araneus*, and *D. anartios* (e.g., Knox et al., 2003; Kahn and Aubry, 2004; Raffi et al., 2005; Agnini et al., 2007; Raffi and De Benardi, 2008), as well as *Coccolithus bownii*, a more delicate form (Jiang and Wise, 2007; Bown and Pearson, 2009). The two species of *Discoaster* are noted for malformation, and other long-ranging *Discoaster* species and a form of *Fasciculithus* were malformed during the event (Raffi and De Benardi, 2008). The malformations have been interpreted as evidence of surface water acidification (e.g., Agnini et al., 2007; Angori et al., 2007; Raffi and De Benardi, 2008) following the experimental results of Riebesell et al. (2000). Bown and Pearson (2009) question this interpretation, casting doubt on whether these forms are malformed, and, even if they are, argue that they are a small fraction of the total assemblage. In addition, the abundance of the excursion taxa and the other proposed malformed taxa increases steadily through the PETM and peaks in the middle of the event, significantly above the interval where surface acidification would have been expected. Moreover, the excursion taxa did not have a global distribution (e.g., Raffi and De Benardi, 2008; Bown and Pearson, 2009), while acidification would have been global. In one shelf setting (New Jersey, likely above the saturation horizon even at the height of the PETM) there is evidence for dissolution intervals toward the base of the event (Gibbs et al., 2006a). In contrast, nanofossils show exceptional preservation throughout

the PETM in Tanzania, with small and fragile taxa present (Bown and Pearson, 2009). Thus, there does not seem to be convincing evidence for surface-water acidification during the PETM.

ANCIENT ANALOGS AND FUTURE PROJECTIONS OF OCEAN ACIDIFICATION

Of all the past events related to ocean acidification, it is the PETM (and associated “hyperthermal” events such as ETM2 [Lourens et al., 2005], which closely followed the PETM during the early to mid Eocene) that arguably comes closest to being a future “analog,” and as a result has been the most closely studied to date. Compared to the end Permian and the late Neoproterozoic events (Figure 1), the PETM is comparatively “close” to the present day, meaning greater similarities in continental configuration, ecosystem structure and function, and global carbon cycling (although important differences, particularly in climatic boundary conditions remain [recent work of author Ridgwell and Daniela Schmidt, University of Bristol]). Furthermore, although the source of carbon is currently not well constrained, even if the initial input was as methane (CH₄) as originally hypothesized by Dickens et al. (1995), the CH₄ would be relatively rapidly oxidized to CO₂, thus driving ocean acidification. It is this association of massive carbon release and contemporaneous transient global warming that parallels society’s great experiment. Quantitatively, how do these events contrast?

Estimates of carbon release across the PETM range from around 2000 Pg C (Dickens et al., 1995; Panchuk et al., 2008) for a dominant biogenic methane

source, to almost 7000 Pg C (Panchuk et al., 2008), with a recent study inferring an initial pulse of 3000 Pg C (Zeebe et al., 2009). The time scale of CO₂ release is more uncertain, and there are no direct observations to constrain it adequately. Indeed, the very nature of the acidification event means that the primary phases used for dating in paleoceanography (carbonate minerals, including the shells of calcareous organisms) tend to be dissolved during the peak of the event, while benthic foraminifera go extinct. Computer models can help by testing and evaluating different time scales to provide the closest fit to multiple observations (Panchuk et al., 2008; Zeebe et al., 2009). Assumptions in models about the time scale of release have ranged from 1 kyr to 10 kyr (Panchuk et al., 2008), with the main phase of carbon input of Zeebe et al. (2009) occurring over 5 kyr. As Figure 6 shows, ~ 2180 Pg C over a relatively short interval (1 kyr) drives a more rapid deterioration in surface ocean conditions, such as in decreasing pH and (aragonite) saturation state as compared to the effects of almost 7000 Pg C over 10 kyr, although the latter ultimately creates a larger magnitude impact.

How marine environmental conditions could change in the future is in stark contrast with estimated changes over the PETM (Figure 6). For example, for a 2180 Pg C total fossil fuel CO₂ burn, the future saturation state change not only far exceeds that estimated for a 2180 Pg C release over 1 kyr during the PETM, but is comparable to ~ 7000 Pg C over 10 kyr. (Although note that while the future pH change seems much larger than during the PETM for the same total CO₂ release, the increase in hydrogen

ion concentration is more comparable.) In addition, the logarithmic increase in atmospheric $p\text{CO}_2$, which scales with the radiative forcing and thus surface temperature increase, is much larger for the modern simulations, implying significantly greater global warming. And while the biotic consequences of the PETM were fairly minor (only the benthic foraminifera suffered a major extinction; see above), the rates of change were markedly slower than those projected for the future. Indeed, the change in both pH and saturation state occurs at a rate over an order of magnitude faster than under the inferred history of PETM CO_2 release, questioning the ability of marine biota to adapt and/or migrate.

Whether the CO_2 release at the PETM could have been more rapid than 1 kyr is difficult to constrain from the geological record. However, it becomes increasingly difficult to envisage by what natural mechanism the carbon could have been transferred from its reservoir to the ocean and atmosphere. Mechanisms of transferring carbon between reservoirs tend to be relatively slow. As we've seen for the Late Permian and Early Aptian, large releases of CO_2 have been hypothesized for the past from extensive flood basalts, perhaps as much as 30,000 Pg C in total. However, the overall rate is likely to have been $< 1 \text{ Pg C yr}^{-1}$ for a 50,000 year event. And it is not at all clear that surface waters reached a critically low saturation state with respect to calcite during these events or the PETM. Existing data, including assemblage and preservational studies, do not demonstrate clear evidence for surface-water acidification during the PETM. Although the fossil record for OAE1a is not as well

preserved, evidence for acidification is stronger than for the PETM.

It is the rate of CO_2 release that makes the current great experiment so geologically unusual, and quite probably unprecedented in Earth history. Indeed, much of industrialization and economic

activity revolves around energy generated from fossil fuels. In other words, much of humanity is, in effect, engaged in a collective and deliberate effort to transfer carbon from geological reservoirs to the atmosphere as CO_2 . The resulting rate of environmental change

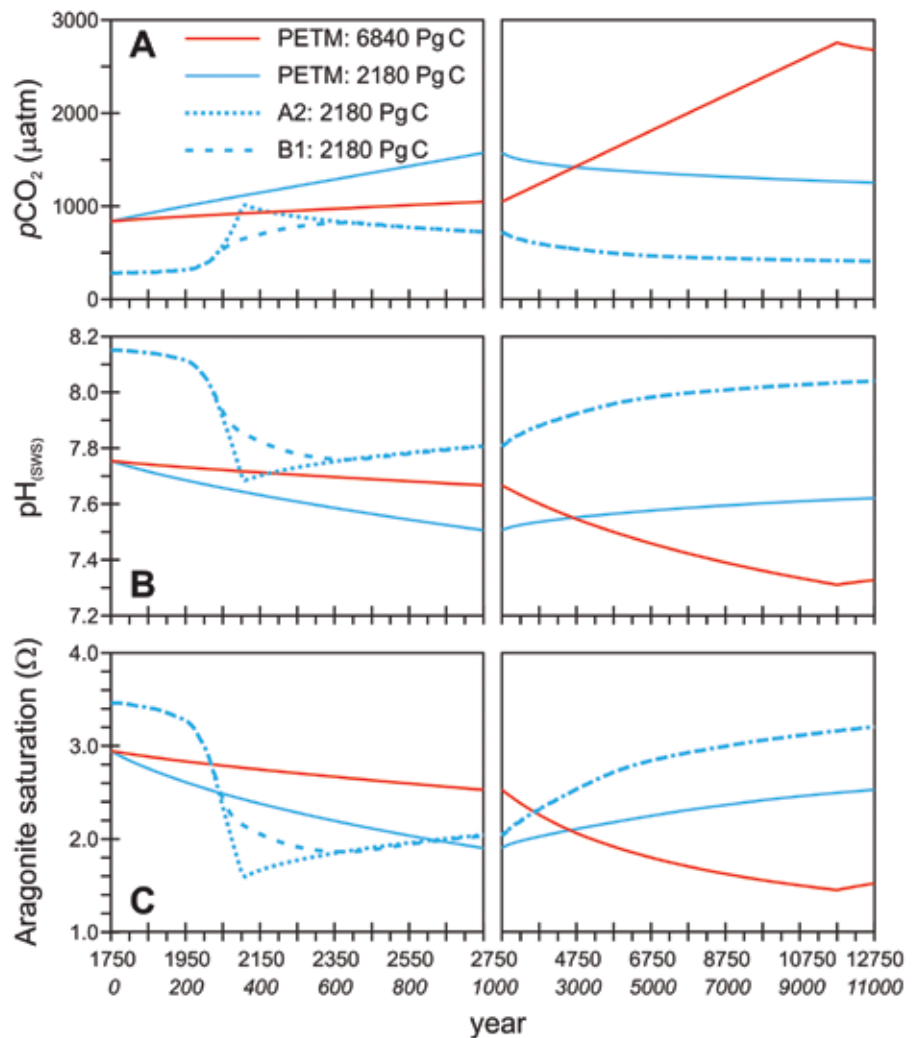



Figure 6. Predicted modern vs. PETM surface ocean impacts. The predicted evolution of global average surface ocean environmental conditions to massive CO_2 release are shown for modern (dashed line) and PETM (solid line) configurations of the same Earth system model (recent work of author Ridgwell and Daniela Schmidt, University of Bristol). Different total CO_2 releases (6840 Pg C in red and 2180 Pg C in blue) and different time scales of release (1 kyr and 10 kyr) are tested for the PETM. For the modern period, the same total (fossil fuel) CO_2 release is used (2180 Pg C) but with two different scenarios for possible future socio-economic development and hence energy usage and fossil fuel dependence, based on the *Intergovernmental Panel on Climate Change Special Report on Emissions Scenarios* (available online at: http://www.grida.no/publications/other/ipcc_sr/?src=/climate/ipcc/emission/).

very likely far exceeds that associated with past greenhouse transient events, and will have been exceeded in the geological record only by bolide impacts of the sort that caused the K/T extinction 66 million years ago (Figure 1). Lesser events in the geologic past have left an indelible imprint on the geologic and biotic record. “Business as usual” combustion of fossil fuels, unless accompanied by an aggressive and successful program of carbon capture and storage, is likely to leave a legacy of the Anthropocene as one of the most notable, if not cataclysmic, events in the history of our planet. 

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