History of Seawater Carbonate Chemistry, Atmospheric CO_2, and Ocean Acidification

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Abstract

Humans are continuing to add vast amounts of carbon dioxide (CO_2) to the atmosphere through fossil fuel burning and other activities. A large fraction of the CO_2 is taken up by the oceans in a process that lowers ocean pH and carbonate mineral saturation state. This effect has potentially serious consequences for marine life, which are, however, difficult to predict. One approach to address the issue is to study the geologic record, which may provide clues about what the future holds for ocean chemistry and marine organisms. This article reviews basic controls on ocean carbonate chemistry on different timescales and examines past ocean chemistry changes and ocean acidification events during various geologic eras. The results allow evaluation of the current anthropogenic perturbation in the context of Earth's history. It appears that the ocean acidification event that humans are expected to cause is unprecedented in the geologic past, for which sufficiently well-preserved records are available.

INTRODUCTION

Since the beginning of the industrial era, anthropogenic emissions of carbon dioxide (CO_2) have increased the concentration of CO_2 in Earth's atmosphere by ~40%. Anthropogenic emissions are primarily due to fossil fuel burning and to a lesser extent due to land use change and cement manufacturing. Increasing levels of CO_2 in the atmosphere are causing changes in the radiative forcing of Earth's climate. Until recently, much of the scientific and public discussion has been focused on the impacts of anthropogenic CO_2 on climate. However, recent studies underline a second, major impact of CO_2 emissions: 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 caused a decrease of surface-ocean pH by ~0.1 units from ~8.2 to ~8.1. Surface-ocean pH has probably not been below ~8.1 during the past 2 million years (Hönisch et al. 2009). If CO_2 emissions continue unabated, surface-ocean pH could decline by approximately 0.7 units by the year 2300 (Zeebe et al. 2008). 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. 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 specific timescales, to be detailed below.

With increasing CO_2 and decreasing pH, the concentration of carbonate ion ($[CO_3^{2-}]$) decreases, whereas that of bicarbonate ion ($[HCO_3^-]$) increases (see sidebar, Carbonate Chemistry). With declining $[CO_3^{2-}]$, the stability of calcium carbonate ($CaCO_3$), the mineral used by many marine organisms to build shells and skeletons, is reduced. Laboratory, shipboard, and mesocosm experiments indicate that many marine organisms react to changes in their geochemical environment that might occur by the end of this century (e.g., Raven et al. 2005, Gattuso & Hansson 2011). Frequently, calcifying organisms produce less $CaCO_3$, whereas some may produce more organic carbon. Extrapolating such experiments would lead us to expect potentially significant changes in ecosystem structure and nutrient cycling. However, several questions arise: Is it appropriate to extrapolate instantaneous environmental changes under experimental conditions to changes occurring on a century timescale? Do organisms have the ability to adapt to ongoing and future ocean acidification, which is occurring on a much shorter timescale than in the laboratory? Simultaneous changes in ocean temperature and nutrient supply as well as in an organism's predation environment may create further stresses or work to ameliorate the effect of changes in ocean chemistry. Either way, the actual future impact on marine organisms may further diverge from projections that are based on simple manipulation experiments.

There is little doubt that the chemistry of the ocean has varied significantly in the past (see below). The geologic record hence may provide clues about what the future will hold for ocean chemistry changes and their effects on marine life. When studying the geologic record, however, the critical task is to identify an appropriate analog for the future. Among other things, this requires a basic understanding of ocean chemistry controls during long-term steady states versus transient events because carbonate chemistry parameters do not have to vary with the same relationship if either the rate of change or the initial chemistry is different. Future versus past comparisons conducted without sufficient knowledge about how the carbon cycle and ocean chemistry are regulated on geologic timescales may ultimately lead to invalid conclusions. In the case of transient events, knowledge of the magnitude and timescale of the acidification event is necessary. Otherwise, geologic periods or events may be studied that are unsuitable for comparison with the future.

CARBONATE CHEMISTRY

Dissolved carbon dioxide (CO_2) in the ocean occurs mainly in three inorganic forms: free aqueous carbon dioxide (CO_2(aq)), bicarbonate ion (HCO_3^-), and carbonate ion (CO_3^{2-}). A minor form is true carbonic acid (H_2CO_3), whose concentration is less than 0.3% of [CO_2(aq)] (brackets denote concentrations). The sum of [CO_2(aq)] and [H_2CO_3] is denoted as [CO_2]. The majority of dissolved inorganic carbon in the modern ocean is in the form of HCO_3^- (>85%). In thermodynamic equilibrium, gaseous carbon dioxide [CO_2(g)] and [CO_2] are related by Henry's law:

$$CO_2(g) \overset{K_0}{=} [CO_2]$$

where K_0 is the temperature- and salinity-dependent solubility coefficient of CO_2 in seawater (Weiss 1974). The concentration of dissolved CO_2 and the fugacity of gaseous CO_2, fCO_2, then obey the equation $[CO_2] = K_0 \times fCO_2$, where the fugacity is virtually equal to the partial pressure, pCO_2 (within ~1%). The dissolved carbonate species react with water, hydrogen ions ($pH = -\log([H^+])$), and hydroxyl ions and are related by these equilibria:

$$CO_2 + H_2O \overset{K_1^*}{=} HCO_3^- + H^+$$

$$HCO_3^- \overset{K_2^*}{=} CO_3^{2-} + H^+.$$

The pK^*s [$= -\log(K^*)$] of the stoichiometric dissociation constants of carbonic acid in seawater are $pK_1{}^* = 5.94$ and $pK_2^* = 9.13$ at temperature $T_c = 15°C$, salinity $S = 35$, and surface pressure $P = 1$ atm (Prieto & Millero 2001). At typical surface-seawater pH of 8.2, the speciation between [CO_2], [HCO_3^-], and [CO_3^{2-}] is 0.5%, 89%, and 10.5%, respectively, showing that most of the dissolved CO_2 is in the form of HCO_3^- and not in the form of CO_2. The sum of the dissolved carbonate species is denoted as total dissolved inorganic carbon (TCO_2):

$$TCO_2 = [CO_2] + [HCO_3^-] + [CO_3^{2-}].$$

This quantity is also referred to as DIC, C_T, TIC, and ΣCO_2, all symbols meaning total dissolved inorganic carbon.

Another essential parameter to describe the carbonate system in seawater is the total alkalinity (TA), a measure of the charge balance in seawater:

$$TA = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H^+] + \text{minor compounds}.$$

TCO_2 and TA are conservative quantities, i.e., their concentrations measured in gravimetric units (mol kg^{-1}) are unaffected by changes in pressure or temperature, for instance, and they obey the linear mixing law. Therefore, they are the preferred tracer variables in numerical models of the ocean's carbon cycle (cf. **Figure 1**). Of all the carbonate species and carbonate system parameters described above, only pCO_2, pH, TCO_2, and TA can be determined analytically (Dickson et al. 2007). However, if any two parameters and total dissolved boron are known, all parameters (pCO_2, [CO_2], [HCO_3^-], [CO_3^{2-}], pH, TCO_2, and TA) can be calculated for a given T, S, and P (cf. Zeebe & Wolf-Gladrow 2001).

The $CaCO_3$ saturation state of seawater is expressed by Ω:

$$\Omega = \frac{[Ca^{2+}]_{sw} \times [CO_3^{2-}]_{sw}}{K_{sp}^*}$$

(*Continued*)

where $[Ca^{2+}]_{sw}$ and $[CO_3^{2-}]_{sw}$ are the concentrations of Ca^{2+} and CO_3^{2-} in seawater, and K_{sp}^* is the solubility product of calcite or aragonite, the two major forms of $CaCO_3$, at the in situ conditions of temperature, salinity, and pressure. Values of $\Omega > 1$ signify supersaturation, and $\Omega < 1$ signifies undersaturation. Because K_{sp}^* increases with pressure (the temperature effect is small), there is a transition of the saturation state from $\Omega > 1$ (calcite-rich) to $\Omega < 1$ (calcite-depleted) in sediments and seawater with depth.

The depth at which $\Omega = 1$ occurs in the ocean is termed the calcite saturation horizon (a water-column property). Although calcite becomes thermodynamically unstable just below this, dissolution proceeds only slowly. The greater depth at which dissolution impacts become noticeable is termed the lysocline (a sediment property). In practice, this is taken as the inflection point in the trend of sedimentary $CaCO_3$ content versus water depth. The depth at which the dissolution flux balances the rain flux of calcite to the sediments is known as the calcite compensation depth (CCD). The CCD is operationally defined and variously taken as the depth at which the $CaCO_3$ content is reduced to values such as 2 or 10 weight percent (wt%).

Furthermore, studying past changes of ocean chemistry allows us to evaluate the current anthropogenic perturbation in the context of Earth's history. For instance, we can ask questions such as: What was the amplitude of natural variations in ocean chemistry immediately prior to industrialization (e.g., during the Holocene, over the past 12,000 years)? Are there past events that are comparable in magnitude and timescale with the present ocean acidification caused by humans, or is it unprecedented in Earth's history? How did the carbon cycle, climate, and ocean chemistry respond to massive carbon input in the past, and on what timescale was the carbon removed from the ocean-atmosphere system by natural sequestration?

This article starts with a brief review of the chemistry of CO_2 in seawater and the basic controls on ocean carbonate chemistry on different timescales. Ocean chemistry changes during various geologic eras are investigated, and past ocean acidification events are examined. Evidence of biotic responses to past changes of ocean chemistry is also discussed (for more information, see Knoll & Fischer 2011, Zeebe & Ridgwell 2011, Hönisch et al. 2012). In the following, *Mya* (million years ago) and *Ma* (mega annum) are used to denote geological dates and durations, respectively.

CHEMISTRY OF CO_2 IN SEAWATER

A few basics of seawater carbonate chemistry are summarized in the sidebar, Carbonate Chemistry, and in **Figure 1**. Additional information can be found elsewhere (e.g., Stumm & Morgan 1996, Zeebe & Wolf-Gladrow 2001, Millero 2006, Dickson et al. 2007). In this section, I emphasize only a few fundamentals and subtleties of seawater carbonate chemistry to aid the discussion below.

Two Out of Six

The carbonate system can be described by six fundamental parameters in thermodynamic equilibrium: total dissolved inorganic carbon (TCO_2), total alkalinity (TA), $[CO_2]$, $[HCO_3^-]$, $[CO_3^{2-}]$, and $[H^+]$ (see sidebar, Carbonate Chemistry). The concentrations of OH^- and partial pressure of carbon dioxide (pCO_2) can be readily calculated using the dissociation constant of water and Henry's law. Given the first and second dissociation constants of carbonic acid and the definitions of TCO_2 and TA, we have four equations with six unknowns. Thus, if the values of two parameters are known, we are left with four equations and four unknowns, and the system can be solved. It follows the fundamental rule that two carbonate system parameters are required to determine the carbonate chemistry. One parameter is insufficient.

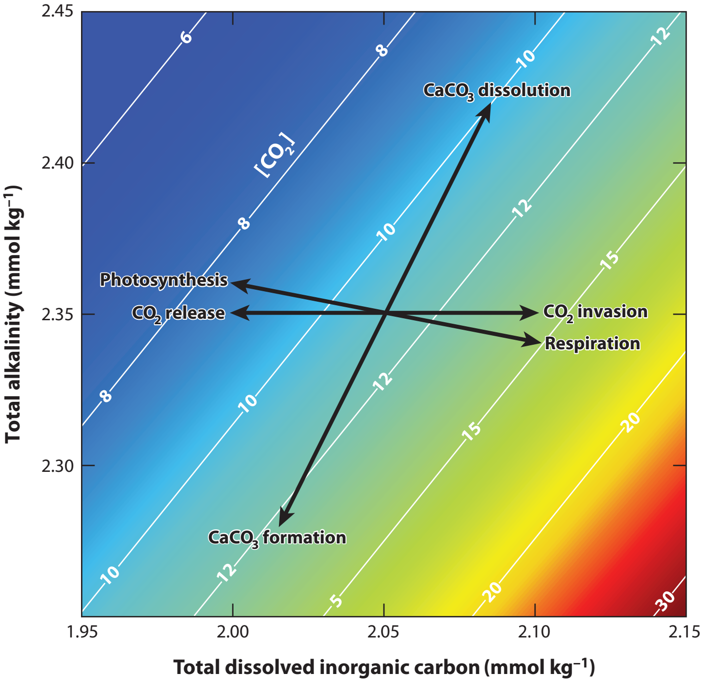


Figure 1

Effects of various processes on the carbonate chemistry parameters total dissolved inorganic carbon (TCO_2), total alkalinity (TA), and $[CO_2]$ at temperature $T_c = 15°C$ (T_c denotes temperature in °C), salinity $S = 35$, and pressure $P = 1$ atm (see sidebar, Carbonate Chemistry, for definitions). Contours indicate lines of constant $[CO_2]$ in μmol kg^{-1}. Invasion and release of CO_2 into/from the ocean changes only TCO_2, whereas photosynthesis and respiration also slightly change TA owing to nitrate uptake and release. $CaCO_3$ formation decreases TCO_2 and TA in a ratio of 1:2, and, counterintuitively, increases $[CO_2]$, although the total inorganic carbon concentration has decreased. $CaCO_3$ dissolution has the reverse effect. Modified from Broecker & Peng (1989) and Zeebe & Wolf-Gladrow (2001).

This rule is frequently ignored, which has led to misinformation in the literature. For instance, future atmospheric CO_2 concentrations have been compared with pCO_2 levels during the Cretaceous (~145 to ~65 Mya), which may have been as high as 2,000 parts per million by volume (ppmv). Although at some point in the future, atmospheric CO_2 levels might approach values similar to those during the Cretaceous, this by no means implies similar surface-ocean chemistry. A surface ocean with $TCO_2 = 2.4$ mmol kg^{-1} in equilibrium with an atmosphere at $pCO_2 = 2{,}000$ ppmv would have a calcite saturation state (Ω_c) of 1.1 [$T_c = 15°C$ (T_c denotes temperature in °C), $S = 35$]. However, at a higher TCO_2 value of 4.9 mmol kg^{-1}, the calcite saturation state Ω_c would be 4.5 (same T_c and S). The latter example illustrates possible Cretaceous seawater conditions and shows that such an ocean would have had surface waters with a favorable carbonate mineral saturation state, despite high pCO_2. For simplicity, the above numbers are based on modern calcium concentrations (for variable calcium, see Tyrrell & Zeebe 2004). The important point is that seawater chemistry comparisons between the Cretaceous, for instance, and the near future cannot be based on one carbonate system parameter alone (see below).

Temperature and Salinity

Temperature and salinity are important factors in setting the carbonate chemistry state, particularly at the surface. For instance, CO_2 is less soluble at higher temperatures, leading to outgassing to the atmosphere and hence locally reduced TCO_2 (**Figure 1**). Conversely, CO_2 uptake takes place predominantly in colder waters, and TCO_2 is higher. Hence, warm regions tend to have higher $[CO_3^{2-}]$ and be more saturated with respect to carbonate minerals than colder regions. As surface-ocean temperatures have varied in the past, both globally as well as regionally (latitudinally), so has carbonate chemistry. Also related to changes in climate is the importance of adding (subtracting) freshwater to (from) the oceans as this will reduce (increase) the concentration of TCO_2 and TA in a 1:1 ratio (they are conservative quantities). For instance, the larger ice volume at the time of the last glacial period, equivalent to the removal of approximately 3% of the water from the ocean (and storage primarily in the great ice sheets of the Northern Hemisphere), would have acted to increase $[CO_2]$ and hence atmospheric pCO_2—just at a time when ice core records of pCO_2 show it was at a record low. A multitude of other factors must then come into play to counter the salinity effect and further drive pCO_2 down to glacial concentrations (see Kohfeld & Ridgwell 2009).

$CaCO_3$ Precipitation and Dissolution

The precipitation of $CaCO_3$ decreases TCO_2 and TA in a ratio of 1:2, and, counterintuitively, increases $[CO_2]$, although the inorganic carbon concentration has decreased (**Figure 1**). Dissolution has the reverse effect. For a qualitative understanding, consider the reaction

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O, \quad (1)$$

which indicates that CO_2 is liberated during $CaCO_3$ precipitation. Quantitatively, however, the conclusion that $[CO_2]$ in solution is increasing by one mole per mole $CaCO_3$ precipitated is incorrect because of buffering. The correct analysis takes into account the decreases of TCO_2 and TA in a ratio of 1:2 and the buffer capacity of seawater. That is, the medium gets more acidic because the decrease in TA outweighs that of total inorganic carbon; hence, $[CO_2]$ increases (**Figure 1**). For instance, at surface-seawater conditions [TCO_2 = 2,000 μmol kg^{-1}, pH_T = 8.2 (total pH scale), T_c = 15°C, S = 35], $[CO_2]$ increases by only ~0.03 μmol per μmol $CaCO_3$ precipitated (for more details, see Zeebe & Wolf-Gladrow 2001).

Thus, $CaCO_3$ production in the surface ocean and its transport to depth tend to increase atmospheric CO_2. This process represents one component of the ocean's biological carbon pump and has been dubbed the $CaCO_3$ counterpump because of its reverse effect relative to the organic carbon pump, which tends to reduce atmospheric CO_2. One ironic consequence of this is that if marine calcifiers were to disappear, the resulting drop in the $CaCO_3$ counterpump would constitute a small negative feedback on rising atmospheric CO_2 levels in the short term (Zondervan et al. 2001, Ridgwell et al. 2007). It is also important that the ocean's carbonate pump on the timescale discussed above leads merely to shifts in the vertical distributions of the ocean's TCO_2 and TA rather than changes in their inventories. This process can be important in changing surface-ocean chemistry and reducing atmospheric CO_2 on timescales shorter than ~10,000 years (see below). On a million-year timescale, on the other hand, the burial of $CaCO_3$ in marine sediments represents one major pathway to remove carbon from the ocean-atmosphere system.

OCEAN CARBONATE CHEMISTRY CONTROLS

The ocean inventories of TCO_2 and TA determine the whole-ocean carbonate chemistry under most natural conditions. Changes in the TCO_2 and TA inventories over time therefore constitute

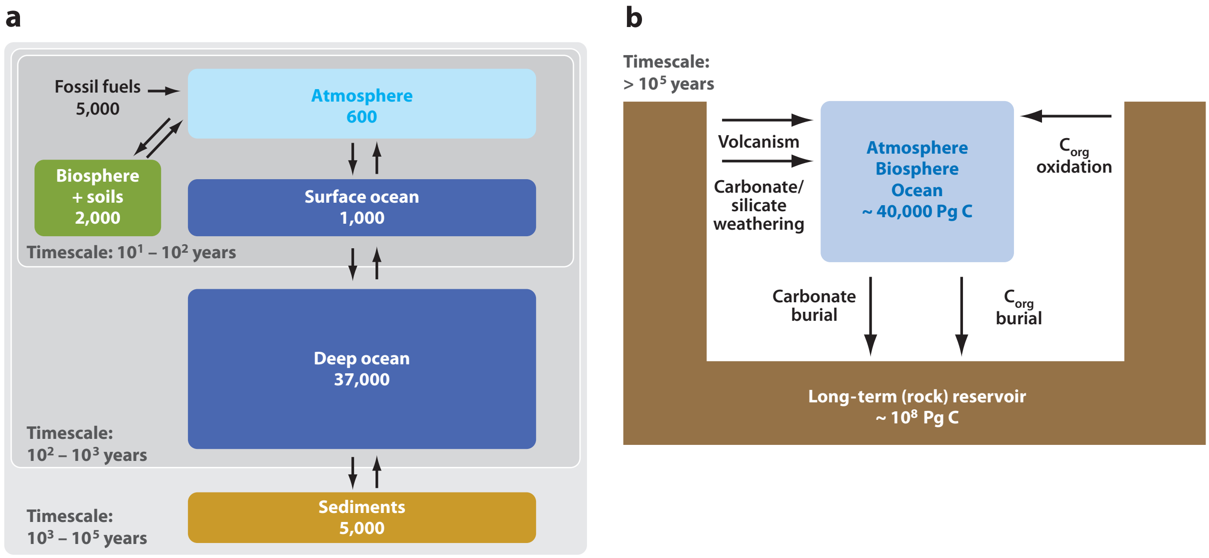


Figure 2

(*a*) Surface (exogenic) carbon cycle. Approximate reservoir sizes are in units of petagrams of carbon, Pg C (1 Pg = 10^{15} g). The gray boxes demarcate reservoirs involved in carbon exchange on the respective timescales. Modified from Zeebe & Ridgwell (2011). (*b*) Long-term carbon cycle. Note that whereas the silicate weathering feedback is critical in controlling atmospheric CO_2, weathering of silicate rocks does not transfer carbon from the rock reservoir to the surface reservoirs. Abbreviation: C_{org}, organic carbon.

the major control on the evolution of the carbonate system in seawater (for carbon cycling, see **Figure 2**). The characterization of the dominant carbon and TA fluxes to and from the ocean on different timescales is hence fundamental to understanding controls on ocean CO_2 chemistry (e.g., Sundquist 1986).

10- to 100-Year Timescale

On timescales shorter than approximately 100 years, the natural reservoirs that exchange carbon at Earth's surface include the atmosphere [preanthropogenic inventory, ~600 petagrams of carbon (Pg C); 1 Pg = 10^{15} g], the biosphere (~500 Pg C), soils (~1,500 Pg C), and the surface ocean (TCO_2 ~ 1,000 Pg C). Combined, these reservoirs hold less than ~4,000 Pg C (see **Figure 2*a***). Fossil fuel reserves, on the other hand, have been estimated at ~5,000 Pg C (excluding hydrates). It is thus immediately clear that the release of several thousands of petagrams of carbon over a few hundred years will overwhelm the capacity of these surface reservoirs to absorb carbon.

1,000-Year Timescale

On timescales on the order of ~1,000 years, the deep ocean reservoir becomes an important component of the surface carbon cycle (modern whole-ocean inventory, TCO_2 ~ 38,000 Pg C; see **Figure 2*a***). In fact, most of the anthropogenic carbon will eventually be absorbed by the ocean and neutralized by reaction with carbonate sediments. Once emissions have ceased and the ocean has had time to fully mix on a ~1,000-year timescale, a new equilibrium is established between ocean and atmosphere, and the CO_2 is partitioned in a ~1:3 ratio between atmosphere and ocean (Archer et al. 1998, Archer 2005). The greater the total release, the larger the exhaustion of oceanic buffering, and hence the greater the final airborne fraction. It is thought that climate change will both warm the ocean surface and increase net precipitation and ice melting at high latitudes, with the result that vertical stratification in the ocean will increase at both low and high latitudes. This is expected to slow the propagation of the TCO_2 and carbonate chemistry anomaly into the ocean interior on a timescale of decades to centuries. Furthermore, a warmer overall ocean will result in a higher airborne CO_2 fraction because of the effects of temperature on the solubility of CO_2. After ~1,000 years, with no additional process operating, the ocean would be left with a reduced pH (i.e., increased hydrogen ion activity), and the atmosphere would be left with a higher level of pCO_2. The carbon has been distributed (or partitioned) between atmosphere and ocean. The subsequent steps of fossil fuel neutralization include carbonate sediment dissolution in the deep sea and terrestrial weathering of carbonate and silicate minerals. Note that near-complete removal of fossil fuel carbon from the atmosphere will take tens to hundreds of thousands of years (e.g., Archer 2005, Uchikawa & Zeebe 2008, Zachos et al. 2008).

The oceanic inventories of TCO_2 and TA can be considered essentially constant on a timescale of ~1,000 years under natural steady-state conditions. Exceptions to this are rapid carbon inputs from otherwise long-term storage reservoirs such as methane hydrates or fossil fuels, which are currently combusted by humans. Other examples include catastrophic events from possible impacts over carbonate platforms, or other abrupt carbon releases from geologic reservoirs (e.g., during the Paleocene-Eocene Thermal Maximum, or PETM; see below). In the case of rapid CO_2 addition to the ocean-atmosphere system, carbonate sediment dissolution may occur on timescales shorter than the usual response time of >1,000 years (see next section).

1,000- to 100,000-Year Timescale

On timescales of 1,000 to 100,000 years, fluxes between reactive carbonate sediments (~5,000 Pg C) and the ocean's inventories of TCO_2 and TA must also be considered. For instance, oceanic inventories may vary during glacial-interglacial cycles (see Calcite Compensation, below). The magnitude of these changes is, however, limited, as are the associated changes in ocean chemistry and atmospheric CO_2. The fate of anthropogenic CO_2 on this timescale involves reaction with deep-sea carbonate sediments and terrestrial carbonates; this reaction will ultimately facilitate carbon removal from the ocean-atmosphere system. (This process is termed fossil fuel neutralization; see Broecker & Takahashi 1977, Sundquist 1986, and Archer et al. 1998.)

Changes in the ocean's carbon pumps can also affect ocean carbonate chemistry on the 1,000- to 100,000-year timescale. Changes in the strength of the pumps can lead to shifts in the vertical distribution of the ocean's TCO_2 and TA, while not affecting their inventories. This process is believed to be important for understanding changes of surface-ocean chemistry and atmospheric CO_2 on glacial-interglacial timescales. Whereas surface-ocean changes during the glacial-interglacial cycles were ~80 ppmv in pCO_2 and ~0.2 units in pH, deep-ocean carbonate chemistry changes were probably much smaller (see below and Zeebe & Marchitto 2010).

>100,000-Year Timescale

A large amount of carbon is locked up in Earth's crust as carbonate carbon (~70 $\times$ 10^6 Pg C) and as elemental carbon in shales and coals (~20 $\times$ 10^6 Pg C). On tectonic timescales (>100,000 years), this reservoir is active; imbalances in the fluxes to and from this pool can lead to large changes in TCO_2, TA, and atmospheric CO_2 (**Figure 2*b***). The balance among long-term carbon fluxes controls atmospheric CO_2 and ocean inventories of TCO_2 and TA on this timescale (e.g., Walker et al. 1981, Berner et al. 1983, Caldeira 1992, Zeebe & Caldeira 2008).

Figure 2 illustrates the fundamental difference between short-term carbon cycling (**Figure 2*a***)—on, for example, a 10- to 100-year timescale—and long-term carbon cycling (**Figure 2*b***). The two distinct cycles involve vastly different reservoir sizes and different sets of controls on atmospheric CO_2 and ocean chemistry. Therefore, carbon cycling and ocean chemistry conditions during long-term steady states (e.g., over millions of years) cannot be compared with rapid, transient events (e.g., over the next few centuries).

Biological Pump

Changes in the strength of the biological pump in the past have modulated the TCO_2 concentration and, by inference, the acidity (pH) at the surface. For instance, it has been hypothesized that during the last glacial period, the strength of the biological pump was greater, meaning lower atmospheric pCO_2 and higher pH. Reconstructions of changes in ocean surface pH based on the boron isotope composition of marine carbonates (boron speciation in seawater being pH-sensitive) suggest that the glacial surface ocean had a pH of 0.1 to 0.2 units higher compared with the pH of interglacial periods (e.g., Sanyal et al. 1995, Hönisch & Hemming 2005, Foster 2008). Of course, rather than changing the inventory of TCO_2, the strength of the biological pump only repartitions TCO_2, primarily vertically.

Calcite Compensation

Calcite compensation maintains the balance between $CaCO_3$ weathering fluxes into the ocean and $CaCO_3$ burial fluxes in marine sediments on a timescale of 5,000 to 10,000 years (e.g., Broecker & Peng 1987, Zeebe & Westbroek 2003). In steady state, the riverine flux of Ca^{2+} and CO_3^{2-} ions from weathering must be balanced by burial of $CaCO_3$ in the sea; otherwise, $[Ca^{2+}]$ and $[CO_3^{2-}]$ would rise or fall. The feedback that maintains this balance works as follows. Assume there is an excess weathering influx of Ca^{2+} and CO_3^{2-} over burial of $CaCO_3$ (system is out of steady state). Then, the concentrations of Ca^{2+} and CO_3^{2-} in seawater increase, leading to an increase of the $CaCO_3$ saturation state. This increase, in turn, leads to a deepening of the saturation horizon and to an increased burial of $CaCO_3$ just until the burial again balances the influx. The new steady-state balance is restored at higher $[CO_3^{2-}]$ than before.

Weathering of Carbonate and Silicate Rocks

Carbonate mineral weathering on continents may be represented by

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^- \tag{2}$$

whereas the reverse reaction (Equation 1) represents the precipitation and subsequent burial of carbonates in marine sediments. As described above, carbonate weathering (input to the ocean) and burial (output) are balanced via calcite compensation on a relatively short timescale (~10,000 years). For each mole of CO_2 taken up during $CaCO_3$ weathering, one mole of CO_2 is also released during $CaCO_3$ precipitation. The net carbon balance for the combined ocean-atmosphere system on timescales over which carbonate weathering is balanced by carbonate burial is therefore zero. For this reason, carbonate weathering and burial are often ignored in models of the long-term carbon cycle over millions of years (see, however, Ridgwell et al. 2003).

Silicate mineral weathering and subsequent burial as calcium carbonate in marine sediments may be represented by

$$CaSiO_3 + CO_2 + H_2O \rightarrow CaCO_3 + SiO_2 + H_2O, \quad (3)$$

which shows that, on a net basis, one mole of carbon in the form of CO_2 is removed from the atmosphere and buried as $CaCO_3$ in sediments. This cycle is balanced by input from volcanic degassing and net organic oxidation on a timescale of 10^5 to 10^6 years (see above).

When this cycle is out of balance during enhanced mineral weathering in response to elevated atmospheric CO_2, for instance, silicate weathering and subsequent carbonate burial remove carbon from the ocean-atmosphere system. Thus, the silicate weathering cycle is ultimately responsible for sequestering carbon in the long term until a balance between sources and sinks is restored. In the case of large anthropogenic fossil fuel emissions (e.g., a total of 5,000 Pg C), it will take hundreds of thousands of years for atmospheric CO_2 to return to climatically relevant levels of, say, 400 ppmv. The exact timing is difficult to forecast, mostly because of uncertainties in the parameterization of weathering processes, which lead to different rates of carbon removal on these timescales (e.g., Uchikawa & Zeebe 2008).

PAST LONG-TERM CHANGES (QUASI-STEADY STATES)

Over several thousands of years, the ocean's carbonate mineral saturation state is controlled by the balance of carbonate mineral weathering on continents (subsequently input to the ocean) and carbonate burial in ocean sediments (output) (e.g., Broecker & Peng 1987, Zeebe & Westbroek 2003, Ridgwell & Schmidt 2010). This balance helps establish fairly constant atmospheric CO_2 concentrations and ocean carbonate chemistry on timescales of >10,000 years. However, the entire system may not be in steady state with long-term processes such as silicate or organic carbon weathering fluxes or volcanic outputs (hence the term quasi-steady state).

Holocene

Considering ocean chemistry changes during the Holocene (the ~12,000-year period prior to industrialization) is useful not because of large variations and/or acidification events but because of its remarkable carbon cycle stability. The stable conditions during the Holocene illustrate the stark contrast to the current anthropogenic disruption, which represents a large and rapid carbon perturbation relative to the natural balance of the Holocene (see **Figure 3*a***). Ice core records reveal that Holocene atmospheric CO_2 varied at most between ~260 and ~280 ppmv, with pCO_2 gradually rising toward the present (Monnin et al. 2004). Ocean chemistry was also quite stable during the same interval. This has been indicated by deep-sea carbonate ion proxy records, although slightly larger changes than those expected to accompany the 20-ppmv rise in atmospheric CO_2 cannot be excluded (Broecker & Clark 2007).

By and large, the data suggest that the Holocene carbon cycle was in or close to steady-state conditions with generally minor imbalances in carbon sources and sinks, some of which were in response to the recovery from the last deglaciation (Elsig et al. 2009). Using the Holocene atmospheric CO_2 record, I have made hindcasts regarding changes in ocean carbonate chemistry using the LOSCAR (Long-term Ocean-atmosphere-Sediment CArbon cycle Reservoir) model (Zeebe et al. 2008, 2009; Zeebe 2011). My results indicate that Holocene ocean carbonate chemistry was nearly constant. For instance, I estimate that the calcite saturation state has varied by less than ~10% and that the pH has varied by less than ~0.04 units in the surface ocean over the past 10,000 years (**Figure 3*b*,*c***). In contrast, I estimate that since the year 1750, anthropogenic CO_2

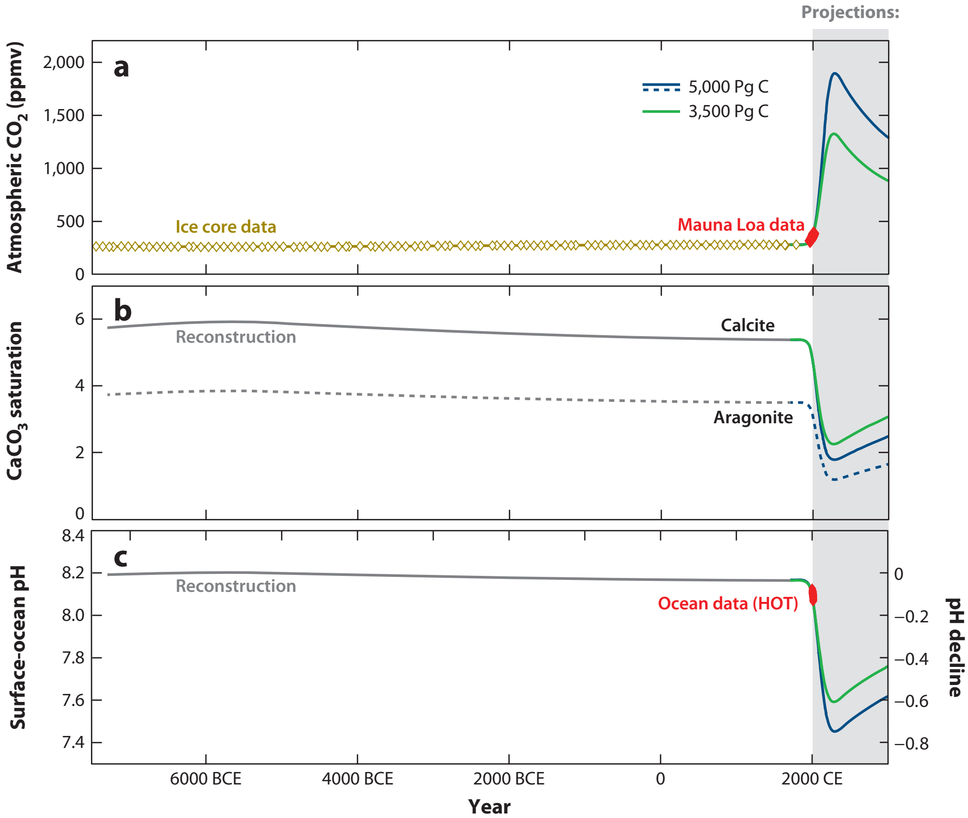


Figure 3

Holocene versus Anthropocene. (*a*) Dark yellow diamonds: Holocene atmospheric CO_2 concentrations from ice cores (Monnin et al. 2004); red diamonds: CO_2 measured at Mauna Loa Observatory, Hawaii (Tans 2009); lines: projections based on carbon input of 5,000 Pg C (*blue*) and 3,500 Pg C (*green*) over ~500 years using the LOSCAR (Long-term Ocean-atmosphere-Sediment CArbon cycle Reservoir) carbon cycle model (Zeebe et al. 2008, 2009; Zeebe 2011). (*b*) Modeled (reconstructed for the past and projected for the future at 5,000 Pg C and 3,500 Pg C) $CaCO_3$ saturation state of surface seawater. Solid lines: calcite saturation; dashed line: aragonite saturation. (*c*) Surface-ocean pH. Lines: model results of reconstructed and future pH for 5,000 Pg C and 3,500 Pg C; red diamonds: Hawaii Ocean Time-series (HOT) pH data at 25°C (Dore et al. 2009).

emissions have led to a decrease of surface-ocean pH by ~0.1 units. If CO_2 emissions continue unabated, surface-ocean calcite saturation state will drop to approximately one-third of its preindustrial value by the year 2300, whereas pH will decline by approximately 0.7 units (**Figure 3*b*,*c***).

Late Pleistocene Glacial-Interglacial Changes

Atmospheric CO_2 has varied periodically between ~200 and ~280 ppmv over the past 800,000 years (Siegenthaler et al. 2005, Lüthi et al. 2008). These glacial-interglacial cycles were accompanied by periodic changes in surface-ocean carbonate chemistry, whereas deep-sea pH and carbonate ion concentration are believed to have been relatively stable (Zeebe & Marchitto 2010). Compared with interglacials, glacial surface-ocean conditions were characterized by lower temperatures, higher pH, and higher carbonate ion concentration (e.g., Sanyal et al. 1995, Hönisch & Hemming 2005, Foster 2008). For example, an interglacial surface-seawater sample at $T_c = 15°C$, $S = 35$, $TCO_2 = 2{,}000\ \mu mol\ kg^{-1}$, and $TA = 2{,}284\ \mu mol\ kg^{-1}$ has a pCO_2 of 280 ppmv, $pH_T = 8.17$, and $[CO_3^{2-}] = 198\ \mu mol\ kg^{-1}$. Corresponding glacial conditions may have been $T_c = 12°C$, $S = 36$, $TCO_2 = 2{,}006\ \mu mol\ kg^{-1}$, and $TA = 2{,}353\ \mu mol\ kg^{-1}$, which yield a pCO_2 of 200 ppmv, $pH_T = 8.30$, and $[CO_3^{2-}] = 238\ \mu mol\ kg^{-1}$. These values indicate a difference in glacial-interglacial saturation state of approximately 20%. Whereas this scenario assumes a 3% higher glacial TA, various other scenarios are possible, which would also modify the calculated pH change (e.g., Archer et al. 2000). Nevertheless, it illustrates the sign and order of magnitude of glacial-interglacial changes in surface-ocean carbonate chemistry.

Considering the time evolution of the system over glacial-interglacial cycles, it is clear that surface-ocean pH and saturation state declined during the course of a deglaciation. One might thus think of a deglaciation as an acidification event, albeit a truly slow and moderate one. In terms of rate and magnitude, it is important to realize that a deglaciation is not a past analog for the current anthropogenic perturbation. For example, the rate of surface-ocean pH change during the most recent deglaciation may be estimated as 0.1–0.2 units per 10,000 years, or 0.001–0.002 units per century on average. In contrast, under Business-as-USual CO_2 emissions, humans may cause a surface-ocean pH change of 0.7 units per 500 years, or 0.14 units per century on average. Thus, surface-ocean chemistry changes during the Anthropocene are expected to be approximately three to seven times larger and 70 times faster than during a deglaciation.

The late Pleistocene changes in surface-ocean carbonate chemistry have been invoked to explain changes in shell weights of surface-dwelling foraminifera. For example, calcite shells of different planktonic foraminiferal species recovered from deep-sea sediment cores in the North Atlantic Ocean and Indian Ocean show higher shell weights during the last glacial period compared with the Holocene (e.g., Barker & Elderfield 2002, de Moel et al. 2009). The authors of these studies suggest that lower pCO_2 and elevated surface $[CO_3^{2-}]$ caused higher initial shell weights during the last glacial stage. On the other hand, shell weights of planktonic foraminifera have been used as an indicator of carbonate sediment dissolution and thus as a proxy for $[CO_3^{2-}]$ in the deep sea rather than at the surface (e.g., Broecker & Clark 2003). Clearly, the issue is complicated by various factors, including possible effects of growth temperature, $[CO_3^{2-}]$, nutrients, and other environmental parameters on initial shell weight, as well as dissolution in sediments and/or the water column (e.g., Bijma et al. 2002). Interrelations among coccolithophore species, coccolith weight/chemistry, primary production, and the carbon cycle appear to be even more complex (for discussions, see Zondervan et al. 2001, Beaufort et al. 2007, Rickaby et al. 2007).

Pleistocene and Pliocene

Records of atmospheric CO_2 in ice cores are limited to the oldest samples available in Antarctic ice cores, which go back at most ~1 Ma. Beyond that, estimates of paleo-pCO_2 levels and ocean chemistry must rely on other proxies. On the basis of stable boron isotopes in foraminifera, glacial pCO_2 levels before the Mid-Pleistocene Transition (~1 Mya) were estimated to have been approximately 30 ppmv higher than after the transition. Estimates of interglacial values before the Mid-Pleistocene Transition appear similar to those obtained from ice cores during the late Pleistocene (Hönisch et al. 2009). Stable boron isotopes are actually a proxy for seawater pH, and one other CO_2 system parameter is required to reconstruct atmospheric CO_2. Regardless, the boron isotope data indicate that surface-ocean pH over the past 2 Ma has varied periodically between ~8.1 and ~8.3 (Hönisch et al. 2009). So far, no major excursions or ocean acidification events have been identified during the Pleistocene. The available Pleistocene data indicate periodic variations in ocean carbonate chemistry during the past 2 Ma. These variations are part of the natural glacial-interglacial climate cycles and are restricted within remarkably stable lower and upper limits (between ~180 and ~300 ppmv for pCO_2 and between ~8.1 and ~8.3 for surface-ocean pH_T).

More estimates of surface-ocean pH and atmospheric CO_2 are now becoming available for the Pliocene epoch (Pagani et al. 2010, Bartoli et al. 2011). Stable boron isotopes indicate variations in surface-ocean pH_T between ~8.0 and ~8.3 and a gradual pCO_2 decline from 4.5 Mya to 2 Mya, with extreme values ranging between ~200 and ~400 ppmv (Bartoli et al. 2011). Over the same time interval, alkenone data suggest a similar pCO_2 decline, with extreme pCO_2 values ranging between ~200 and ~525 ppmv (Pagani et al. 2010). Alkenone-based pCO_2 estimates derive from records of the carbon isotope fractionation that occurred during marine photosynthetic carbon fixation. Several lines of evidence suggest that the carbon isotope fractionation depends on CO_2 levels (e.g., Pagani et al. 2010). These reconstructions have large uncertainties. Nevertheless, taking the results at face value, one may estimate the maximum change in surface-ocean saturation state of calcite over the past 4 Ma. The cold periods may be characterized by $pH_T = 8.3$ and $pCO_2 = 200$ ppmv, which yield $\Omega_c = 6.1$ ($T_c = 15°C$, $S = 35$). The warm Pliocene periods (~4°C warmer than the preindustrial period) may be characterized by $pH_T = 8.0$ and $pCO_2 = 525$ ppmv, which yield $\Omega_c = 4.6$ ($T_c = 19°C$, $S = 35$). By and large, the combined evidence for the Pliocene and Pleistocene periods suggests that over the past 4 Ma, ocean carbonate chemistry has experienced relatively slow changes on timescales of >10,000 years, with atmospheric CO_2 varying roughly between 200 and 500 ppmv.

Cenozoic and Phanerozoic

One approach to reconstruct ocean chemistry over the Cenozoic (the past ~65 Ma) is based on estimates of past atmospheric CO_2 concentrations and the ocean's carbonate mineral saturation state (e.g., Sundquist 1986, Broecker & Sanyal 1998, Zeebe 2001). Deep-sea sediment cores reveal that the long-term steady-state position of the calcite compensation depth (CCD) over the past 100 to 150 Ma did not vary dramatically; rather, it gradually deepened slightly toward the present (for a summary, see Tyrrell & Zeebe 2004 and **Figure 4**). This suggests a more or less constant carbonate mineral saturation state of the ocean over the Cenozoic, except for the Eocene-Oligocene transition (~34 Mya), when the CCD rapidly deepened permanently by several hundred meters. A recent study indicates a more dynamic CCD on shorter timescales—for instance, during the Eocene in the Equatorial Pacific (Pälike et al. 2009). Nevertheless, on long timescales, the ocean's carbonate chemistry over the Cenozoic may be reconstructed on the basis of saturation state estimates and paleo-pCO_2 reconstructions (e.g., Tyrrell & Zeebe 2004, Ridgwell 2005, Goodwin et al. 2009, Stuecker & Zeebe 2010).

Although the details of the reconstructions can vary substantially—mostly depending on the different paleo-pCO_2 estimates—several trends appear to be robust. Atmospheric CO_2 concentrations were higher during the early Cenozoic and have declined from a few thousand parts per million by volume to 200–300 ppmv during the late Pleistocene (**Figure 4**). Whereas surface-ocean saturation state was nearly constant over this period of time, surface-ocean pH_T was lower during the early Cenozoic (perhaps ~7.6) and has gradually increased to its modern value of approximately 8.2 (see **Figure 4** and Tyrrell & Zeebe 2004, Ridgwell & Zeebe 2005). These are long-term trends that do not resolve possible large short-term variations during ocean acidification events such as the PETM (see below). Furthermore, low surface-ocean pH during multimillion-year periods of the Paleocene or Cretaceous, for instance, are no analogs for the centuries to come because of different seawater carbonate mineral saturation states (see below).

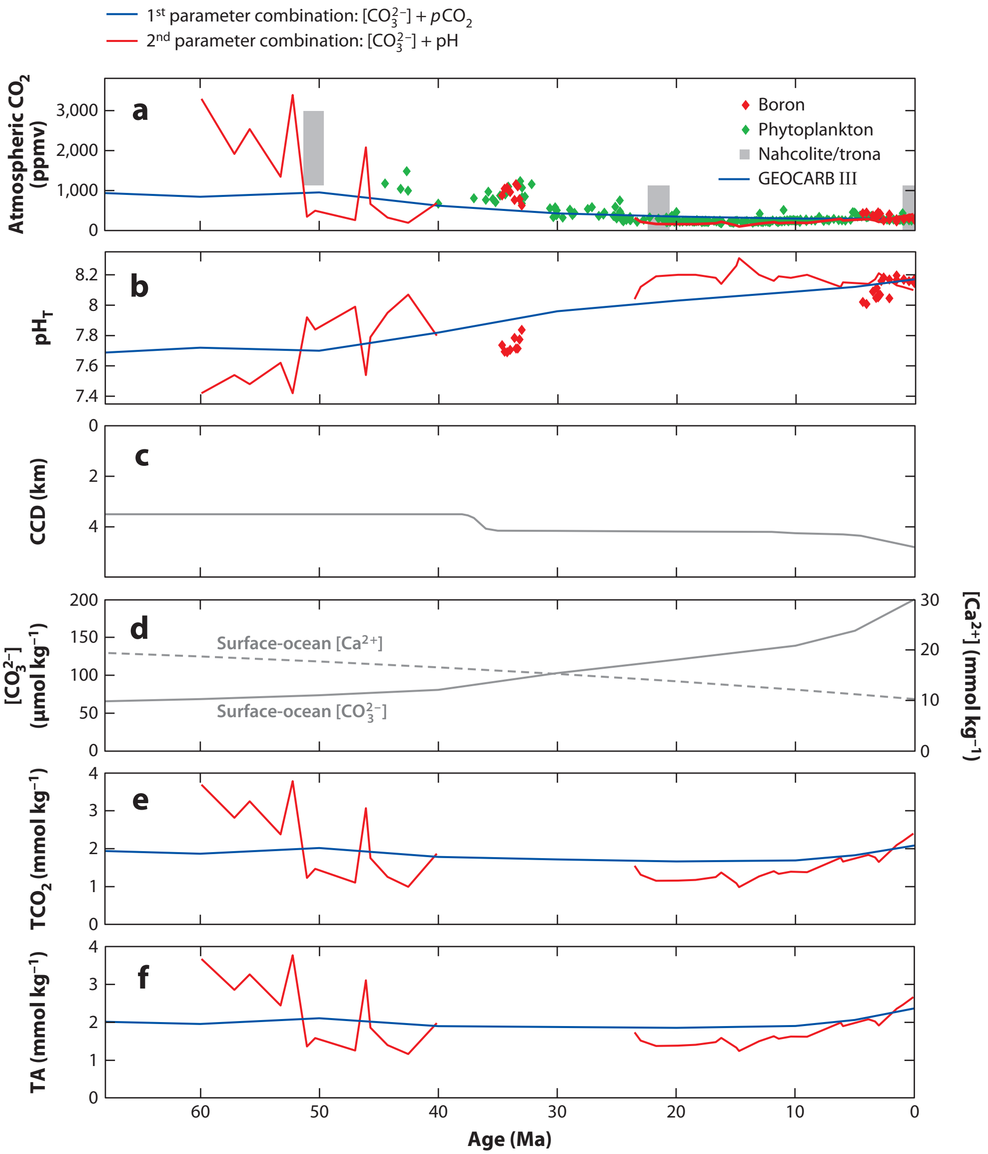


Figure 4

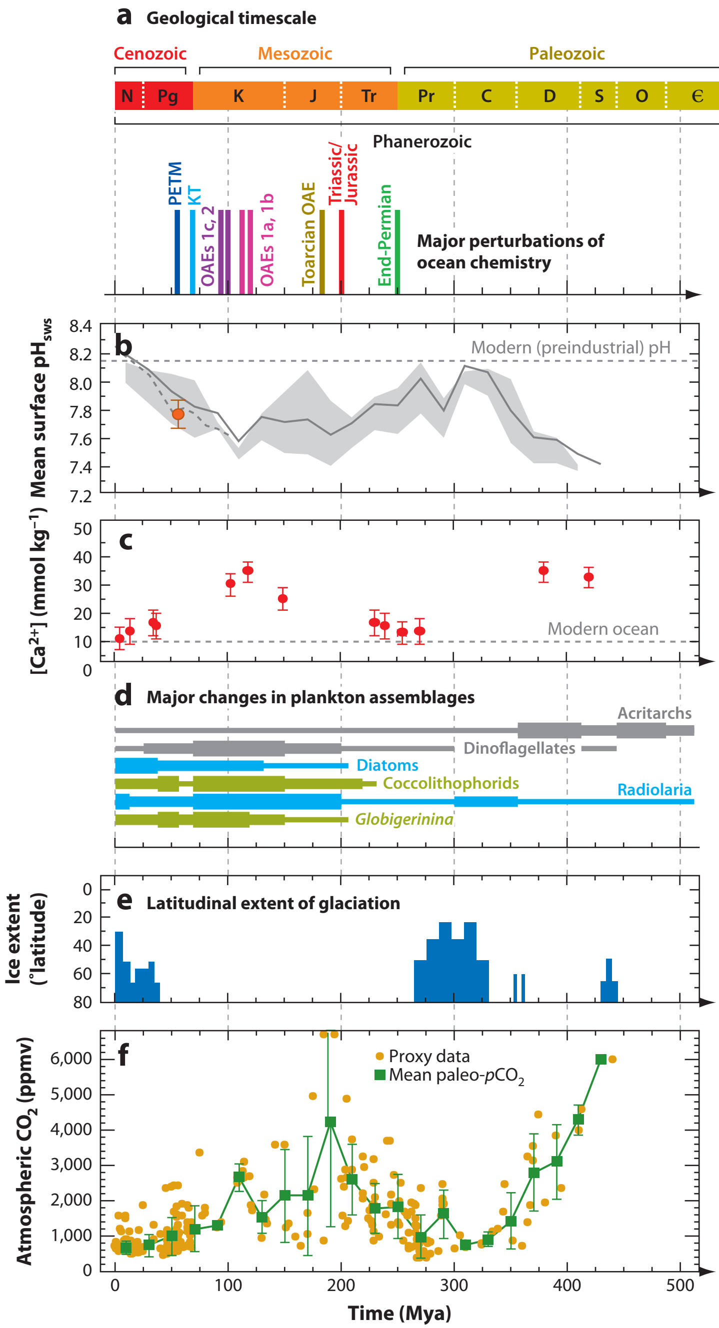
Atmospheric CO_2 and carbonate chemistry reconstruction of surface seawater over the Cenozoic, based on two different parameter combinations: (1) [CO_3^{2-}] and pCO_2 (*blue lines*) and (2) [CO_3^{2-}] and pH (*red lines*). Modified from Tyrrell & Zeebe (2004). (*a*) pCO_2 reconstructions based on proxies (Freeman & Hayes 1992; Pagani et al. 1999a,b, 2005; Pearson & Palmer 2000; Pearson et al. 2009; Seki et al. 2010; Beerling & Royer 2011), from the carbon cycle model GEOCARB III (*blue line*; Berner & Kothavala 2001), and based on combination 2 (*red line*). Nahcolite = $NaHCO_3$, trona = $NaHCO_3 \cdot Na_2CO_3 \cdot 2H_2O$. (*b*) pH_T (total pH scale) based on combination 1 (*blue line*) and from stable boron isotopes (*red line*; Pearson & Palmer 2000). (*c*) Global mean calcite compensation depth (CCD). Note the minor CCD changes over time, indicating nearly constant carbonate mineral saturation state of the ocean (except for rapid fluctuations, not shown). (*d*) Surface-ocean concentrations of CO_3^{2-} (*solid line*; derived from saturation state indicators) and Ca^{2+} (*dotted line*; from fluid inclusions). (*e*) Total dissolved inorganic carbon (TCO_2), calculated based on the two different parameter combinations. (*f*) Total alkalinity (TA), calculated based on the two different parameter combinations.

The question arises whether the long-term trends in ocean carbonate chemistry throughout the Cenozoic had any effect on the evolution of marine calcifying organisms. However, if species evolution were sensitive to carbonate mineral saturation state, little effect is to be expected because saturation state appears to have been nearly constant over the Cenozoic. Regarding coccolithophores, a trend toward smaller cell sizes in the Oligocene (~34 to ~23 Mya) relative to the Eocene (~55 to ~34 Mya) has been suggested on the basis of deep-sea sediment records (Henderiks & Pagani 2008). Henderiks & Pagani (2008) speculated that the size trend in the haptophyte algae may reflect a response to increased CO_2 limitation associated with the decline in atmospheric CO_2 across the Eocene-Oligocene transition. If so, this would represent a CO_2-related effect on photosynthesis and cell growth rather than on calcification. Regarding planktonic foraminifera, a trend toward larger test sizes in low-latitude species has been reported, particularly since the end of the Miocene (Schmidt et al. 2004). Schmidt et al. (2004) suggested that the size increase was a response to intensified surface-water stratification in low latitudes. Changes in Cenozoic carbonate chemistry appear unlikely to have caused the shell-size increase in foraminifera, emphasizing the importance of other functional correlations with shell size. For example, surface-water changes in CO_2 at the end of the Miocene (~23 to ~5 Mya) seem rather small compared with those during the Paleogene. Thus, if dissolved CO_2 or pH were important factors in determining shell size in planktonic foraminifera, one would expect large changes during the Paleogene (~65 to ~23 Mya). This is not the case.

Lastly, one could ask whether long-term changes in ocean carbonate chemistry could have influenced features such as the distribution of coral reefs throughout the Cenozoic. On the basis of geologic evidence in the continental United States, Opdyke & Wilkinson (1993) suggested a ~10° latitudinal reduction in areal extent of reefal/oolitic carbonate accumulation between the Cretaceous and the Holocene, with a gradual decrease toward the present. These authors focused mostly on carbonate mineral saturation state and sea-surface temperature as environmental parameters that control the latitudinal extent of reefs. In this context, a recent study suggests rapid poleward range expansion of tropical reef corals around Japan over the past 80 years in response to rising sea-surface temperatures (Yamano et al. 2011). In contrast, on the basis of an extensive data set of paleolatitudinal distribution of reef sites, Kiessling (2001) concluded that neither the width of the tropical reef zone nor the total latitudinal range of reefs is correlated with paleotemperature estimates. He inferred a fairly wide reef zone during the Cretaceous and early Paleogene and an exceptionally wide tropical reef zone in the late Paleocene and Eocene, relative to the modern latitudinal boundaries. The bottom line is that these studies do not seem to indicate any obvious relationships between the distribution of reefs and changes in seawater CO_2 or pH, for example, over the Cenozoic (see **Figure 4**). As mentioned above, no significant relationships are to be expected because the ocean's long-term saturation state appears to have been nearly constant throughout the Cenozoic. In contrast, rapid short-term ocean acidification events such as the PETM (~55 Mya) have been identified as the cause for ancient reef crises (e.g., Kiessling & Simpson 2011). Long-term changes in ocean carbonate chemistry over the past 500 Ma are summarized in **Figure 5** (see Ridgwell 2005, Ridgwell & Zeebe 2005, Kump et al. 2009).

The Cretaceous Is Not an Analog for the Near Future

As pointed out above, comparisons between the Cretaceous and the near future are frequently made to suggest that marine calcification will not be impaired in a future high-CO_2 world. The evidence cited for this is usually based on the occurrence of massive carbonate deposits during the Cretaceous such as the White Cliffs of Dover—carbonate formations that consist of coccolithophore calcite. Given the basics of carbon cycling and controls on seawater carbonate chemistry as reviewed above, it is obvious that such comparisons are invalid (see also Zeebe & Westbroek 2003, Ridgwell & Schmidt 2010). This applies not only to the Cretaceous in particular but also to past long-term, high-CO_2 steady states in general. Briefly, because two carbonate system parameters are required to determine the carbonate chemistry, similar CO_2 concentrations do not imply similar carbonate chemistry conditions (for instance, carbonate mineral saturation states can be completely different).



The anthropogenic perturbation represents a transient event with massive carbon release over a few hundred years. In contrast, the Cretaceous, for instance, represents a long-term steady-state interval over millions of years. As a result, the timescales involved (centuries versus millions of years), reservoir sizes (a few thousand petagrams of carbon versus 10^8 Pg C), and controls on carbonate chemistry are fundamentally different (see above).

The carbonate mineral saturation state of the ocean is generally well regulated by the requirement that on long (>10,000 years) timescales, $CaCO_3$ sources (weathering) and sinks (shallow- and deep-water $CaCO_3$) must balance (Ridgwell & Schmidt 2010). In contrast, as pH reflects the balance between dissolved CO_2 and carbonate ion concentration, it is governed primarily by pCO_2 (controlling CO_2 for a given temperature) and Ca^{2+}/Mg^{2+} (controlling CO_3^{2-} for a given Ω) rather than by weathering. It follows, for instance, that there was no late Mesozoic carbonate crisis because Ω was probably high and decoupled from pH. Only events involving geologically rapid (<10,000 years) CO_2 release overwhelm the ability of the ocean and sediments to regulate Ω, producing a coupled decline in both pH and saturation state and hence providing a future-relevant ocean acidification analog.

PAST OCEAN ACIDIFICATION EVENTS

I use the term ocean acidification event to describe episodes in Earth's history that involve geologically rapid changes of ocean carbonate chemistry, including reductions in both pH and $CaCO_3$ saturation states on timescales shorter than ~10,000 years. I limit the discussion to a few episodes that appear most relevant in relation to the ongoing anthropogenic acidification event. The list is not comprehensive, and other events in Earth's history may deserve more attention in the context of ocean acidification (see, e.g., Kump et al. 2009, Knoll & Fischer 2011, Hönisch et al. 2012).

Aptian Oceanic Anoxic Event

The Aptian Oceanic Anoxic Event (OAE1a, ~120 Mya; see **Figure 5**) is characterized by the widespread deposition of organic-rich sediments and represents a possible ocean acidification example. It has been suggested that a marine calcification crisis occurred during OAE1a (e.g.,

Figure 5

The geological context for past changes in ocean carbonate chemistry. Modified from Kump et al. (2009). (*a*) Major global carbon cycle events during the past ~500 Ma. Abbreviations: Є, Cambrian; C, Carboniferous; D, Devonian; J, Jurassic; K, Cretaceous; KT, Cretaceous-Tertiary boundary; N, Neogene; O, Ordovician; OAE, Oceanic Anoxic Event; PETM, Paleocene-Eocene Thermal Maximum; Pg, Paleogene; Pr, Permian; S, Silurian; Tr, Triassic. (*b*) Evolution of ocean surface pH_{sws} (seawater pH scale) (Tyrrell & Zeebe 2004, Ridgwell 2005, Ridgwell & Zeebe 2005, Ridgwell & Schmidt 2010). Gray line: response of the global carbonate cycle to the mean paleo-pCO_2 reconstruction; gray-filled envelope: response to the uncertainty (one standard deviation) in paleo-pCO_2; orange-filled circle: estimates for the late Paleocene. (*c*) Reconstructed Ca^{2+} concentrations (Lowenstein et al. 2001). (*d*) Major changes in plankton assemblages (Martin 1995). Calcifying taxa are highlighted in green; noncalcifying taxa are shown in gray and blue. The rise during the early- to mid-Mesozoic of the importance of *Globigerinina* is shown as broadly representative of the timing of changes of planktonic foraminiferal taxa in general, although the evolution of the first foraminifera taxon occurred somewhat earlier in the mid-Paleozoic (Martin 1995). (*e*) Latitudinal extent of glaciation (Crowley & Burke 1998). (*f*) Phanerozoic evolution of atmospheric pCO_2 reconstructed from proxy records (*orange-filled circles*) by Royer et al. (2004). Paleo-pCO_2 data have been binned into 20-Ma intervals, with the mean indicated by green squares and one standard deviation indicated by error bars. The geological timescale for all panels is shown in panel *a*.

Erba & Tremolada 2004). However, rather than being transient (e.g., showing a decay pattern after an initial perturbation), the event was long-lasting, with a total duration of ~1 Ma. The timescale of its onset has been estimated at ~20,000 to 44,000 years ago (Li et al. 2008, Méhay et al. 2009), and the onset was most likely slower than the onset of the PETM, for example. Also, the substantial decline in nannoconid abundance (calcareous nannoplankton, proposed as an indicator of the calcification crisis) started ~1 Ma prior to the onset of the event (Erba & Tremolada 2004, Méhay et al. 2009). As the ocean carbonate mineral saturation state is generally well buffered on timescales of >10,000 years, it is improbable that effects on calcification would have lasted over millions of years (Gibbs et al. 2011). This view is supported by the fact that other heavily calcified taxa peaked in abundance precisely during the interval of minimum nannoconid abundance (Erba & Tremolada 2004). Some species such as the coccolithophore *Watznaueria barnesiae* show little change in abundance during the onset of the event (Méhay et al. 2009).

End-Permian and Cretaceous-Tertiary Boundary

The end-Permian mass extinction (~252 Mya) is believed to have invoked rapid and massive input of CO_2 to the ocean-atmosphere system, which is associated with one of the largest eruptions of flood basalts documented in the geologic record. The extinctions appear to show a pattern of selectivity with respect to physiological and ecological features of the biota. For example, hypercalcifiers with limited ability to pump ions across membranes show nearly complete extinction, whereas other groups that can modulate the composition of the calcifying fluid survived comparatively well. A comprehensive summary of the end-Permian mass extinction can be found elsewhere (e.g., Knoll 2003, Kump et al. 2009, Knoll & Fischer 2011, Payne & Clapham 2012). Unfortunately, no direct proxy records of seawater carbonate chemistry changes for the end-Permian appear to be available at this time.

The Paleocene-Eocene Thermal Maximum

The PETM (~55 Mya) is probably the closest analog for the future that has been identified in the geologic record. The onset of the PETM was marked by a global increase in surface temperatures by 5–9°C within a few thousand years (e.g., Kennett & Stott 1991, Thomas & Shackleton 1996, Zachos et al. 2003, Sluijs et al. 2006). At nearly the same time, a substantial carbon release occurred, as evidenced by a large drop in the $^{13}C/^{12}C$ ratios of surficial carbon reservoirs. The carbon release led to ocean acidification and widespread dissolution of deep-sea carbonates (e.g., Zachos et al. 2005, Zeebe et al. 2009, Ridgwell & Schmidt 2010). Different sources for the carbon input have been suggested, leading to speculations concerning the mechanism. Some mechanisms, such as volcanic intrusion, imply that the carbon drove the warming. Others, such as the destabilization of oceanic methane hydrates, imply that the carbon release is a feedback mechanism that can exacerbate warming (Dickens et al. 1995, Dickens 2000, Pagani et al. 2006, Dickens 2011). With respect to ocean acidification, whether the carbon source was CO_2 or methane is of minor importance, as methane would have been oxidized rapidly to CO_2 in the water column and/or the atmosphere. Remarkably, even the lower estimates for the carbon release during the onset of the PETM (~1 Pg C per year) appear to be of similar order of magnitude to that over the past 50 years from anthropogenic sources.

The PETM shows several characteristics that are essential for a meaningful comparison with the anthropogenic perturbation. First, it was a transient event with a rapid onset (not a long-term steady state); second, it was associated with a large and rapid carbon input. In contrast to aberrations that occurred in the more distant past, the PETM is relatively well studied because numerous well-preserved terrestrial and marine paleorecords for this time interval are available (on the marine side accessible through ocean drilling). The PETM may therefore serve as a case study for ocean acidification caused by CO_2 released by human activities. However, it is important to keep in mind that the climatic and carbon cycle boundary conditions before the PETM were significantly different from those today—including different continental configuration, absence of continental ice, and a different baseline climate. Moreover, ocean carbonate chemistry prior to the event was different from modern conditions, and the sensitivity to a carbon perturbation was likely reduced (Goodwin et al. 2009, Stuecker & Zeebe 2010). These aspects limit the PETM's suitability as the perfect future analog. Nevertheless, the PETM provides invaluable information on the response of the carbon cycle, climate, and ocean carbonate chemistry to massive carbon input. It also allows us to estimate the timescale over which carbon was removed from the ocean-atmosphere system by natural sequestration.

For the PETM, different carbon input scenarios have been proposed (e.g., Dickens et al. 1995, Panchuk et al. 2008, Zeebe et al. 2009). For example, the scenario proposed by Zeebe et al. (2009) requires an initial carbon pulse of approximately 3,000 Pg C over ~6,000 years to be consistent with the timing and magnitude of stable carbon isotope records and the deep-sea dissolution pattern (Zachos et al. 2005, Leon-Rodriguez & Dickens 2010). I have compared this PETM scenario with a Business-as-USual scenario of fossil fuel emissions of 5,000 Pg C over ~500 years (**Figure 6**). The 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 would be expected for the future

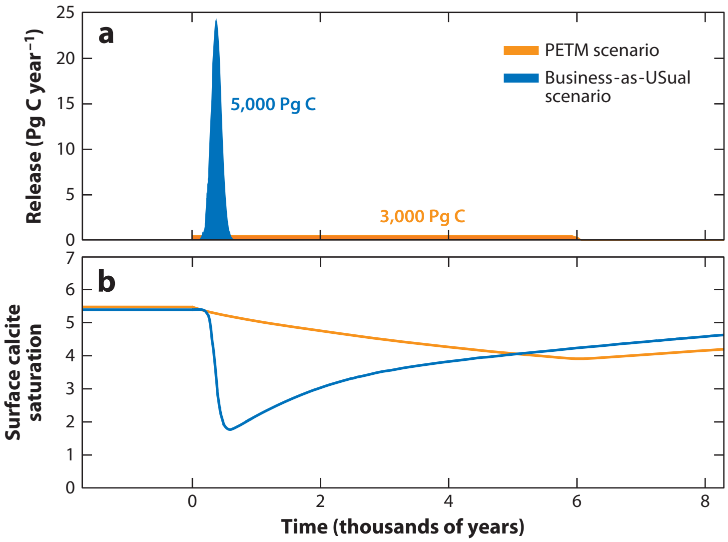


Figure 6

Paleocene-Eocene Thermal Maximum (PETM) versus Anthropocene. Modified from Zeebe & Ridgwell (2011). (*a*) Carbon emission scenarios as projected for the future under the Business-as-USual scenario [5,000 Pg C over ~500 years (Zeebe et al. 2008)] and as observed for the PETM [3,000 Pg C over 6,000 years (Zeebe et al. 2009)]. The onset of industrialization has been aligned with the onset of the PETM. (*b*) Changes in surface-ocean calcite saturation state (Ω_c) simulated with the LOSCAR (Long-term Ocean-atmosphere-Sediment CArbon cycle Reservoir) model (Zeebe 2011) in response to the carbon input shown in panel *a*.

(Zeebe & Zachos 2007, Ridgwell & Schmidt 2010). As pointed out above, both the magnitude and the timescale of the carbon input are 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 (**Figure 2*a***). As a result of a 5,000–Pg C input over $\sim$500 years, the surface-ocean calcite saturation state (Ω_c) would drop from approximately 5.4 to $<$2 within a few hundred years. In contrast, the PETM scenario suggests a corresponding decline of Ω_c from 5.5 to $\sim$4 within a few thousand years. I emphasize, however, that the PETM scenario may be subject to revision, depending on the outcome of future studies that will help better constrain the timescale of the carbon input.

Our suggestion that the PETM carbon input had a moderate impact on surface-ocean saturation state (Zeebe et al. 2009) is consistent with the results of Gibbs et al. (2006), who studied nannoplankton origination and extinction during the PETM. They concluded that the perturbation of the surface-water saturation state across the PETM was not detrimental to the survival of most calcareous nannoplankton taxa. In contrast, the Paleocene-Eocene boundary marks a major extinction event of benthic foraminifera, affecting 30–50% of species globally (e.g., Thomas 1990, 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 (for discussion, see Ridgwell & Schmidt 2010). In summary, the direct effects of ocean acidification on surface calcifiers during the PETM may have been limited because of a relatively slow carbon input rate (slow on human timescales, rapid on geologic timescales). Possible acidification effects on benthic organisms are difficult to quantify because of competing effects from other environmental changes (see also Knoll & Fischer 2011).

Among the ocean acidification events hitherto identified in Earth's history, the PETM may be the closest analog for the future. Yet the evidence suggests that the carbon input rate from human activities may exceed that during the PETM. Thus, it seems that the ocean acidification event that humans may cause over the next few centuries is unprecedented in the geologic past for which sufficiently well-preserved paleorecords are available.

SUMMARY

The geologic record provides valuable information about the response of the Earth system to massive and rapid carbon input. Analyses and evaluation of the information should ultimately lead to improved future predictions. In particular, studies of past changes in ocean chemistry teach us a lesson about the effects that ocean acidification may have on marine life in the future. In addition, they provide the necessary background to assess the current anthropogenic perturbation in the context of Earth's history. The assessment presented in this review shows that when studying the past, a good understanding of the relevant timescales involved is of utmost importance. For instance, short-term carbon cycling on a timescale of 10 to 100 years and long-term carbon cycling on a timescale of millions of years involve two distinct cycles with vastly different reservoir sizes and different sets of controls on atmospheric CO_2 and ocean chemistry (**Figure 2**). Thus, the pertinent timescales of paleo-pCO_2 and paleochemistry records require thorough examination if these records are to qualify as appropriate future analogs.

The survey of long-term changes of ocean carbonate chemistry during Earth's history (quasi-steady states) revealed that natural variations are generally slow and small on timescales relevant to the near future (see **Figure 7** for a summary). Because ocean saturation state is usually well regulated and decoupled from pH over tens of thousands of years, past events that involve geologically rapid changes of ocean carbonate chemistry are of particular interest. Among the ocean acidification events discussed here, the PETM may be the closest analog for the future.

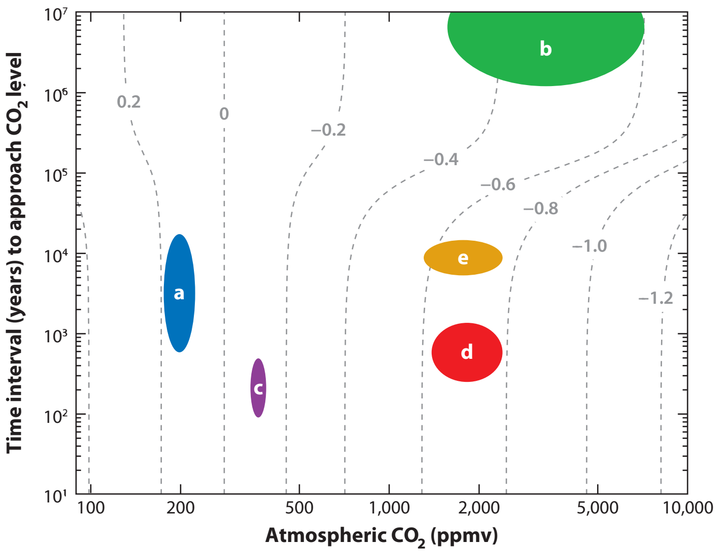


Figure 7

Estimated maximum change in surface-ocean pH (*gray labeled contour lines*) as a function of final atmospheric CO_2 partial pressure, and the transition time over which this CO_2 partial pressure is linearly approached from 280 ppmv. Modified from Caldeira & Wickett (2003). (*a*) Glacial-interglacial CO_2 changes. (*b*) Slow changes over the past 300 Ma. (*c*) Historical changes in ocean surface waters. (*d*) Unabated fossil fuel burning over the next few centuries. (*e*) The range of the timescale of carbon input and pCO_2 estimates during the Paleocene-Eocene Thermal Maximum (PETM), which was likely approached from a CO_2 level significantly higher than 280 ppmv. Surface-ocean pH changes were probably much smaller during the PETM than suggested in the figure because of lower sensitivity to carbon perturbations and substantially higher initial pCO_2 (e.g., Zeebe et al. 2009, Stuecker & Zeebe 2010).

However, the anthropogenic rate of carbon input appears to be greater than during any of the ocean acidification events identified so far, including the PETM.

DISCLOSURE STATEMENT

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