The role of the global carbonate cycle in the regulation and evolution of the Earth system

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Abstract

We review one of the most ancient of all the global biogeochemical cycles and one which reflects the profound geochemical and biological changes that have occurred as the Earth system has evolved through time – that of calcium carbonate ($CaCO_3$). In particular, we highlight a Mid Mesozoic Revolution in the nature and location of carbonate deposition in the marine environment, driven by the ecological success of calcareous plankton. This drove the creation of a responsive deep-sea sedimentary sink of $CaCO_3$. The result is that biologically driven carbonate deposition provides a significant buffering of ocean chemistry and of atmospheric CO_2 in the modern system. However, the same calcifying organisms that under-pin the deep-sea carbonate sink are now threatened by the continued atmospheric release of fossil fuel CO_2 and increasing acidity of the surface ocean. We are not yet in a position to predict what the impact on $CaCO_3$ production will be, or how the uptake of fossil fuel CO_2 by the ocean will be affected. This uncertainty in the future trajectory of atmospheric CO_2 that comes from incomplete understanding of the marine carbonate cycle is cause for concern.

Keywords: Earth system; carbon cycle; carbonate; calcifiers; ocean chemistry, CO_2, fossil fuel

1. Introduction

The geochemical or long-term carbon cycle primarily involves the exchange of carbon between the 'surficial' and 'geologic' reservoirs [*1*]. The former comprise atmosphere, oceans, biosphere, soils, and exchangeable sediments in the marine environment (Figure 1) while the latter include crustal rocks and deeply buried sediments in addition to the underlying mantle. How carbon is partitioned between the various reservoirs of the surficial system and between surficial and geologic reservoirs is what sets the concentration of CO_2 in the atmosphere. Life, and the cycle of organic carbon, as well as its geological (and subsequent fossil fuel exhumation) is of particular importance in this regard. The cycle of carbon in its inorganic, calcium carbonate ($CaCO_3$) [1] form also affects atmospheric CO_2, but by more subtle means. It also plays a fundamental role in regulating ocean chemistry and *p*H – a major factor in the viability of calcareous marine organisms.

Before exploring some of the roles that the global carbonate cycle plays in the functioning of the Earth system (Section 2) we first discuss the two constituent parts of this cycle; (a) precipitation and burial of $CaCO_3$, and (b) weathering and geologic recycling, illustrated in Figure 1a and 1b, respectively. Then, in Sections 3 and 4 we highlight the ways in which carbonate cycling on Earth has evolved through time, and look to the future and the increasing impact that fossil fuel CO_2 release will have on the system. We finish with a brief perspective on the implications for future research. Readers are referred to the Box for a brief primer on aqueous carbonate chemistry and $CaCO_3$ thermodynamics.

1.1 Carbonate precipitation and burial

Today, the surface of the ocean is everywhere more than saturated ('over-saturated') with respect to the solid carbonate phase, with a mean value for the saturation state ('Ω' – see Box) of calcite of 4.8. In other words, the minimum thermodynamical requirement for calcite to precipitate is exceeded by a factor of almost 5 (for aragonite, Ω is 3.2). Despite this, the spontaneous precipitation of $CaCO_3$ from the water column is not observed in the ocean [*2*]. This is because the initial step of crystal nucleation is kinetically unfavorable, and experimentally, spontaneous (homogeneous) nucleation does not occur in sea water solutions until $\Omega_{calcite} > \sim 20$ - 25 [*3*]. Although $CaCO_3$ precipitation occurs as cements and coatings in the marine environment, it is primarily associated with the activities of living organisms, particularly corals, benthic shelly animals, plankton species such as coccolithophores and foraminifera, and pteropods, and where it takes place under direct metabolic control. In comparison, carbonate deposition in fresh-water systems is of only minor importance globally, and will not be discussed further here.

While not in itself sufficient to drive substantial abiotic precipitation, the saturation state of the modern ocean surface is favorable to the preservation of carbonates deposited in shallow water (neritic) environments. Long-term accumulation of this material can result in the formation of extensive marine topographical features such as barrier reefs and carbonate banks and platforms. A different fate awaits $CaCO_3$ precipitated in the open ocean by plankton such as coccolithophores and foraminifera, however. This is because oceanic waters become increasingly less saturated with depth. Below the depth of the saturation horizon, conditions become under-saturated ($\Omega < 1.0$) and carbonate will start to dissolve. In the modern ocean the calcite saturation horizon (see Box) lies at about 4500 m in the Atlantic and ~3000 m in the Pacific Ocean. Within a further 1000 m sediments are often completely devoid of carbonate particles (the carbonate compensation depth, or 'CCD'). Topographic highs on the ocean floor such as the mid-Atlantic ridge can thus be picked out by sediments rich in $CaCO_3$ while the adjacent deep basins are low in $\%CaCO_3$ (Figure 3). The visual effect has been likened to 'snow-capped mountains'. The pressure induced surface-to-deep vertical contrast in Ω is further enhanced by

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[1] For the purposes of this review we simply refer to 'calcium carbonate', but recognize that carbonates exhibit a range of

the respiration of organic matter and release of metabolic CO_2 in the ocean interior which suppresses the ambient carbonate ion concentration and thus Ω (see Box). The greater accumulation of metabolic CO_2 in the older water masses of the deep Pacific explains why the sea-floor there is much poorer in %$CaCO_3$ compared to the Atlantic at a similar depth [*4*] (Figure 3).

Unfortunately, the carbonate cycle does not conform to this simple picture, and a significant fraction of $CaCO_3$ appears to dissolve in the water column even before it can reach the sediment surface [*4-6*]. This has been something of an enigma because the reduction in carbonate flux measured by sediment traps occurs well above the depth at which calcite becomes thermodynamically unstable. Dissolution of carbonate particles in acidic digestive conditions of zooplankton guts has been one proposed mechanism [*6*]. Acidic micro-environments within individual 'marine snow' aggregates may also be important [*7*]. Another possible explanation surrounds the aragonite polymorph because it becomes susceptible to dissolution at much shallower depths than calcite under the same ambient conditions. In support of this are recent estimates of the depth at which most $CaCO_3$ dissolution occurs in the ocean which appears to correspond to the aragonite saturation horizon [*4,5*]. However, calculations suggest that solute release from sinking pteropod shells, the main aragonite product in the open ocean, should mostly occur much deeper than this [*8*]. Dissolution of aragonite also does not help explain how 65% of calcitic foraminiferal tests can be lost at shallow depths [*9*]. This uncertainty is of concern because a full appreciation of the controls of atmospheric CO_2 and response to global change requires an understanding of the dissolution and the depth of recycling of $CaCO_3$ in the water column.

Overall, more than 80% of all carbonate precipitated in the open ocean dissolves either in the water column or within the uppermost layers of the underlying sediments [*4,10,11*]. The remainder, some 1 Gt $CaCO_3$ yr^{-1} accumulates in deep-sea sediments. This burial loss, to which can be added as much as another 1 Gt $CaCO_3$ yr^{-1} of deposition in neritic environments (although the uncertainty in this

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substitutions of Ca^{2+} by Mg^{2+} with a generic composition of $Mg_x \cdot Ca_{\cdot(1-x)} \cdot CO_3$.

figure is substantial) [*11,12*], must somehow be balanced if the ocean is not to run out of calcium ions! This is achieved through the weathering of carbonate and silicate rocks.

1.2 Weathering and carbonate recycling

The weathering of calcium-carbonate and calcium-silicate minerals in soils and at exposed rock surfaces helps balance the $CaCO_3$ sedimentation loss by unlocking Ca^{2+} from the geologic reservoir. Alteration of ocean crust by percolating fluids adds an additional but more minor contribution [*13*]. The weathering reactions (see Figure 1b; #5 and #7) provide the other raw material necessary for carbonate precipitation – bicarbonate ions (HCO_3^-). However, because the transformation $2CO_2 \rightarrow 2HCO_3^-$ (Figure 1b; #7) is internal to the surficial system and does not represent a source of 'new' carbon, the component of $CaCO_3$ burial derived from silicate rock weathering represents a loss of carbon to the geologic reservoir. This must be replaced on the long-term, achieved through the release of CO_2 to the atmosphere from volcanic sources [2] [*1*]. (In contrast, the weathering and burial of $CaCO_3$ results in no net loss or gain of CO_2 to the surficial system.)

A powerful regulatory mechanism of the Earth system arises because weathering rates respond to surface temperature and atmospheric CO_2 while simultaneously silicate weathering rates control the rate of transformation $CO_2 \rightarrow HCO_3$- and thus rate of loss of carbon through $CaCO_3$ burial. This is a negative feedback system [*14*] and acts to regulate the concentration of CO_2 in the atmosphere over hundreds of thousands of years [*1*].

Buried carbonate is eventually recycled back from the geologic reservoir. This can occur if carbonates laid down in shallow seas such as limestones or chalks are subsequently uplifted and exposed to weathering as a result of mountain building episodes. However, carbonates deposited in open ocean sediments are only infrequently exposed at the Earth's surface, as ophiolite complexes –

portions of the oceanic crust and overlying sediments that have been trapped between colliding cratonic blocks and uplifted. Instead, the primary recycling of deep-sea $CaCO_3$ occurs through subduction into the upper mantle and decarbonation (see Figure 1b; #6).

At this point it is important to recognize that carbonate burial represents the principal geologic mechanism of CO_2 removal from the ocean and atmosphere. However, the act of precipitating $CaCO_3$ has the effect of re-partitioning dissolved carbon in the surface ocean into $CO_{2(aq)}$, raising ambient pCO_2 and pH (see Box). Thus, precipitation and deposition of $CaCO_3$ has the short-term effect of increasing the concentration of CO_2 in the atmosphere at the expense of the ocean carbon inventory, but at the same time represents the ultimate long-term sink for CO_2.

2. The role of the global carbonate cycle in the Earth system

Over millions of years the silicate rock weathering feedback controls the concentration of CO_2 in the atmosphere [*1,14*]. On time-scales shorter than ca. 100 kyr, however, the weathering feedback is ineffective and the marine carbonate cycle plays an important role in determining atmospheric CO_2. We illustrate this by considering some of the global changes that marked the end of the last ice age 18 thousand years ago (18 ka), when CO_2 rose from a glacial minimum of 189 ppm to 265 ppm at the beginning of the Holocene [*15*].

The demise of the great Northern Hemisphere ice sheets was marked by a rise in sea-level of about 120 m [*16*]. With the flooding of the continental shelves came a 4-fold increase in the area of shallow water environments available for coral growth [*17*]. Because an increase in the rate of $CaCO_3$ deposition will drive more CO_2 into the atmosphere, this mechanism was once proposed as an explanation for the 70-80 ppm deglacial rise in atmospheric CO_2 – known as the 'coral reef' hypothesis

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[2] Imbalances between the rates of burial of organic carbon and weathering of ancient organic matter (kerogens) exposed at the land surface affects the inventory of carbon in the surficial reservoirs and thus atmospheric CO_2. The details of how this particular sub-cycle fits into the Earth system picture lies outside the scope of this review, however.

[*18*]. Subsequent ice core measurements made it apparent that the main increase in CO_2 occurred prior to the rise in sea-level [*19*]. However, one cannot reject a role for corals out of hand because reconstructions of the time-history of reef building episodes are unambiguous in demonstrating a profound increase in $CaCO_3$ deposition following the end of the last glacial [*20-22*]. *A priori* geochemical reasoning argues that this must translate into a net re-partitioning of CO_2 from the ocean to atmosphere. The solution to this is that the 'coral reef' mechanism is essentially a Holocene phenomenon, with post-glacial coral re-colonization and reefal buildup potentially explaining much of the 20 ppm increase in CO_2 observed in ice cores that starts at around 8 ka [*23*].

The global carbonate cycle plays other interesting biogeochemical games. Since the last glacial, the expansion of ecosystems to higher latitudes and stimulation of productivity by rising atmospheric CO_2 resulted in an increase in the amount of carbon contained in the terrestrial biosphere (vegetation plus soils). The estimates for this increase vary – from around 600 GtC based on deep-ocean ^{13}C changes [*24*] (but see [*25*] for a new re-assessment), ~850 GtC according to global vegetation models [*26*], to 1300 GtC (and higher) in some paleo vegetation reconstructions [*27*]. A transfer of carbon into the terrestrial biosphere of just 500 GtC should have driven atmospheric CO_2 downwards by some 40 ppm [*28*], yet ice cores show an increase between glacial and early Holocene of 70-80 ppm [*15*]. However, as CO_2 is sucked out of the atmosphere and ocean, oceanic CO_3^{2-} concentrations (and *p*H) increase (Figure 2) enhancing the stability of $CaCO_3$ in deep-sea sediments. Increased carbonate burial drives more CO_2 into the atmosphere, countering about 60% of the impact of re-growth in the terrestrial biosphere to leave a net CO_2 fall of just 17 (rather than 40) ppm [*28*]. This amelioration of a perturbation of atmospheric CO_2 by changes induced in the preservation of $CaCO_3$ in deep-sea sediments is known as 'carbonate compensation' [*29*] and represents a critical regulatory mechanism in the modern global carbon cycle on time-scales of 5-10 kyr. (Carbonate compensation also represents an additional way of helping to explain the 20 ppm late Holocene rise in atmospheric CO_2 [*30*], to which a rise in sea-surface temperature (SST) [*31*] and a reduction in terrestrial carbon storage could also have contributed [*32,33*].) Carbonate compensation on its own does not explain why atmospheric CO_2 should have risen during deglaciation at about the same time as the terrestrial biosphere was accumulating carbon. Clearly, there must be additional carbon cycle mechanisms operating at this time to explain the ice core CO_2 record, the main candidates being: higher SSTs, reduced sea-ice cover, a more restricted iron supply to the ocean biota, and increased ventilation of the deep ocean [*23,28*].

Yet another possible way of explaining an increase in atmospheric CO_2 arises because the saturation state of the deep-sea sedimentary pore-waters where $CaCO_3$ dissolution takes place is determined not only by Ω of the overlying waters but also by the amount of metabolic CO_2 released by the *in situ* respiration of particulate organic carbon (POC) [*34,35*]. Any change in the POC flux to the sediments will therefore alter the fraction of $CaCO_3$ that dissolves. (Strictly, it is the ratio between $CaCO_3$ and POC fluxes, the $CaCO_3$:POC 'rain ratio' that is the critical parameter rather than the absolute POC or $CaCO_3$ flux, *per se*). Models predict an atmospheric CO_2 sensitivity of about 1.6 ppm per percent reduction in $CaCO_3$:POC [*36,37*]. A 67% increase in pelagic POC production (or 40% decrease in $CaCO_3$) could therefore theoretically account for the entire deglacial CO_2 rise. Thus, although the responsiveness of deep-sea sedimentary $CaCO_3$ preservation offers a means of stabilizing ocean chemistry through carbonate compensation, the atmospheric CO_2 control setting on this carbonate regulator can be adjusted by changing surface ocean productivity and $CaCO_3$:POC rain ratio. However, despite its potential for explaining the ice core CO_2 record, a primary role for the rain ratio mechanism does not appear consistent with reconstructed shifts in the CCD and lysocline and model analysis [*38,39*]. Recent interpretations of sediment trap data also questions whether changes in the $CaCO_3$:POC rain ratio at the surface would be transmitted to the abyssal sediments [*40,41*] (see Section 4).

A different facet of the carbonate cycle is in its role as regulator of the saturation state of the ocean. Understanding past changes in surface saturation (Ω) provides the environmental context for the geological interpretation of primary carbonate mineralogy, particularly the occurrence of abundant environmentally controlled carbonates such as marine cements and ooids [*42*]. The occurrence of extremes in Ω may also be important in understanding the evolutionary driving force behind the advent of biomineralizing species [*43*]. Furthermore, given the partial pressure of CO_2 (pCO_2), knowledge of Ω (plus temperature and major cation composition) uniquely determines the state of the entire aqueous carbonate system [*44*]. Thus, as proxy-based reconstructions of paleo atmospheric CO_2 for the Phanerozoic improve [*45*] an understanding of how ocean Ω has also changed through time would enable all the properties of the aqueous carbonate state to be deduced, providing critical information in the interpretation of Earth history [*46*].

3. Evolution of the global carbonate cycle through Earth history

We review the history of global carbonate cycling in two parts; the Precambrian (up to 542 Ma), when inorganic geochemical processes tended to dominate the nature and location of carbonate deposition, and the Phanerozoic (542 Ma to present), when life became the single most important factor.

3.1 Carbonate cycling in the Precambrian – when geochemistry ruled the roost

The requirements for carbonate cycling to begin on the early Earth are fairly minimal – the contact of basaltic rock with water and dissolved CO_2 to initiate chemical weathering [*47*]. With the weathering of silicate rocks comes the delivery of solutes to the ocean, making an over-saturated surface and the eventual precipitation of carbonates inevitable. The early start to this biogeochemical cycle is reflected in the dated carbonate record which extends back to at least 3800 Ma [*48*] and deposition of the first facies would have occurred well before this.

Early Precambrian carbonates are characterized by sea-floor encrustations, crystal fans, and thick cement beds, all indicative of a relatively rapid and ‘abiotic’ mechanism of $CaCO_3$ precipitation. Progressively younger Precambrian rocks show a decreasing abundance of such inorganically precipitated carbonates [*49*]. This secular trend in carbonate fabric most likely reflects a progressive decline in the degree of ocean over-saturation. However, the reasons for this are not entirely clear. One possibility is because as the atmosphere and surface ocean become more oxygenated towards the end of the Precambrian, sea-water concentrations of Mn^{2+} and Fe^{2+} whould have declined [*49,50*]. Since these cations inhibit the precipitation of $CaCO_3$, a reduction in their concentration would mean that a lower degree of over-saturation is required to achieve the same global carbonate deposition rate. Alternatively, the gradual accretion of continental crust and associated increase in area of shallow water depositional environments means that a lower precipitation rate per unit area (and thus Ω) would be required to balance the same global weathering flux, [*51*]. Whatever the reasons, the Precambrian inorganic geochemical age was brought to a relatively abrupt end as life stepped on the evolutionary accelerator and drove the Earth system through a succession of new modes of carbonate cycling.

3.2 Carbonate cycling in the Phanerozoic – enter the biota

The advent of carbonate biomineralization occurred around the time of the Cambrian-Precambrian boundary [*52*] when evolutionary innovation conferred on organisms the ability to precipitate carbonate structures (skeletons). Prior to this there could have been no significant biologically driven production of $CaCO_3$, and carbonate deposition would have been primarily restricted to heterogeneous nucleation and crystal growth on organic and inorganic surfaces in warm shallow water environments [*49*]. Because biomineralization enabled the more efficient removal of weathering products from the ocean by the expenditure of metabolic energy, a lower thermodynamic driving force for carbonate precipitation would have been required in the ambient marine environment. The result would have been a reduction in ocean saturation (Ω) as the Phanerozoic got under way.

A second major development took place several hundred million years (Myr) later, with the Mesozoic proliferation of planktic calcifiers [*53*] and the establishment of the modern mode of carbonate cycling in a 'Mid Mesozoic Revolution' [*46*]. We illustrate the profound importance of this by considering the response of the marine carbonate cycle to two environmental forcings; (i) sea-level, which varies over hundreds of million years by up to 300 m (Figure 4a), and (ii) the cation chemistry of the ocean; particularly Magnesium (Mg^{2+}) and Calcium (Ca^{2+}) ion concentrations (Figure 4c). Although global temperatures and continental paleo-latitude also affect global carbonate deposition by determining the latitudinal extent of carbonate production by warm-water corals [*43,54*] we will restrict our analysis to just two factors.

Times of high sea-level such as the Mid Paleozoic produced flooding extents in excess of 50% on some cratons [*55*] and the creation of extensive inland (epeiric) seas. This in turn facilitated widespread carbonate platform development and shallow water carbonate accumulation [*43,54*] which would have driven a lower Ω. Conversely, times of low sea-level and restricted depositional area would produce a tendency towards high ocean Ω [*56*]. Superimposed on this is a variation in the oceanic ratio of Mg^{2+} to Ca^{2+} by a factor of three [*57-59*]. In order to maintain the same global rate of carbonate production, higher ambient Mg^{2+}/Ca^{2+} requires a more over-saturated ocean because Mg^{2+} inhibits calcite precipitation [*60*]. (The inhibition is predominantly a result of the Mg^{2+} interaction with the solid calcite phase, rather than a solution effect involving Mg^{2+}-CO_3^{2-} complexation. The latter effect reduces CO_3^{2-} activity but is independent of the $CaCO_3$ polymorph present in solution – see [*61*] and references therein.) At higher Ω, aragonite becomes more common in abiotic cements and hyper-calcifying organisms, which we observe in the geological record as distinctive times of relatively abundant shallow water carbonate aragonite [*62,63*] – periods dubbed 'aragonite seas' [*64*] (Figure 4d).

The coincidence of times of low sea-level and low Ca^{2+} concentrations (Figure 4) should have given rise to a highly over-saturated ocean. This is consistent with the widespread occurrence of abundant environmentally controlled carbonates such as cements, calcified cyanobacteria, and thick precipitated beds during parts of the Permian and Triassic [*42,65,66*], all indicative of comparatively rapid and 'abiotic' modes of carbonate precipitation. However, despite similar sea-level and cation chemistry, environmentally controlled carbonates are rare in the modern ocean. The difference is a direct consequence of the proliferation of calcareous plankton during the Mesozoic and creation of a new and substantive sink for $CaCO_3$ [*46,65,66*].

Although benthic foraminifera and other bottom-dwelling calcifiers evolved early in the Phanerozoic, it is not until the Mesozoic that a marked proliferation in coccolithophore and planktic foraminiferal diversity and abundance is observed [*53,67*] (Figure 4b). Only then would a substantive deep-sea sedimentary carbonate sink have been possible. This supposition is supported by the observed composition of Phanerozoic ophiolite suites which indicate that pelagic carbonate accumulation was comparatively rare in Paleozoic ocean sediments [*68*] (Figure 4e). Conversely, the mean area of platform carbonates during the Mesozoic and Cenozoic is much reduced compared to the Paleozoic (Figure 4f). One might speculate whether the ca. 200 Myr gap between the first appearance of calcifying planktic foraminifera and coccolithophorids and their rise to relative dominance in global pelagic ecosystems [*53*] is related to extreme ocean over-saturation in the late Permian and early Triassic, a potential environmental driving force favoring calcifiers. A similar thesis can be advanced to help explain the timing of the advent of metazoan biomineralization following the inferred occurrence of extreme oceanic saturation events during the late Precambrian [*69*].

The establishment of a substantive deep-sea carbonate sink is important because it introduced a new stabilizing mechanism to the Earth system – 'carbonate compensation' (see Section 2). Indeed, the absence of a responsive deep-sea carbonate sink in the Precambrian would have made the carbon-climate system much more sensitive to perturbation. Ice ages of near-global extent and multi million-year duration deduced for the end of the Precambrian [*70*] could have been facilitated by the weak ‘buffering’ of the Precambrian carbon cycle and atmospheric CO_2 [*71,72*]. This view is also consistent with the widespread occurrence of strange ‘cap’ carbonate facies deposited during postglacial flooding of the shelves. Other explanations for the genesis of cap carbonates in the aftermath of extreme late Precambrian glaciation have been proposed, such as the removal of the solutes derived from of rapid rock weathering under a high CO_2 atmosphere [*73,74*] and the overturning of a stagnant ocean [*42*]. However, all hypotheses recognize extreme changes taking place in global carbonate cycling at this time.

As well as adding new mechanisms for stabilizing atmospheric CO_2, the establishment of a substantive deep-sea sedimentary $CaCO_3$ sink would have also had a destabilizing effect. For instance, episodes of high weathering rates and sequestration of carbon in pelagic carbonates could subsequently lead to periods of enhanced metamorphic CO_2 out-gassing to the atmosphere as the sea-floor $CaCO_3$ is subducted and undergoes decarbonation [*75*]. The subduction of carbonates as ocean basins close and are destroyed would also result in episodic enhanced CO_2 release [*76,77*]. Both mechanisms predict secular oscillation in metamorphic CO_2 out-gassing rates on tectonic time-scales, and both would not have been possible before the Mid Mesozoic Revolution in carbonate deposition.

3.3 Synthesis

This evolution in global carbonate cycling over geologic time can be neatly conceptualized as three distinct marine carbonate cycle modes, termed ‘Strangelove’, ‘Neritan’, and ‘Cretan’ ocean modes by [*39*]. The geochemistry-ruled Precambrian mode of $CaCO_3$ cycling resembles a carbonate-‘Strangelove’ ocean, in which biogenic precipitation of $CaCO_3$ is essentially absent. It is characterized by high-supersaturation and generally inorganic (at most partly biologically-mediated) formation of carbonates. Following the advent of biomineralization in the Cambrian, biologically controlled carbonate precipitation in shallow-water (neritic) environments became significant. Its conceptual analog is the ‘Neritan’ ocean, in which the dominant mode of Ca^{2+} and CO_3^{2-} removal from seawater is biogenic, neritic carbonate deposition. The saturation state of the Neritan ocean is highly susceptible to changes in the population or ecological success of shallow-water calcifiers. The Mesozoic shift towards widespread pelagic biomineralization finally led to a significant stabilization of the marine $CaCO_3$ saturation state, termed the 'Cretan' ocean. Large and rapid shifts between e.g. the Neritic- and Cretan-ocean mode have likely occurred in the aftermaths of catastrophic events such as the Cretaceous-Tertiary bolide impact [*78*].

4. Back to the future: carbon cycling in the Anthropocene

The ocean is capable of absorbing about 70% of all the CO_2 released by fossil fuel combustion [*79*]. For a 4000 GtC 'burn' this means that the equivalent of ~600 ppm CO_2 will remain in the atmosphere after hundreds of years [*80*]. An atmospheric CO_2 concentration of ~1000 ppm is about three times the present-day (year 2003) value of 376 ppm [*81*] and represents a very significant long-term radiative forcing of the climate system. The terrestrial biosphere is unlikely to be of much help and may well become a net source of CO_2 to the atmosphere in the coming centuries as the Earth's surface warms [*82,83*], further exacerbating the problem. Fortunately, geochemical interactions between the ocean and deep-sea sediments intervene and on a time-scale of 5-8 kyr, carbonate compensation will remove a further 10-20% of fossil fuel CO_2 emitted to the atmosphere [*79*]. Ultimately, on a time-scale of 1 Myr, higher silicate rock weathering rates induced by enhanced greenhouse warming will remove the remaining fraction.

This has been the view of the response of the global carbonate cycle to anthropogenic perturbation – largely predictable and beneficial. New research paints a much murkier picture.

When CO_2 gas dissolves in water there is a reduction in carbonate ion concentrations and an increase in ocean acidity (see Box). As a result of historical fossil fuel CO_2 emissions surface *p*H has already been reduced by some ~0.1 *p*H units [*80,81*]. A further fall over the next few hundred years of more than 0.6 *p*H units is possible [*80*] (Figure 5). Because carbonate is thermodynamically less stable under such conditions, the metabolic cost to organisms of building carbonate shells and skeletons will be greater. Experimental studies have indeed demonstrated that corals are adversely affected at higher pCO_2 [*84-86*] with the implications for coral reef ecosystems already starting to be widely appreciated [*87,88*]. In contrast, much less attention has been paid to the open ocean environment. Only more recently has the extent to which calcifying plankton could be affected started to be recognized [*89-91*] (Figure 6). This has important implications for the marine carbon cycle.

The precipitation of $CaCO_3$ and subsequent removal from surface ocean layers through gravitational settling has the effect of driving surface ocean pCO_2 higher. This decreases the air-sea CO_2 gradient and opposes the uptake of fossil fuel CO_2 from the atmosphere. If carbonate production was reduced, surface ocean pCO_2 would fall and the rate of CO_2 invasion into the ocean would be enhanced – acting as a 'brake' (negative feedback) on rising atmospheric CO_2 [*89-91*]. Preliminary estimates suggest an increase in the rate of CO_2 uptake of 0.5-1.0 GtC yr^{-1} is possible [*91*]. In this respect, decreasing calcification and $CaCO_3$ export rates would play a direct and 'helpful' role in ameliorating future global change.

However, a strong association between particulate organic carbon (POC) and $CaCO_3$ fluxes recognized in deep-sea sediment trap data [*92,40*] may reflect a 'ballasting'[3] of organic matter by carbonate particles [*92,93*]. A decrease in $CaCO_3$ production would then drive a reduction in the efficiency with which POC is transported to depth, weakening the biological pump, and driving higher surface ocean pCO_2 [*94*]. This would reduce the flux of fossil fuel CO_2 into the ocean [*95*] and exacerbate future climate change.

Which is it? Unfortunately, the respective importance of these two mechanisms is poorly constrained and even the sign of the net impact is uncertain [*95*]. Underlying this is uncertainty in the

[3] The enhancement of the sinking rate of POC through the water column due to a greater mean aggregate density.

interpretation of the observed relationship between sinking fluxes of $CaCO_3$ and POC because alternative explanations require no direct link between the degree of calcification and the efficiency of particulate organic matter transport [*40,41*].

5. Summary and Perspectives

The trajectory that the concentration of CO_2 in the atmosphere takes will largely dictate the rate and magnitude of future climate change. In order to make sufficiently informed choices regarding the maximum fossil fuel CO_2 release that will keep global change within 'acceptable' limits, the natural pathways of CO_2 removal from the atmosphere must be fully characterized. Of primary importance is the oceanic sink, which already accounts for the equivalent of almost half of all CO_2 emissions due to fossil fuel burning and cement manufacture [*96*]. Improving our understanding of the role of the marine carbonate cycle in this and how it might change in the future is essential.

To put the possible environmental changes facing us into some perspective, one would have to turn the clock back at least 100 million years to find analogous surface ocean *p*H conditions (Figure 5b). One must recognize, however, that the calcifying species involved and relative importance of shallow vs. deep-water carbonate deposition have both changed over this period. More importantly, this also excludes transient perturbations of the carbon cycle – 'catastrophic' events such as associated with the 'Paleocene/Eocene Thermal Maximum' (PETM) at 55.5 Ma [*97*]. Indeed, the early Eocene could have seen significant surface ocean acidification in response to inferred CO_2 release to the ocean and atmosphere. Events such as the PETM represent a possible geologic analogue for future global change [*97,98*]. Understanding the PETM may prove critical in being able to correctly predict the long-term impact of continued fossil fuel CO_2 release, as well as what (if any) species of marine calcifying organisms might go extinct. However, we are still far from achieving this understanding and even the source and magnitude of the carbon release is currently hotly debated [*99*].

Given the importance of managing future global change, we believe that new impetus should be given to elucidating the role of the global carbonate cycle in the regulation and evolution of the Earth system. We identify several key priorities; (i) better quantification of the modern global carbonate budget, especially of neritic deposition, (ii) elucidating the response of planktic calcifiers and ecosystem composition to depressed ambient *p*H, (iii) understanding the reasons for the dissolution of carbonate particles sinking in the water column (and the general controls on the $CaCO_3$:POC 'rain' ratio at the sediment surface), and (iv) application of coupled carbon-climate models in the quantitative interpretation of 'catastrophic' geological events such as the PETM.

Box: Carbonate chemistry '101' and jargon buster

The mineral *calcium carbonate* ($CaCO_3$) has a crystal lattice motif comprising one calcium ion (Ca^{2+}) ionically bound to one carbonate ion (CO_3^{2-}), configured in different polymorphic forms; e.g., *calcite*, a trigonal structure, or *aragonite*, which is orthorhombic. Precipitation may be described by the following reaction: $Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_{2(aq)} + H_2O$. Of the reactants required for this, Ca^{2+} is naturally abundant in sea-water and at one of the highest concentrations of all ionic species in the ocean. *Bicarbonate ions* (HCO_3^-) are also ubiquitous in sea-water and are formed through the dissolution of CO_2 gas. Under typical marine conditions, carbon dioxide will largely hydrate to form a proton (H^+) and a bicarbonate ion (HCO_3); $H_2O + CO_{2(aq)} \rightarrow H^+ + HCO_3^-$ (see Figure 2), while true *carbonic acid* (H_2CO_3) is only present in very small concentrations. A fraction of HCO_3^- dissociates to form a *carbonate ion* (CO_3^{2-}); $HCO_3^- \rightarrow H^+ + CO_3^{2-}$. The sum total; $CO_{2(aq)}$ (+ H_2CO_3) + HCO_3^- + CO_3^{2-} is collectively termed *dissolved inorganic carbon* ('DIC').

The climatic importance of the $CaCO_3$ precipitation reaction arises because although the sum total of dissolved carbon species (DIC) is reduced, the remaining carbon is re-partitioned in favor of $CO_{2(aq)}$, resulting in a higher *partial pressure* of CO_2 (pCO_2) in the surface ocean. (Another way of thinking about this is in terms of removing CO_3^{2-} and shifting the aqueous carbonate equilibrium reaction $CO_{2(aq)} + CO_3^{2-} + H_2O \leftrightarrow 2HCO_3^-$ to the left to compensate.) The counter-intuitive and often confusing consequence of all this is that the precipitation of carbonate carbon drives an increase in ocean pCO_2, and with it, an increase in atmospheric CO_2 concentration. Conversely, dissolution of $CaCO_3$ drives a pCO_2 (and atmospheric CO_2) decrease.

Whether $CaCO_3$ precipitates or dissolves depends on the relative stability of its crystal structure. This can be directly related to the ambient concentrations (strictly, activities) of Ca^{2+} and CO_3^{2-} by the *saturation state* (also known as the *solubility ratio*) Ω of the solution, defined; $\Omega = [Ca^{2+}]\times[CO_3^{2-}]/K_{sp}$, where K_{sp} is a solubility constant [*44*]. The precipitation of calcium carbonate from sea-water is thermodynamically favorable when Ω is greater than unity and occurs at a rate taking the form of a proportionality with $(\Omega\text{-}1)^n$ [*100*], where *n* is a measure of how strongly the precipitation rate responds to a change in CO_3^{2-}. Conversely, $CaCO_3$ will tend to dissolve at $\Omega < 1.0$, and at a rate proportional to $(1\text{-}\Omega)^n$ [*101*].

As well as the concentrations of Ca^{2+} and CO_3^{2-}, depth in the ocean is also important because K_{sp} scales with increasing pressure. Since K_{sp} and Ω are inversely related, the greater the depth in the ocean the more likely the ambient environment is to be under-saturated (i.e., $\Omega < 1.0$). The depth at which $\Omega = 1.0$ occurs is termed the equilibrium *calcite saturation horizon* (CSH). (Similar terminology can be applied to the aragonite polymorph.) Although calcite becomes thermodynamically unstable just below this, dissolution proceeds only extremely slowly. The (greater) depth at which dissolution impacts become noticeable is termed the *calcite lysocline* [*102*]. In practice this is taken as the inflection point in the trend of sedimentary $CaCO_3$ content vs. water depth. For want of a more robust definition, a *chemical lysocline* is sometimes defined at $\Omega = 0.8$, a value which marks a distinct increase in dissolution rate [*6*]. Deeper still, and dissolution becomes sufficiently rapid for the dissolution flux back to the ocean to exactly balance the rain flux of calcite to the sediments. This is known as the *calcite* (or *carbonate*) *compensation depth* (CCD). Because in the real World the boundary in depth between sediments that have carbonate present and those in which it is completely absent is gradual rather than sharp, the CCD is operationally defined, and variously taken as the depth at which the $CaCO_3$ content is reduced to 2 or 10 wt%.

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Figure 1. The global biogeochemical cycling of calcium carbonate.

(a) Modes of $CaCO_3$ transformation & recycling within the surficial system and loss to the geological reservoir (labeled '1' through '4'). #1 Precipitation of calcite by coccolithophores and foraminifera in the open ocean; $Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_{2(aq)} + H_2O$. #2 Carbonate reaching deep-sea sediments will dissolve during early diagenesis if the bottom water is under-saturated and/or the organic matter flux to the sediments is sufficiently high. #3 Precipitation of $CaCO_3$ by corals and shelly animals, with a significant fraction as the aragonite polymorph. Because modern surface waters are over-saturated relatively little of this carbonate dissolves *in situ*, and instead contributes to the formation of reefal structures or is exported to the adjoining continental slopes. #4 Precipitation of $CaCO_3$ results in higher pCO_2 at the surface, driving a net transfer of CO_2 from the ocean to the atmosphere.

(b) Modes of $CaCO_3$ transformation & recycling within the geologic reservoirs and return to the surficial system (labeled '5' through '8'). #5 $CaCO_3$ laid down in shallow seas as platform and reef carbonates and chalks can be uplifted and exposed to erosion through rifting and mountain-building episodes. $CaCO_3$ can then be directly recycled; $CO_2 + H_2O + CaCO_3 \rightarrow Ca^{2+} + 2HCO_3^-$. #6 Thermal breakdown of carbonates subducted into the mantle or deeply buried. The decarbonation reaction involved is essentially the reverse of silicate weathering, and results in the creation of calcium silicates and release of CO_2; $CaCO_3 + SiO_2 \rightarrow CO_2 + CaSiO_3$. #7 Weathering of silicate rocks; $2CO_2 + H_2O + CaSiO_3 \rightarrow Ca^{2+} + 2HCO_3^- + SiO_2$. #8 Emission to the atmosphere of CO_2 produced through decarbonation. This closes the carbon cycle on the very longest time-scales.

Figure 2. The concentrations of the dissolved carbonate species as a function of *p*H (referred to as the Bjerrum plot, cf. [*44*]): Dissolved carbon dioxide ($CO_{2(aq)}$), bicarbonate (HCO_3^-), carbonate ion (CO_3^{2-}), hydrogen ion (H^+), and hydroxyl ion (OH^-). At modern seawater *p*H, most of the dissolved inorganic carbon is in the form of bicarbonate. Note that in seawater, the relative proportions of CO_2, HCO_3^-, and CO_3^{2-} control the *p*H and not vice versa.

Figure 3. Distribution of the calcium carbonate content of the surface sediments of the deep sea [*10*]. There is an apparent predominance of $CaCO_3$ accumulation taking place in the Atlantic and Indian

Oceans compared to much more sparse accumulation in the Pacific. This is primarily a consequence of the greater accumulation of metabolic CO_2 in deep Pacific waters which drives a greater degree of under-saturation and lowers the depth of the lysocline (see Box). The virtual absence of $CaCO_3$ in sediments of the Southern Ocean is due to a combination of much lower $CaCO_3$:POC rain ratio to the sediments and relatively corrosive bottom-waters. 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.

Figure 4. Evolution of global carbonate cycling through the Phanerozoic – major driving forces (panels *a* though *c*) and responses of the system recorded in the geological record (panels *d* through *f*).
FORCINGS: (a) Eustatic sea-level plotted relative to modern [*103*]. (b) Major changes in plankton assembledges [*53*]. Calcifying taxa are highlighted in black with non-calcifying taxa shown in grey. Although the rise of planktic foraminiferal taxa (for which we take *Globigerinina* as broadly representative) occurs during the early- to mid-Mesozoic, the evolution of the first calcifying foraminifera taxa occurred somewhat earlier in the mid-Paleozoic [*53*]. (c) Paleo marine Ca^{2+} concentrations as recorded in fluid inclusions contained in marine halite crystals [*57*] (vertical grey bars) as well as the model predictions of [*62*] (black curve).
RESPONSES: (d) Ascribed characterisitic periods of aragonite and calcite 'seas' [*62,63*], corresponding to times of high and low Mg^{2+}/Ca^{2+} ratios, respectively. (e) Percent occurrence of carbonates in ophiolite complexes for which sedimentary composition has been reported [*68*]. The comparative rarity of carbonate sediments in ophiolite complexes of Paleozoic age is noteable. (f) Reconstructed changes in the total area of platform (shallow water) carbonates [*43*]. A general poleward movement of the major continents through the Phanerozoic has been proposed as the reason for the apparent long-term decline in areal extent [*43*]. However, the general shape of the curve is also consistent with an oscillation in sea-level, with a step reduction in the importance of shallow water carbonate after the Mid Mesozoic Revolution [*46*].
The geological periods from the end-Precambrian to end-Phanerozoic are delineated at the top, running

from Ediacran ('E') (600 to 542 Ma) at the far right through to Paleogene ('Pg') and Neogene ('N') on the left-hand side.

Figure 5. A geologic perspective on current anthropogenic perturbation of the global carbon cycle. (a) Phanerozoic evolution of atmospheric CO_2 reconstructed from proxy records by [*45*]. Paleo CO_2 data has been binned into 20 Myr intervals, with the mean and error (one standard deviation) for each interval shown as horizontal black dash and vertical grey bar, respectively. The left hand side of the figure shows the historical atmospheric CO_2 trend (year 1800 to 2000) followed by the range in trajectories that would occur if between 4000 and 8000 GtC fossil fuel resources were to be combusted (and also depending on the assumed rate of CO_2 emissions) [*104*]. A peak value of between ~1000 and 3000 ppm is reached before the end of this millennium, indicated by the pair of horizontal dashed lines. (b) Model-predicted evolution of mean surface *p*H through the Phanerozoic (but only considering the case of a modern mode of carbonate cycling) [*46*]. The solid black line represents the response of the global carbonate cycle to the mean paleo pCO_2 reconstruction while the grey-filled envelope reflects the response to the error (1 s.d.) in paleo CO_2. The model is also forced with changes in ambient ocean Ca^{2+} concentrations (see Figure 4c) following 62], which has the effect of additionally supressing ocean *p*H by up to ~0.25 *p*H units during periods of elevated [Ca^{2+}] such as the early-to-mid Paleozoic, and mid-to-late Mesozoic. Further factors affecting carbonate cycling have a comparatively smaller effect and are excluded for clarity. For instance, the absence of a significant deep-sea sedimentary carbonate sink prior to ca. 200 Ma would increase *p*H and make the earlier Phanerozoic ocean slightly less acidic compared to the curve shown here, but by no more than ~0.1 *p*H units [*46*]. The predicted historical and future trajectory of mean surface ocean *p*H in response to the same range of CO_2 emission scenarios as detailed in (a) above [*104*] is shown on the left hand side of the figure. Future surface ocean *p*H reaches a minimum in the range 7.7 to 7.25 (indicated by the pair of horizontal dashed lines).

Figure 6. Scanning electron microscopy (SEM) photographs of coccolithophorids cultured under different CO_2 concentrations [*90*]. (a), (b), (d), (e), *Emiliania huxleyi*; and (c), (f), *Gephyrocapsa Oceanica*. Scale bars represent 1μm. Coccolith structure is notably different, with distinct malformations and a reduced degree of calcification in cells grown at elevated CO_2 levels (and lower

*p*H) (d,e,f) compared to cultures incubated at preindustrial CO_2 levels (a,b,c). With copyright permission from Nature Publishing Group.

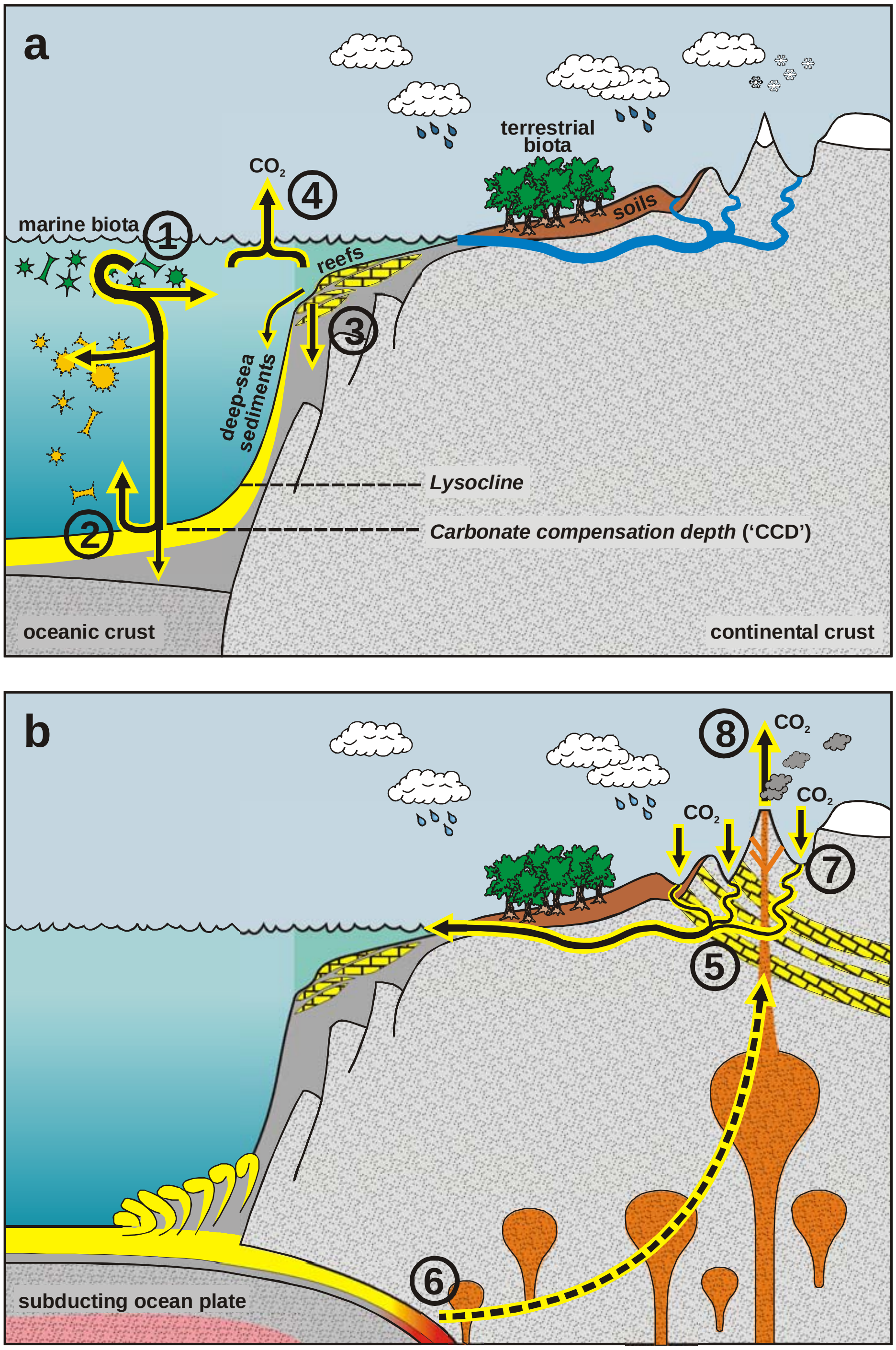

a
marine biota
1
CO$_2$
4
reefs
3
terrestrial biota
soils
deep-sea sediments
Lysocline
2
Carbonate compensation depth ('CCD')
oceanic crust
continental crust
b
8
CO$_2$
CO$_2$
CO$_2$
7
5
6
subducting ocean plate

figure_1

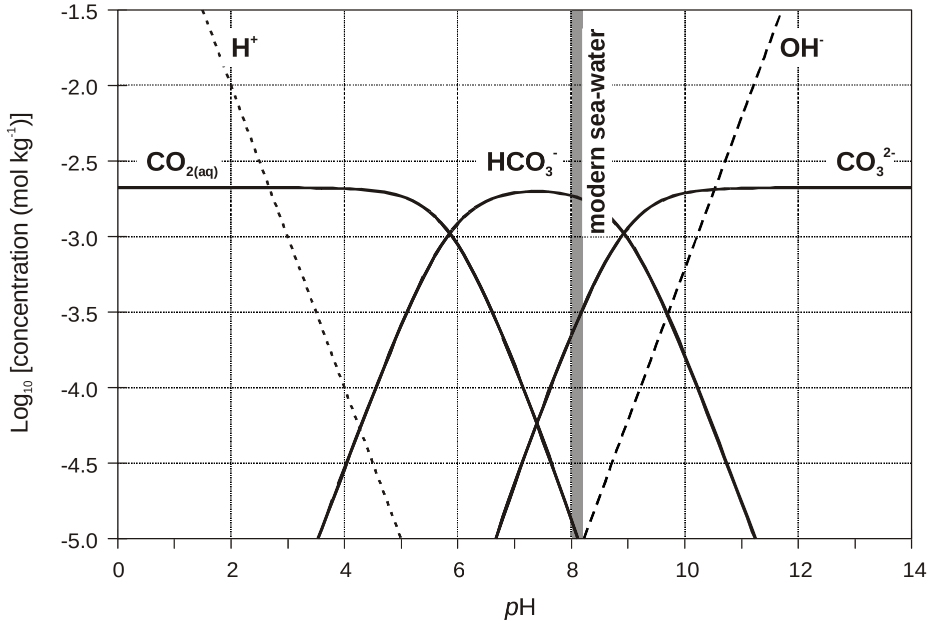

H$^+$
OH$^-$
CO$_{2(aq)}$
HCO$_3^-$
CO$_3^{2-}$
modern sea-water
Log$_{10}$ [concentration (mol kg^{-1})]
-1.5
-2.0
-2.5
-3.0
-3.5
-4.0
-4.5
-5.0
0
2
4
6
8
10
12
14
pH

figure_2

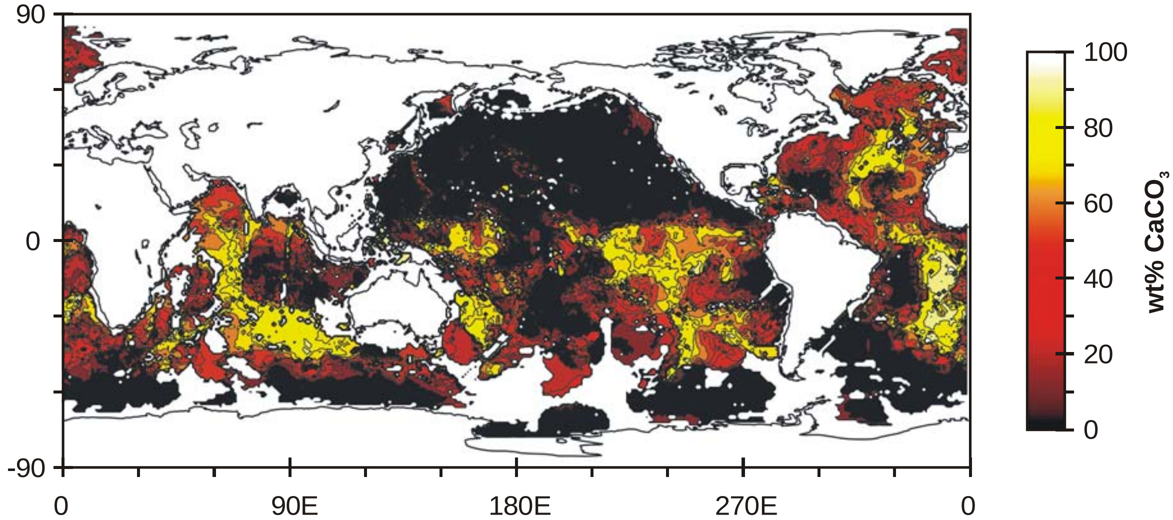


figure_3

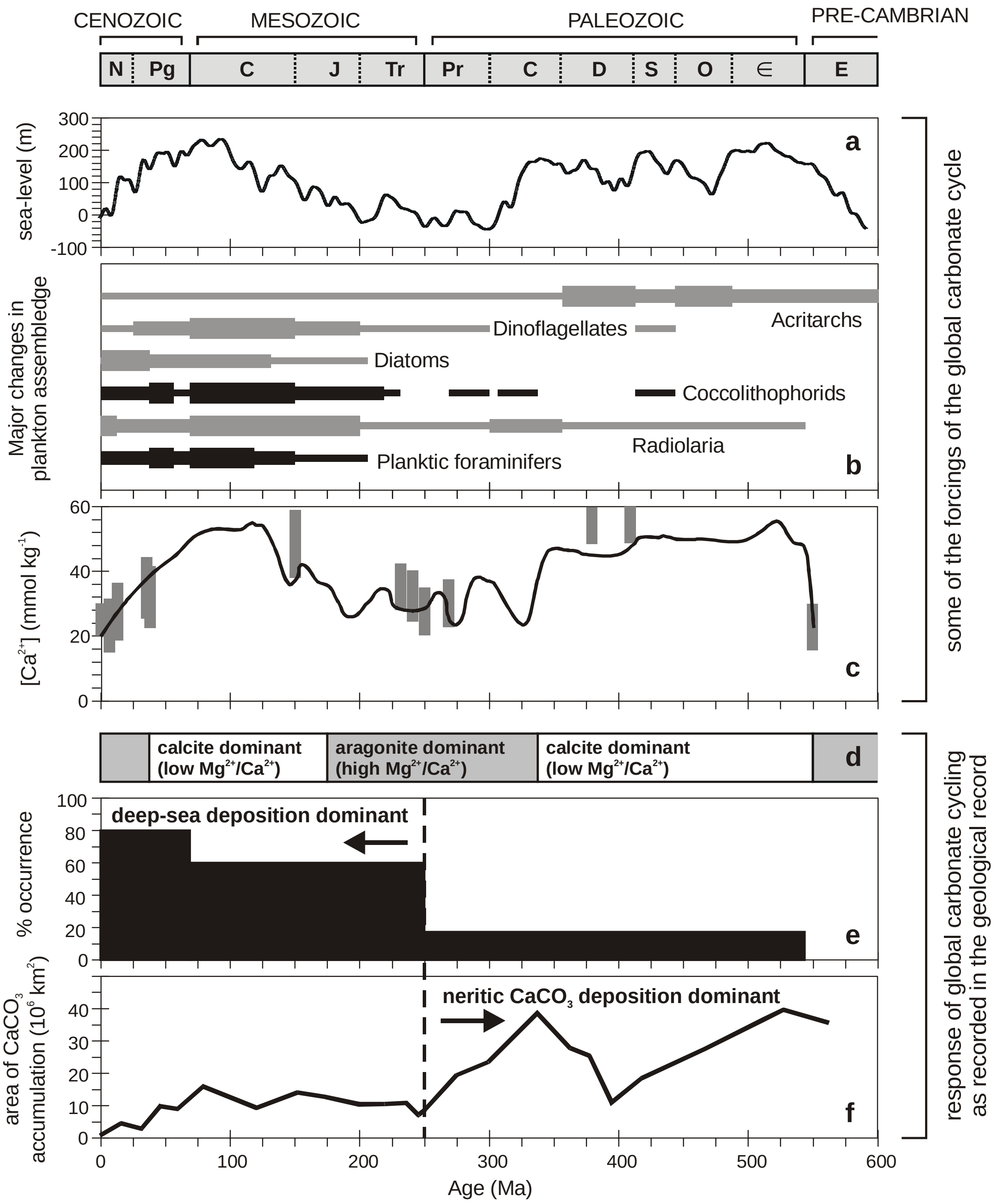
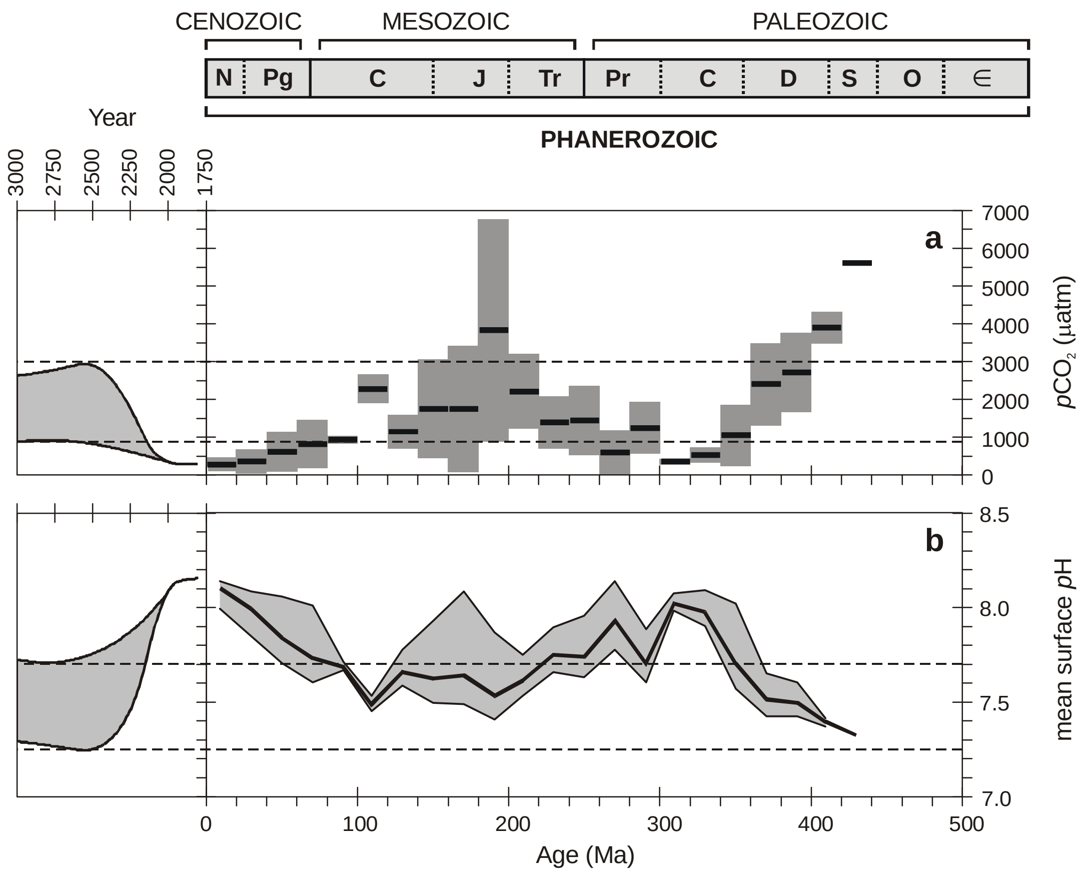

CENOZOIC
MESOZOIC
PALEOZOIC
PRE-CAMBRIAN
N
Pg
C
J
Tr
Pr
C
D
S
O
∈
E
sea-level (m)
a
Major changes in plankton assemblage
Acritarchs
Dinoflagellates
Diatoms
Coccolithophorids
Radiolaria
Planktic foraminifers
b
[Ca2+] (mmol kg-1)
c
some of the forcings of the global carbonate cycle
calcite dominant (low Mg2+/Ca2+)
aragonite dominant (high Mg2+/Ca2+)
calcite dominant (low Mg2+/Ca2+)
d
% occurrence
deep-sea deposition dominant
e
area of CaCO3 accumulation (10^6 km^2)
neritic CaCO3 deposition dominant
f
Age (Ma)
response of global carbonate cycling as recorded in the geological record

figure_4



CENOZOIC
MESOZOIC
PALEOZOIC
N
Pg
C
J
Tr
Pr
C
D
S
O
∈
PHANEROZOIC
Year
3000
2750
2500
2250
2000
1750
a
b
7000
6000
5000
4000
3000
2000
1000
0
pCO2 (µatm)
8.5
8.0
7.5
7.0
mean surface pH
0
100
200
300
400
500
Age (Ma)

fiigure_5

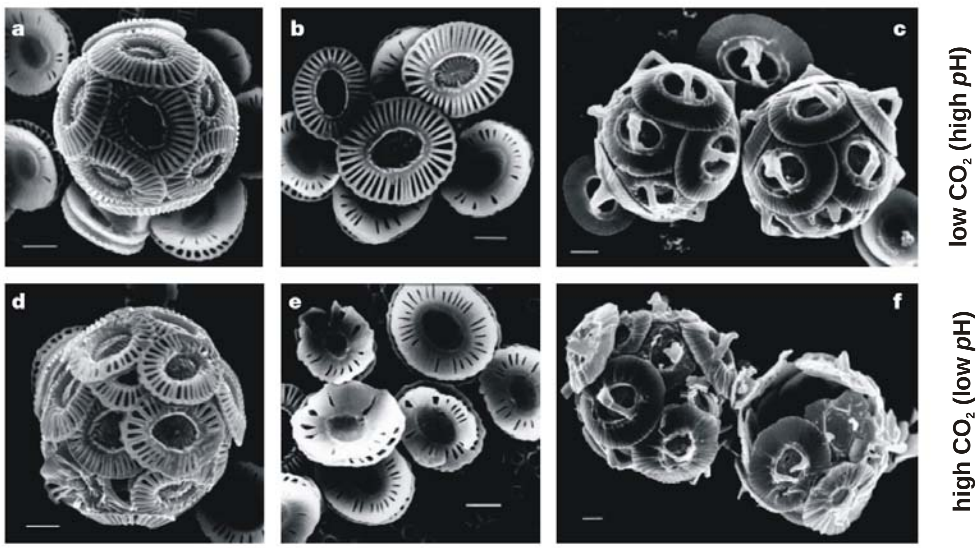


figure_6