

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 important geochemical and biological changes that have occurred as the Earth system has evolved through time – that of calcium carbonate. 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. The resulting creation of a responsive deep-sea sedimentary sink of CaCO_3 provides a significant buffering of ocean chemistry and of atmospheric CO_2 in the modern system. The importance of biologically driven carbonate deposition is consistent with the apparent relative instability of the Precambrian Earth system, prior to the advent of carbonate secreting organisms.

Today, the same calcifying organisms that under-pin the deep-sea carbonate sink are threatened by the continued atmospheric release of fossil fuel CO_2 and increasing acidity of the surface ocean. The degree of acidification possible is without precedent in the recent geological record and with the exception of catastrophic events such as at the onset of the Eocene some 55 Myr ago, we conclude that similar geochemical oceanographic conditions may not have occurred in at least 100 million years. Much progress has recently been made in revealing different ways in which the marine carbon cycle will be affected by anthropogenic acidification of the ocean. However, we do not yet know what the overall response of global carbonate cycling 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 is cause for concern. We argue that not only is further research into the role of global carbonate cycling in the regulation and evolution of the Earth system essential, but geo-engineering options such as deep injection of CO_2 in the ocean that could mitigate the degree of surface acidification should be more seriously considered.

Keywords: Earth system; carbon cycle; carbonate; 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 [Berner and Caldeira, 1997], 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 sets the concentration of CO₂ in the atmosphere. Life, and the cycle of organic carbon is of particular importance in this regard as it affects atmospheric CO₂ via a variety of mechanisms, such as the sinking to depth in the ocean of carbon that has been photosynthetically removed from solution by biological activity at the surface and terrestrial productivity, which affects the amount of carbon stored in vegetation and soils. On geologic time-scales the burial of organic carbon in sediments and transfer to the geologic reservoir becomes important. Changes in the cycling of carbonate carbon in the form of calcium carbonate (CaCO₃)¹ also affects atmospheric CO₂, but by more subtle means. It also plays a fundamental role in regulating ocean chemistry and pH – a major factor in the viability and fitness 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; precipitation and burial of CaCO₃, and weathering and recycling, illustrated in Figure 1a and 1b, respectively. (Readers are referred to the Box for a primer on aqueous carbonate chemistry and CaCO₃ thermodynamics.) Then, in Sections 3 and 4 we journey from the distant past, highlighting the ways in which carbonate cycling on Earth has evolved through time, and look to the future and the increasing impact that fossil

¹ For the purposes of this review we simply refer to ‘calcium carbonate’, but recognizing that carbonates exhibit a range of substitutions of Ca²⁺ by Mg²⁺, giving a general composition of Mg_x·Ca_(1-x)·CO₃.

fuel carbon will have on the system. We finish with a brief perspective on the implications for future research.

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 Ω_{calcite} and $\Omega_{\text{aragonite}}$ of 4.8 and 3.2, respectively (see Box). In other words, the minimum thermodynamical requirement for calcite to precipitate is exceeded by a factor of almost 5 (and just over 3 for aragonite). Despite this, the spontaneous precipitation of CaCO_3 from the water column is not observed in the ocean [Morse *et al.*, 2003]. This is because the initial step of crystal nucleation is kinetically unfavorable. Experimentally, spontaneous (homogeneous) nucleation does not occur in sea water solutions until $\Omega_{\text{calcite}} > \sim 20 - 25$ [Morse and He, 1993]. It is only in extreme chemical environments, such as the mixing zones surrounding thermal springs that apparent inorganic-physiochemical 'whittings' are observed [Arp *et al.*, 1999]. Instead, much of marine carbonate precipitation today is controlled directly by metabolic processes in living organisms, particularly corals, benthic shelly animals, plankton species such as coccolithophores and foraminifera, and pteropods. Precipitation of CaCO_3 cements and coatings also occurs but is predominantly restricted to shallow seas and makes a lesser contribution globally.

The over-saturated nature of the ocean surface favors the preservation of carbonate 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. A different fate awaits CaCO_3 precipitated in the open ocean by plankton such as coccolithophores and foraminifera, however. This is because the 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 CSH (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 'CCD'). Topographic highs on the ocean floor such as the mid-Atlantic ridge can thus be picked out by sediments rich in CaCO₃ while deep basins are low in %CaCO₃ (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 the respiration of organic matter in the water column. The addition of metabolic CO₂ reduces the ambient carbonate ion concentration (one can think of an equilibrium $\text{CO}_{2(\text{aq})} + \text{CO}_3^{2-} + \text{H}_2\text{O} \leftrightarrow 2\text{HCO}_3^-$ shifting to the right to remove excess CO₂) and thus Ω . The greater accumulation of metabolic CO₂ in the older water masses of the deep Pacific explains why the sea-floor there is much poorer in %CaCO₃ compared to in the Atlantic at a similar depth [Feely *et al.*, 2004] (Figure 3).

The marine carbonate cycle is not quite so straightforward, and a significant fraction of CaCO₃ appears to dissolve in the water column even before it can reach the sediment surface [Chung *et al.*, 2003; Feely *et al.*, 2004; Milliman *et al.*, 1999]. This has been something of an enigma because the reduction carbonate flux measured by sediment traps occurs well above the depth of the CSH. Dissolution of carbonate particles in acidic digestive conditions of zooplankton guts has been one proposed mechanism [Milliman *et al.*, 1999]. The presence of acidic micro-environments within individual 'marine snow' aggregates may also be important [Jansen *et al.*, 2002]. 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 made of the depth at which the maximum rate of CaCO₃ dissolution occurs and which appear to correspond to the ASH [Chung *et al.*, 2003; Feely *et al.*, 2004]. However, theoretical analysis of the sinking and dissolution in the water column of aragonite pteropod shells suggests that the solute release would be much deeper [Byrne *et al.*, 1984]. Dissolution of aragonite also does not help explain the estimated loss at shallow depths of 65% of calcitic foraminiferal tests [Schiebel, 2002].

Overall, the marine environment exhibits a relatively high degree of internal recycling with more than 80% of all carbonate precipitated in the open ocean dissolving either in the water column or within the uppermost layers of the underlying sediments [Archer, 1996; Feely *et al.*, 2004; Milliman and Droxler, 1996] (Figure 1a). The remainder, some 1 Gt CaCO₃ yr⁻¹ accumulates in deep-sea sediments. Shallow water deposition accounts for perhaps another 1 Gt yr⁻¹ of carbonate burial [Milliman and Droxler, 1996; Vecsei, 2004]. However, a paucity of data for a number of the fluxes gives rise to substantial uncertainties in the global budget [Vecsei, 2004]. This is of concern because a full appreciation of the controls of atmospheric CO₂ and response to global change requires an understanding of the dissolution and the depth of recycling of CaCO₃ in the water column. In the marine carbonate cycle, ‘ignorance is not bliss’ [Milliman and Droxler, 1996].

1.2 Rock weathering and carbonate recycling

The weathering of calcium-silicate minerals in soils and at exposed rock surface helps balance CaCO₃ sedimentation loss by unlocking Ca²⁺ from the geologic reservoir. Alteration of ocean crust by percolating fluids adds an additional but more minor contribution [Caldeira, 1995]. The weathering reactions (see Figure 1, #5 and #7) provide the other raw material necessary for carbonate precipitation – bicarbonate ions (HCO₃⁻). However, because the transformation CO₂ → HCO₃⁻ is internal to the surficial system and does not represent a source of ‘new’ carbon, burial of CaCO₃ represents a loss of carbon to the geologic reservoir. Obviously, this must be balanced on the long-term and which is achieved through the release of CO₂ to the atmosphere from volcanic sources² [Berner and Caldeira, 1997].

A powerful regulatory mechanism of the Earth system arises because weathering rates respond to surface temperature and atmospheric CO₂ while simultaneously weathering rates are controlling the

rate of transformation $\text{CO}_2 \rightarrow \text{HCO}_3^-$ and thus loss of carbon through CaCO_3 burial. This is a negative feedback system [Berner, 1999] which acts to regulate the concentration of CO_2 in the atmosphere on time-scales corresponding to the residence time of volcanic CO_2 in the surficial system – of order 100 kyr [Berner and Caldeira, 1997].

Buried carbonate can eventually be recycled back from the geologic reservoir. CaCO_3 that is subducted into the upper mantle or buried sufficiently deeply will undergo decarbonation (see Figure 1 #6) with the eventual release of CO_2 to the atmosphere. More direct re-cycling can occur if carbonates layer down in shallow seas such as limestones or chalks are subsequently uplifted and exposed to weathering. This can occur through continental collision and mountain building episodes. Carbonates deposited in deep-sea sediments can only be exposed at the Earth's surface through the infrequent creation of ophiolite complexes – portions of the oceanic crust and overlying sediments that have been trapped between colliding cratonic blocks and uplifted.

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

Over millions of years the silicate rock weathering feedback dictates the concentration of CO_2 in the atmosphere [Berner, 1999; Berner and Caldeira, 1997]. On time-scales shorter than ca. 100 kyr, however, the weathering feedback becomes ineffective and carbonate cycling plays an important role in determining 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 when CO_2 rose from a glacial minimum of 189 ppm to 265 ppm at the start of the Holocene [Monnin *et al.*, 2001].

The demise of the great Northern Hemisphere ice sheets was marked by a rise in sea-level of about 120 m [Siddall *et al.*, 2003]. With the flooding of the continental shelves came a 4-fold increase

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.

in the area of shallow water benthic environments [Kleypas, 1997]. In addition, warming of the ocean's surface would have extended the latitudinal limits of conditions favorable for coral growth. Because the consequence of an increase in the rate of CaCO₃ deposition is higher *p*CO₂ (see Box), this mechanism was once proposed as an explanation for the 70-80 ppm deglacial rise in atmospheric CO₂ – called the ‘coral reef’ hypothesis [Berger, 1982]. Subsequent ice core measurements made it apparent that much of the CO₂ increase occurred before any substantial sea-level rise, arguing against this explanation [Broecker and Henderson, 1998]. Despite this, reconstructions of the time-history of reef building episodes are unambiguous in demonstrating a profound increase in CaCO₃ deposition since the end of the last glacial [Montaggioni, 2000; Ryan *et al.*, 2001; Vecsei and Berger, 2004]. *A priori* geochemical reasoning argues that this must translate into a net re-partitioning of CO₂ from the ocean to atmosphere. How can we reconcile this with the ice-core CO₂ data? Because the rate of sea-level rise at the deglacial transition was too rapid for immediate coral re-colonization [Montaggioni, 2000], the CO₂ impact would have been delayed until the Holocene. Models suggest that this is consistent with the 20 ppm increase in CO₂ that started at around 8 ka [Ridgwell *et al.*, 2003a]. The ‘coral reef’ mechanism is then in essence a Holocene phenomenon.

The global carbonate cycle plays other interesting biogeochemical games. Due to the expansion of ecosystems to higher latitudes and stimulation of productivity by rising CO₂ during deglaciation the inventory of carbon in the terrestrial biosphere increased by an estimated 850 GtC [Kaplan *et al.*, 2002; Otto *et al.*, 2002]. This should have driven atmospheric CO₂ about 67 ppm lower [Archer *et al.*, 2000]. Ice cores, in contrast, show a generally rising trend in CO₂ at this time [Monnin *et al.*, 2002]. However, as CO₂ is sucked out of the atmosphere and ocean, oceanic CO₃²⁻ concentrations (and *pH*) increase (Figure 2), enhancing the stability of CaCO₃ in deep-sea sediments. Increased carbonate burial subsequently drives higher surface *p*CO₂, countering about 60% of the effect on atmospheric CO₂ that carbon removal by the terrestrial biota would have had on its own. The action of additional carbon

cycle mechanisms are then able to turn the relatively small residual decrease of 29 ppm into a rising deglacial CO₂ trend [Archer *et al.*, 2000; Ridgwell *et al.*, 2003a]. This amelioration of a perturbation of atmospheric CO₂ by an induced change in the preservation of CaCO₃ in deep-sea sediments is known as ‘carbonate compensation’ [Broecker and Peng, 1987] and represents a critical regulatory mechanism in the modern global carbon cycle on time-scales of 5-10 kyr.

There are further levels to the complexity of ocean-sediment interactions. The saturation state of the deep-sea sedimentary pore-waters where CaCO₃ dissolution takes place is determined not only by Ω of the overlying waters but also by the amount of metabolic CO₂ released by the *in situ* respiration of particulate organic carbon (POC) [Archer *et al.*, 2002, Hales, 2003]. Any change in the POC flux to the sediments will therefore alter the fraction of CaCO₃ that dissolves. (Strictly, it is the ratio between CaCO₃ and POC fluxes, the CaCO₃:POC ‘rain ratio’ that is the critical metric rather than the absolute CaCO₃ flux, *per se*). Models predict an atmospheric CO₂ sensitivity of about 1.6 ppm per percent reduction in CaCO₃:POC [Archer and Maier-Reimer, 1994; Ridgwell *et al.*, 2002]. A 40% decrease in pelagic CaCO₃ production (or 67% increase in POC production) could therefore theoretically account for the entire deglacial CO₂ rise. However, this hypothesis does not predict the decoupling of the CSH and lysocline that is required by paleoceanographic evidence [Sigman *et al.*, 1998; Zeebe and Westbroek, 2003]. Recent interpretations of sediment trap data also questions whether changes in the CaCO₃:POC rain ratio at the surface would be transmitted to the abyssal sediments [Ridgwell, 2003] (see Section 4).

Although the responsiveness of deep-sea sedimentary CaCO₃ preservation offers a means of stabilizing ocean chemistry and atmospheric CO₂ through carbonate compensation, there is the potential to alter for the control setting on this carbonate regulator by a change in surface ocean productivity and CaCO₃:POC rain ratio. One way to do this is through the silicic acid (H₄SiO₄) supply to diatoms – siliceous phytoplankton which compete with calcifying phytoplankton for limiting

nutrients common to both such as nitrate and iron. A change in the rate of H_4SiO_4 supply from aeolian dust [Harrison, 2000] or continental rock weathering [Tréguer and Pondaven, 2000], or by a meridional redistribution of H_4SiO_4 within the ocean [Brzezinski *et al.*, 2002; Ganeshram, 2002; Matsumoto *et al.*, 2002] could all achieve this. The implications of this ‘silicate switch’ [Ridgwell *et al.*, 2002] are that a full appreciation of the open ocean carbonate cycle also requires an adequate understanding of both ecosystem dynamics and the marine silica cycle.

A different facet to the carbonate cycle is its role in regulating the saturation state of the ocean. Understanding past changes in surface saturation 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 [Grotzinger and Knoll, 1995]. The occurrence of extremes in Ω may also be important in understanding the evolutionary driving force behind the advent of biomineralizing species [Walker *et al.*, 2002]. Furthermore, given $p\text{CO}_2$, knowledge of Ω uniquely determines the state of the entire aqueous carbonate system. Although the associated uncertainties are still quite substantial, proxy-based reconstructions of paleo atmospheric CO_2 are available spanning much of the Phanerozoic [Royer *et al.*, 2004]. In contrast, long-term predictions of oceanic Ω are a relatively new undertaking [Ridgwell, submitted, Royer *et al.*, 2004; Tyrrell and Zeebe, 2004]. As paleo CO_2 estimates improve, an understanding of how ocean Ω has changed through time would enable all the properties of the aqueous carbonate state to be interrogated, providing critical information in the interpretation of Earth history. For instance, ocean $p\text{H}$ (or CO_3^{2-}) is required in the calculation of ocean temperature from carbonate $\delta^{18}\text{O}$ [Spero *et al.*, 1997; Zeebe, 2001], while the interpretation of boron isotopes ($\delta^{11}\text{B}$) as surface $p\text{CO}_2$ requires DIC (or CO_3^{2-}) [Caldeira and Berner, 1999; Pearson and Palmer, 1999, 2000]. Assumptions regarding the oceanic (and atmospheric) carbon inventory also underlie all mass-balance interpretations of $\delta^{13}\text{C}$ excursions (e.g. Dickens *et al.* [1995]; Jiang *et al.* [2003]; Kennedy *et al.* [2001]).

3. Evolution of the global carbonate cycle through Earth history

We divide the history of global carbonate cycling into two periods; the Precambrian (up to 542 Ma), when 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 the initiation of carbonate cycling on the early Earth are fairly minimal – the contact of basaltic rock with water and dissolved CO₂ [Sleep and Zahnle, 2001]. With chemical weathering comes the delivery of solutes to the ocean, making an over-saturated surface and the eventual precipitation of carbonates inevitable. This is reflected for instance in the record of isotopically analyzed carbonates which extends back to 3800 Ma [Shields and Veizer, 2002].

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 CaCO₃ precipitation. Progressively younger Precambrian rocks show a decreasing abundance of such inorganically precipitated carbonates [Grotzinger and James, 2000]. 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 that as the atmosphere and surface ocean became more oxygenated towards the end of the Precambrian, sea-water concentrations of Mn²⁺ and Fe²⁺ which inhibit the precipitation of CaCO₃ declined [Grotzinger and James, 2000; Grotzinger and Kasting, 1993]. Alternatively, the gradual accretion of continental crust and associated increase in the global area of shallow water depositional environments would have required a lower precipitation rate per unit area in order to balance a given weathering flux, resulting in a progressively less saturated ocean [Des Marais, 2001]. The observations may also reflect a reduction in the rate of CO₂ out-gassing from the

mantle and progressively lower rate of silicate rock weathering. Whatever the reasons were for the long-term and progressive changes in carbonate deposition, the Precambrian 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 Phanerozoic saw fundamental events taking place in global carbonate cycling. Sea-level varied over hundreds of million years by up to 300 m (Figure 4a) and was one driver of change. Times of high sea-level such as the Mid Paleozoic produced flooding extents in excess of 50% on some cratons [Algeo and Sessler, 1995] and led to the creation of extensive inland (epeiric) seas. This in turn facilitated widespread carbonate platform development and shallow water carbonate accumulation [Walker *et al.*, 2002] and would have driven a lower degree of over-saturation in the ocean.

Conversely, times of low sea-level and restricted depositional area produces a tendency towards high Ω . Global temperatures contribute by determining the latitudinal extent of carbonate deposition [Opdyke and Wilkinson, 1993]. Continental paleo-latitude has an analogous influence, and determines the proportion of shallow seas falling within the latitudinal limits of coral growth [Walker *et al.*, 2002].

Another driving force is the cation chemistry of the ocean; particularly Magnesium (Mg^{2+}) and Calcium (Ca^{2+}) ion concentrations. Past records of these concentrations are recorded in the fluid inclusions contained in marine halite crystals [Horita *et al.*, 2002; Lowenstein *et al.*, 2001, 2003] (e.g., Figure 4b) while the ratio between them can also be read from the analysis of primary skeletal carbonates [Dickson, 2002; Stanley *et al.*, 2002]. Associated with this are shifts in the relative abundance of aragonite in shallow water carbonates [Stanley and Hardie, 1998, 1999] which appear as distinctive time periods in the geological record. The linking mechanism is the inhibition of calcite precipitation at higher Mg^{2+} concentrations by a reduction in its stability [Davis *et al.*, 2000]. A high $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio suppresses calcite precipitation, driving ocean Ω up until aragonite becomes common

in abiotic cements and hyper-calcifying organisms. An ‘aragonite sea’ is recorded in the geological record.

The superimposition of low sea-level with high Mg^{2+}/Ca^{2+} would have given rise to a high degree of ocean over-saturation. 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 [*Grotzinger and Knoll, 1995; Riding, 1993; Sumner and Grotzinger, 1996*], all indicative of comparatively rapid and ‘abiotic’ modes carbonate precipitation. The cold, polar location of the super-continent Pangea would have produced unfavorable conditions for corals and thus contributed to the effect. However, despite low sea-level, high Mg^{2+}/Ca^{2+} , and a predominance of continental area sited at high latitudes, the saturation state of the modern ocean does not appear to be particularly high and environmentally controlled carbonates are rare. The difference is due to the fundamental impact that the proliferation of calcareous plankton during the Mesozoic had in creating a substantive sink for $CaCO_3$ in the deep-sea [*Riding, 1993; Sumner and Grotzinger, 1996*].

The establishment of the modern mode of carbonate cycling in a Mid Mesozoic Revolution can be viewed as a two-step process [*Sumner and Grotzinger, 1996*]; (1) the advent of biomineralization around the time of the Cambrian-Precambrian boundary [*Wood et al., 2002*], and (2) the Mesozoic proliferation of planktic calcifiers [*Martin, 1995*]. The initial critical step was the evolutionary innovation that was the ability to precipitate carbonate structures (skeletons). Prior to this there could have been no significant biologically driven $CaCO_3$ production, and carbonate deposition would have been primarily restricted to heterogeneous nucleation and crystal growth on organic and inorganic surfaces in warm shallow water environments [*Grotzinger and James, 2000*]. The advent of biomineralization enabled the more efficient removal of weathering products from the ocean by the expenditure of metabolic energy.

Although there is some evidence that planktic biomineralizers evolved much earlier in the Phanerozoic, it is not until the Mesozoic that a marked proliferation in coccolithophore and foraminiferal diversity and abundance is observed [Hart *et al.*, 2003; Martin, 1995] (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 [Boss and Wilkinson, 1991] (Figure 4d). Conversely, even allowing for secular oscillation driven by sea-level, the area of platform carbonates is conspicuously much greater before the Mesozoic compared to afterwards (Figure 4e). One might speculate whether the ca. 200 Myr gap between the first appearance of calcifying foraminifera and coccolithophorids and their rise to relative dominance in global pelagic ecosystems [Martin, 1995] might not be related to the occurrence of an interval of extreme ocean oversaturation in the late Permian and early Triassic. This could have served as an 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 [Brennan *et al.*, 2004].

The establishment of a substantive deep-sea carbonate sink is important because it introduced a new stabilizing mechanism to the Earth system – ‘carbonate compensation’. 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. Positive feedback involving sea-level fall, loss of neritic area, and draw-down of atmospheric CO₂ could help explain the extremity of glaciation that has been deduced for the end of the Precambrian [Ridgwell *et al.*, 2003b; Ridgwell and Kennedy, in press] – the time of so-called ‘snowball Earths’ [Hoffman *et al.*, 1998; Kirschvink, 1992]. In this view ice ages of near-global extent and multi million-year duration are facilitated by the weak ‘buffering’ of the Precambrian carbon cycle in the absence of a responsive deep-sea carbonate sink. The existence of an extreme

saturation at end of the glacial is also consistent with the widespread occurrence of strange ‘cap’ carbonate facies, deposited during postglacial flooding of the shelves. Other explanations exist such as enhanced ‘greenhouse’ weathering [*Hoffman et al.*, 1998; *Hoffman and Schrag*, 2002] and the overturning of a stagnant ocean [*Grotzinger and Knoll*, 1995]. However, all invoke extreme changes in global carbonate cycling.

In contrast to its millennial-scale buffering capability, the establishment of a substantive deep-sea sedimentary CaCO₃ sink would have also led to new mode of recycling which could have given rise to a destabilizing effect, but on much longer time-scales. For instance, episodes of high weathering rates and sequestration of carbon in pelagic carbonates could subsequently lead to periods of enhanced metamorphic CO₂ out-gassing to the atmosphere as the sea-floor CaCO₃ is subducted and undergoes decarbonation [*Caldeira*, 1991]. A related effect is that carbonate buried in sediments at comparatively shallow water depths close to spreading ridges would later be subducted with the closing and destruction of ocean basins, again results in enhanced CO₂ release [*Edmond and Huh*, 2003; *Schrag*, 2002]. Both effects would lead to a secular oscillation in metamorphic CO₂ 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

The evolution of CaCO₃ precipitation and burial over geologic time outlined above may be sketched by three distinctly different stages, referred to as the ‘Strangelove’, the ‘Neritan’, and the ‘Cretan’ ocean by *Zeebe and Westbroek* [2003]. The geochemistry-ruled Precambrian mode of CaCO₃ cycling resembles a carbonate-‘Strangelove’ ocean, in which biogenic precipitation of CaCO₃ 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 [Zeebe and Westbroek, 2003]. Large and rapid shifts between e.g. the Neritic- and Cretan-ocean mode likely have occurred in aftermaths of catastrophic events such as the Cretaceous-Tertiary bolide impact [Caldeira & Rampino, 1993].

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

The current rising trend in atmospheric carbon dioxide results from our failure to limit the release of fossil fuel CO_2 to the maximum rate at which the ocean and terrestrial biosphere can absorb it from the atmosphere. Since the start of the Industrial Revolution (the late 1700s) atmospheric CO_2 has risen by about 100 ppm, reaching 376 ppm by the year 2003 [Keeling and Whorf, 2004]. Depending on the rate and total amount of fossil fuel burned a concentration of between 1000 and 3000 ppm could be reached sometime over the thousand years [Tyrrell *et al.*, submitted] (Figure 5). However, the modern ocean has a limited capacity to store CO_2 and if 4000 GtC or more of the remaining fossil fuel reserves were burned over the coming few centuries some 30% of these emissions equal to ~600 ppm CO_2 would remain in the atmosphere [Archer *et al.*, 1997, 1998; Caldeira and Wickett, 2003]. A residual atmospheric inventory of 1000 ppm CO_2 represents a very significant long-term radiative warming of the Earth system. It should be noted that the terrestrial biosphere is unlikely to be of much help and is predicted to become a net source of CO_2 to the atmosphere in the coming centuries as the Earth’s surface warms [Cox *et al.*, 2000; Lenton, 2000], further exacerbating the problem.

Fortunately, on millennial time-scales and longer, geochemical interactions between the ocean and deep-sea sediments intervene [Archer *et al.*, 1997, 1998]. The first ocean-sediment process that comes into play is the chemical reaction between CaCO₃ already present in deep-sea sediments and the overlying water, with dissolution of CaCO₃ in effect neutralizing a portion of the CO₂. With a shallower lysocline and reduced marine carbonate sedimentation flux, the excess of weathering over burial will lead to a further adjustment of neutralization of CO₂ until deep-sea carbonate ion concentrations reduce to their pre-perturbation value. Thus, on a time-scale of 5-8 kyr carbonate compensation will remove a further 10-20 of fossil fuel CO₂ emissions. Ultimately, on hundreds of thousands of years, the higher silicate rock weathering rates induced by greenhouse warming will remove the final fraction.

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

When CO₂ 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 CO₂ emissions surface pH has already be reduced by some ~0.1 pH units [Kleypas *et al.*, 1999; Caldeira and Wickett, 2003]. A further fall over the next few hundred years of more than 0.6 pH units is possible [Caldeira and Wickett, 2003; Tyrrell *et al.*, submitted] (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 pCO₂ [Gattuso *et al.*, 1998; Leclercq *et al.*, 2000; Marshall and Clode, 2002] with the implications for coral reef ecosystems already widely appreciated [Hughes *et al.*, 2003; Kleypas *et al.*, 2001]. In contrast, relatively little attention has been paid to the open ocean environment and it is only much more recently that the extent to which calcifying plankton could be affected has started to be recognized

[*Barker and Elderfield, 2002; Riebesell et al., 2000; Zondervan et al., 2001*] (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 $p\text{CO}_2$ higher. This decreases the air-sea CO_2 gradient and opposes the uptake of fossil fuel CO_2 from the atmosphere. If carbonate production decreases, surface ocean $p\text{CO}_2$ will fall and the rate of CO_2 invasion into the ocean will be enhanced – acting as a ‘brake’ (negative feedback) on rising atmospheric CO_2 [*Barker et al., 2003; Zeebe and Westbroek, 2003; Zondervan et al., 2001*]. Preliminary estimates suggest an increase in the rate of CO_2 uptake of 0.5-1.0 GtC yr⁻¹ is possible [*Zondervan et al., 2001*]. In this respect, decreasing calcification and CaCO_3 export rates will play a direct and ‘helpful’ role in ameliorating future global change [*Elderfield, 2002; Zeebe and Westbroek, 2003; Zondervan et al., 2001*].

However, a strong association between particulate organic carbon (POC) and CaCO_3 fluxes recognized in deep-sea sediment trap data [*Armstrong et al., 2002; Francois et al., 2002; Klaas and Archer, 2002*] may reflect a ‘ballasting’³ of organic matter [*Armstrong et al., 2002; Klaas and Archer, 2002*]. 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 $p\text{CO}_2$. This secondary impact would reduce the flux of fossil fuel CO_2 into the ocean [*Barker et al., 2003*].

Currently, the respective importance of these two mechanisms is poorly constrained and even the sign of the net impact is uncertain [*Barker et al., 2003*]. Underlying this is uncertainty in the interpretation of the observed relationship between sinking fluxes of CaCO_3 and POC [*Francois et al., 2002; Passow, 2004*]. Alternative explanations require no direct link between calcification and the efficiency of organic matter transport.

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

Finally, the revelation that a significant change in the flux of CaCO_3 to the sediments could occur adds a new and currently unexplored dimension to the interaction between ocean and deep-sea sediments. A reduction in sedimentary CaCO_3 burial would drive $p\text{CO}_2$ slowly lower, aiding the removal of fossil fuel CO_2 on millennial time-scales. However, if carbonate ballasts POC, the reduced release of metabolic CO_2 in deep-sea sediments would enhance carbonate preservation and lead to increasing CO_2 . Little consideration has yet been given to this aspect of response of carbonating cycle to global change.

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, society will require that the natural pathways of CO_2 removal from the atmosphere are fully characterized. Of primary importance in this is the ocean, which has already absorbed the equivalent of almost half of all CO_2 emissions due to fossil fuel burning and cement manufacture [*Sabine et al.*, 2004]. Understanding how the oceanic carbon sink changes in the future is essential.

With the anthropogenic acidification of the marine environment the ability of certain species of plankton to make calcium carbonate shells will be seriously diminished. What the impact of this will be on the rate at which the ocean takes up fossil fuel CO_2 is not yet well understood. Indeed, even the sign of the impact is uncertain, and anthropogenic acidification of the ocean could give rise to a strong negative (stabilizing) feedback on rising atmospheric CO_2 or could exacerbate future global change. Closer collaboration between experimentalists, observationalists, and models of carbon cycling and global change will be essential in addressing this.

Furthermore, the degree of acidity that could be reached in the surface ocean over the coming centuries appears to be without precedent in recent geologic history (Figure 5). Depending on how proxies for ocean pH are derived [Pearson and Palmer, 1999; Caldeira and Berner, 1999] and what assumptions are made regarding how carbonate deposition has changed during the Phanerozoic [Ridgwell, submitted] we believe that one would have to turn the clock back at least 100 million years to find analogous surface ocean conditions. This analysis excludes transient perturbations of the carbon cycle, however. Catastrophic events such as a hypothesized clathrate CH₄ release associated with the ‘Paleocene/Eocene Thermal Maximum’ at 55.5 Ma [Dickens *et al.*, 1995] could have potentially driven pH much lower for thousands of years. Such events are likely to be the best analogues for future global change. More work is thus required in not only understanding the controls on the long-term cycle of calcium carbonate and saturation state, but also the impact that infrequent catastrophic events have on global carbon cycling.

It is possible to mitigate anthropogenic acidification of the ocean and its associated impact on the global carbonate cycle. This will require not only in a re-doubling of efforts towards substantive emissions control and reductions targets but a more serious consideration of ‘geo-engineering’ solutions such as transferring or ‘sequestering’ carbon captured from power plants directly into the deep ocean [Kheshgi and Archer, 2004; Wickett *et al.*, 2003]. Deep injection would help avoid the environmental impact associated with the passage of CO₂ from the atmosphere through the comparatively shallow and resistive uppermost layer of the ocean where it then drives extreme acidification [Caldeira and Wickett, 2003]. One could argue the case because the ocean is ‘naturally’ sequestering anthropogenic CO₂ [Wickett *et al.*, 2003] and most fossil fuel CO₂ released to the atmosphere will end up in solution in the deep ocean over the next few hundred years anyway and in essence, deep-injection is speeding up a ‘natural’ transfer process. However, sequestration does come

with some environmental cost and there would be local or regional impacts on the benthic biota associated with the deep injection site [Hu *et al.*, 2003].

Given the importance of understanding and 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.

Box: Carbonate chemistry ‘101’ and terminology

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 either of two polymorphic forms; *calcite*, a trigonal structure, or *aragonite*, which is orthorhombic. Precipitation of both proceeds by the following reaction: $\text{Ca}^{2+} + 2\text{HCO}_3^- \rightarrow \text{CaCO}_3 + \text{CO}_{2(\text{aq})} + \text{H}_2\text{O}$. 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, dissolved carbon dioxide ($\text{CO}_{2(\text{aq})}$) will largely hydrate to form *carbonic acid* (H_2CO_3) (see Figure 2). Carbonic acid, in turn, rapidly dissociates to form a proton (H^+) and a bicarbonate ion (HCO_3^-); $\text{H}_2\text{O} + \text{CO}_{2(\text{aq})} \rightarrow \text{H}^+ + \text{HCO}_3^-$. A fraction of HCO_3^- undergoes further dissociate to form a *carbonate ion* (CO_3^{2-}); $\text{HCO}_3^- \rightarrow \text{H}^+ + \text{CO}_3^{2-}$. The sum total $\text{CO}_{2(\text{aq})} + \text{H}_2\text{CO}_3 + \text{HCO}_3^- + \text{CO}_3^{2-}$ is collectively termed *dissolved inorganic carbon* (‘DIC’).

The climatic importance of CaCO_3 precipitation arises because the carbonic acid released in the reaction drives an increase in the concentration of $\text{CO}_{2(\text{aq})}$ and a decrease in ambient *pH*. Another way of thinking about this is in terms of removing CO_3^{2-} and shifting the aqueous carbonate equilibrium reaction $\text{CO}_{2(\text{aq})} + \text{CO}_3^{2-} + \text{H}_2\text{O} \leftrightarrow 2\text{HCO}_3^-$ to the left to compensate. Thus, although CaCO_3 precipitation reduces the sum total of dissolved carbon species (DIC), the remaining carbon is re-

partitioned in favor of $\text{CO}_{2(\text{aq})}$. The resulting higher partial pressure of CO_2 ($p\text{CO}_2$) in the surface ocean will drive a loss of CO_2 to the atmosphere. The counter-intuitive and often confused result is that the precipitation of carbonate carbon drives an increase in atmospheric CO_2 . Conversely, dissolution of CaCO_3 drives a 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; $\Omega = [\text{Ca}^{2+}] \times [\text{CO}_3^{2-}] / K_{\text{sp}}$, where K_{sp} is a solubility constant [Zeebe and Wolf-Gladrow, 2001]. 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 $(\Omega - 1)^n$ [Zhong and Mucci, 1993], where n is a measure of how strongly precipitation rate responds to a change in CO_3^{2-} . Conversely, CaCO_3 will tend to dissolve at $\Omega < 1.0$.

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 $\Omega = 1.0$ with respect to the calcite polymorph is termed the equilibrium *calcite saturation horizon* (CSH). Below this depth calcite particles will start to dissolve. However, one must go deeper than this for dissolution to be sufficiently rapid that all CaCO_3 reaching the sediment surface dissolves before it can be buried in the accumulating sediments. This is the *calcite compensation depth* (CCD) (also referred to in general as the *carbonate compensation depth*). Lying somewhere in between the CSH and CCD there is a visual transition from CaCO_3 -rich sediments to sediments with increasingly less abundant CaCO_3 . This is the calcite *lysocline*. Similar terminology is applied to the aragonite polymorph.

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Figure 1. The global biogeochemical cycling of calcium carbonate.

TOP PANEL: Modes of CaCO_3 transformation recycling within the surficial system and loss to the geological reservoir. (1) Precipitation of calcite by coccolithophores and foraminifera in the open ocean; $\text{Ca}^{2+} + 2\text{HCO}_3^- \rightarrow \text{CaCO}_3 + \text{CO}_{2(\text{aq})} + \text{H}_2\text{O}$. (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 [Archer *et al.*, 2002]. (3) Precipitation of CaCO_3 by corals and shelly animals, mainly 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 a higher partial pressure of CO_2 at the surface, driving a net transfer of CO_2 from the ocean to the atmosphere.

BOTTOM PANEL: Modes CaCO_3 transformation recycling within the geologic reservoirs and from geologic to the surficial system. (5) CaCO_3 layed 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; $\text{CO}_2 + \text{H}_2\text{O} + \text{CaCO}_3 \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^-$. (6) Thermal breakdown of carbonates subduction 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 CO_2 ; $\text{CaCO}_3 + \text{SiO}_2 \rightarrow \text{CO}_2 + \text{CaSiO}_3$. (7) Weathering of silicate rocks; $2\text{CO}_2 + \text{H}_2\text{O} + \text{CaSiO}_3 \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^- + \text{SiO}_2$. (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 $p\text{H}$ (referred to as the Bjerrum plot, cf. Zeebe and Wolf-Gladrow [2001]): Dissolved carbon dioxide ($\text{CO}_{2(\text{aq})}$), bicarbonate (HCO_3^-), carbonate ion (CO_3^{2-}), hydrogen ion (H^+), and hydroxyl ion (OH^-). At modern seawater $p\text{H}$, 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 $p\text{H}$ and not vice versa.

Figure 3. Distribution of calcium carbonate in the surface sediments of the deep sea [Archer, 1996]. There is an apparent predominance of CaCO₃ 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 CO₂ 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 CaCO₃ in sediments of the Southern Ocean is due to a combination of much lower CaCO₃:POC rain ratio to the sediments and relatively corrosive bottom-waters. Topographic ‘highs’ can be picked out as areas of higher %CaCO₃ compared to sediments elsewhere in the same basin at similar latitudes.

Figure 4. Evolution of global carbonate cycling through the Phanerozoic – major driving forces (panels *a* through *c*) and responses of the system recorded in the geological record (panels *d* and *e*).

FORCINGS: (a) Eustatic sea-level plotted relative to modern [Haq *et al.*, 1988]. (b) Major changes in plankton assemblages [Martin, 1995]. Calcifying taxa are highlighted in black with non-calcifying taxa shown in grey. The rise during the early- to mid-Mesozoic of the importance of *Globigerinina* is shown as broadly representative of the timing of changes of planktic foraminiferal taxa in general, although the evolution of the first foraminifera taxa occurred somewhat earlier in the mid-Paleozoic [Martin, 1995]. (c) Fluid inclusion analysis of paleo marine Ca²⁺ concentrations [Horita *et al.*, 2002] (vertical grey bars) as well as the model predictions of Stanley and Hardie [1998] (black curve).

RESPONSES: (d) Percent occurrence of carbonates in ophiolite complexes for which sedimentary composition has been reported [Boss and Wilkinson, 1991]. The comparative rarity of carbonate sediments in ophiolite complexes of Paleozoic age is notable. (e) Reconstructed changes in the total area of platform (shallow water) carbonates [Walker *et al.*, 2002]. 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 [Walker *et al.*, 2002]. 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 [Ridgwell, submitted].

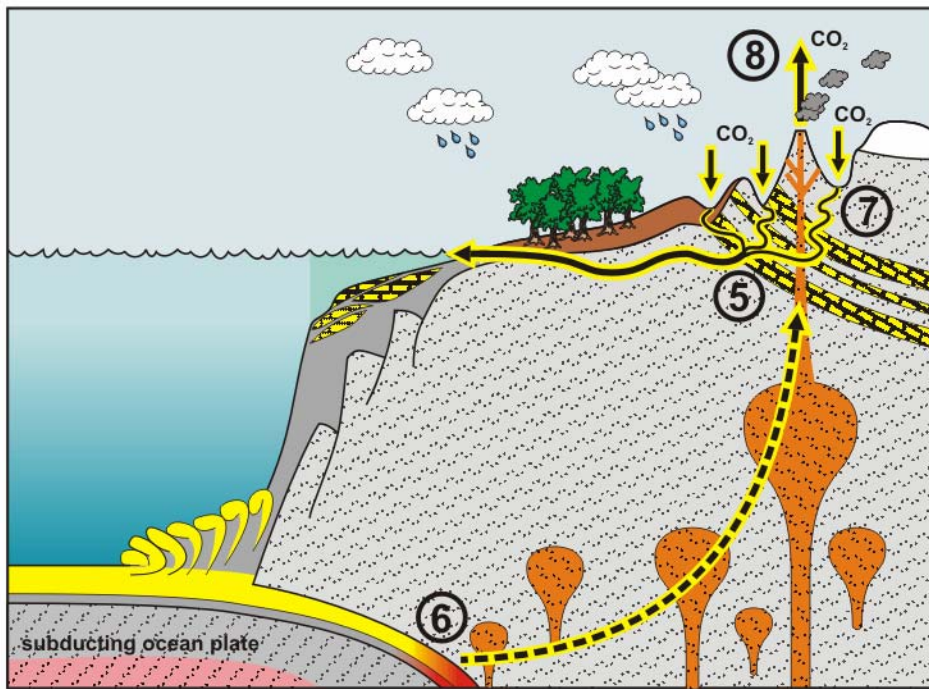
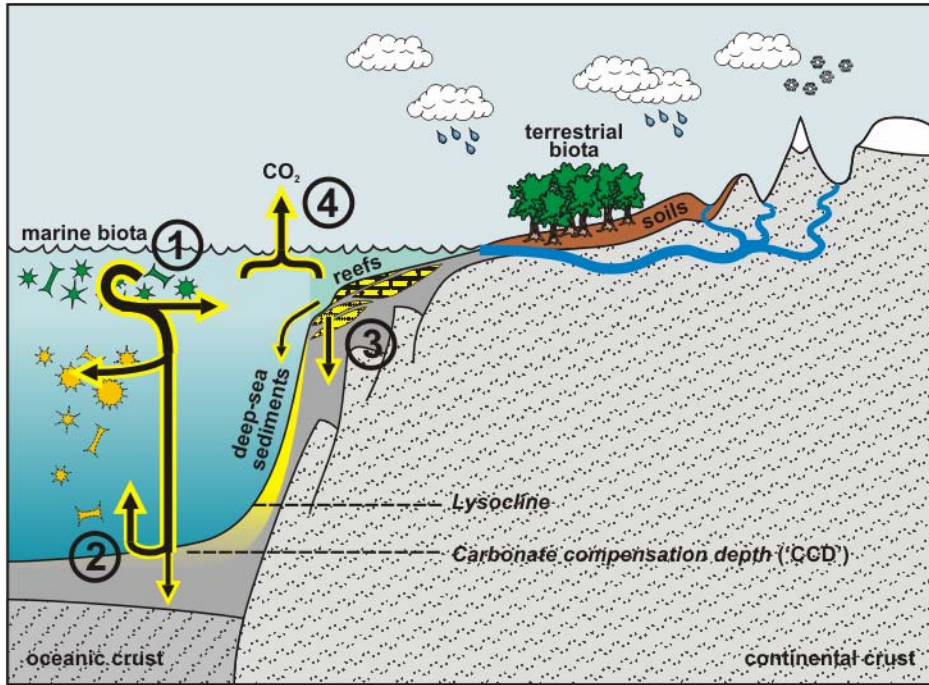
The geological periods of the end Precambrian and Phanerozoic are delineated at the top, running from

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

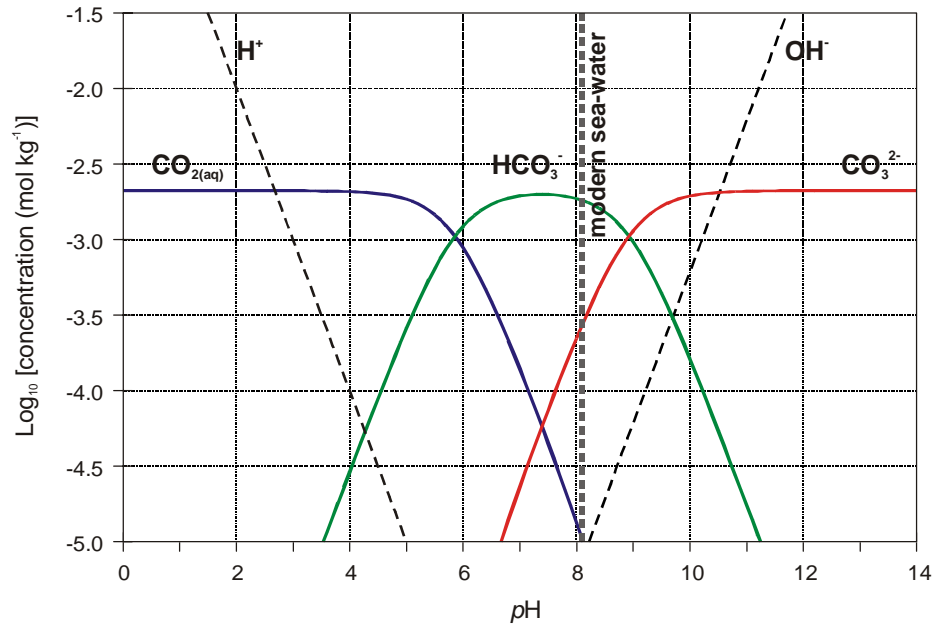
Figure 5. A geologic perspective to current anthropogenic perturbation of the global carbon cycle. (a) Phanerozoic evolution of atmospheric CO₂ reconstructed from proxy records by *Royer et al.* [2004]. Paleo CO₂ data has been binned into 20 Myr intervals, with the mean and error (one standard deviation) for each interval shown as horizontal black dash and vertical grey bar, respectively. The left hand side of the figure shows the historical atmospheric CO₂ trend (year 1800 to 2000) followed by the range in trajectories that would occur if between 4000 or 8000 GtC fossil fuel resources were to be combusted (and also depending on the assumed rate of CO₂ emissions) [*Tyrrell et al.*, submitted]. 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 pH through the Phanerozoic [*Ridgwell*, submitted] but only considering the case of a modern mode of carbonate cycling. The solid black line represents the response of the global carbonate cycle to the mean paleo pCO₂ reconstruction while the grey-filled envelope reflects the response to the error (1 s.d.) in paleo CO₂. The model is also forced with changes in ambient ocean Ca²⁺ concentrations (see Figure 4c) following *Stanley and Hardie* [1998], which has the effect of additionally suppressing ocean pH by up to ~0.25 pH units during periods of elevated [Ca²⁺] 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 pH and make the earlier Phanerozoic ocean slightly less acidic compared to the curve shown here, but only by no more than ~0.1 pH units [*Ridgwell*, submitted]. The predicted historical and future trajectory of mean surface ocean pH in response to the same range of CO₂ emission scenarios as detailed in (a) above [*Tyrrell et al.*, submitted] is shown on the left hand side of the figure. Future surface ocean pH 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 CO₂ concentrations [*Riebesell et al.*, 2000]. (a), (b), (d), (e), *Emiliania huxleyi*; and (c), (f),

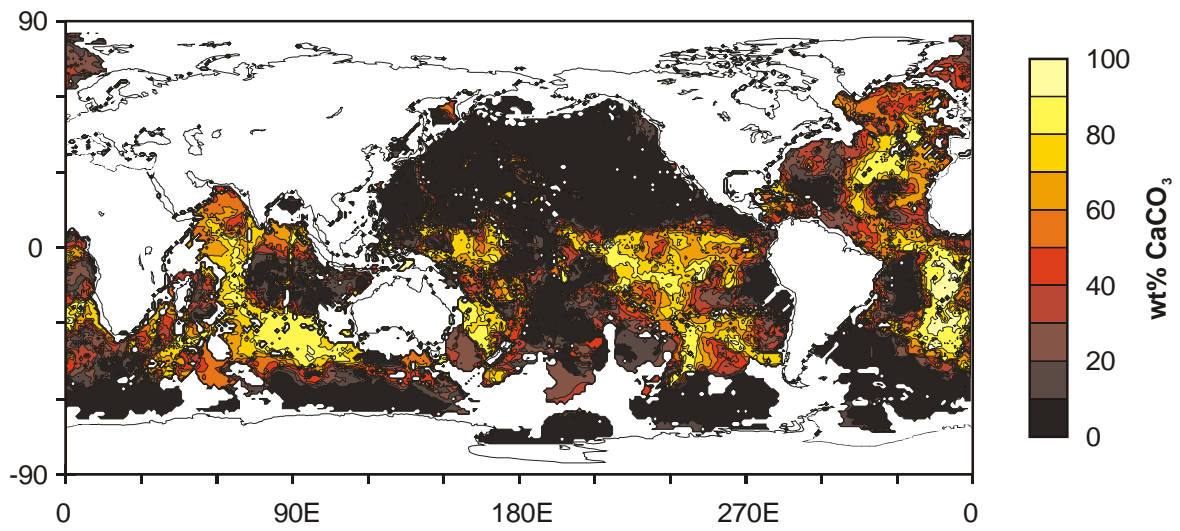
Gephyrocapsa Oceanica. Scale bars represent 1 μm . Coccolith structure is notably different, with distinct malformations and a reduced degree of calcification in cells grown at elevated CO_2 levels (and lower $p\text{H}$) (d,e,f) compared to cultures incubated at preindustrial CO_2 levels (a,b,c). With copyright permission from Nature Publishing Group.



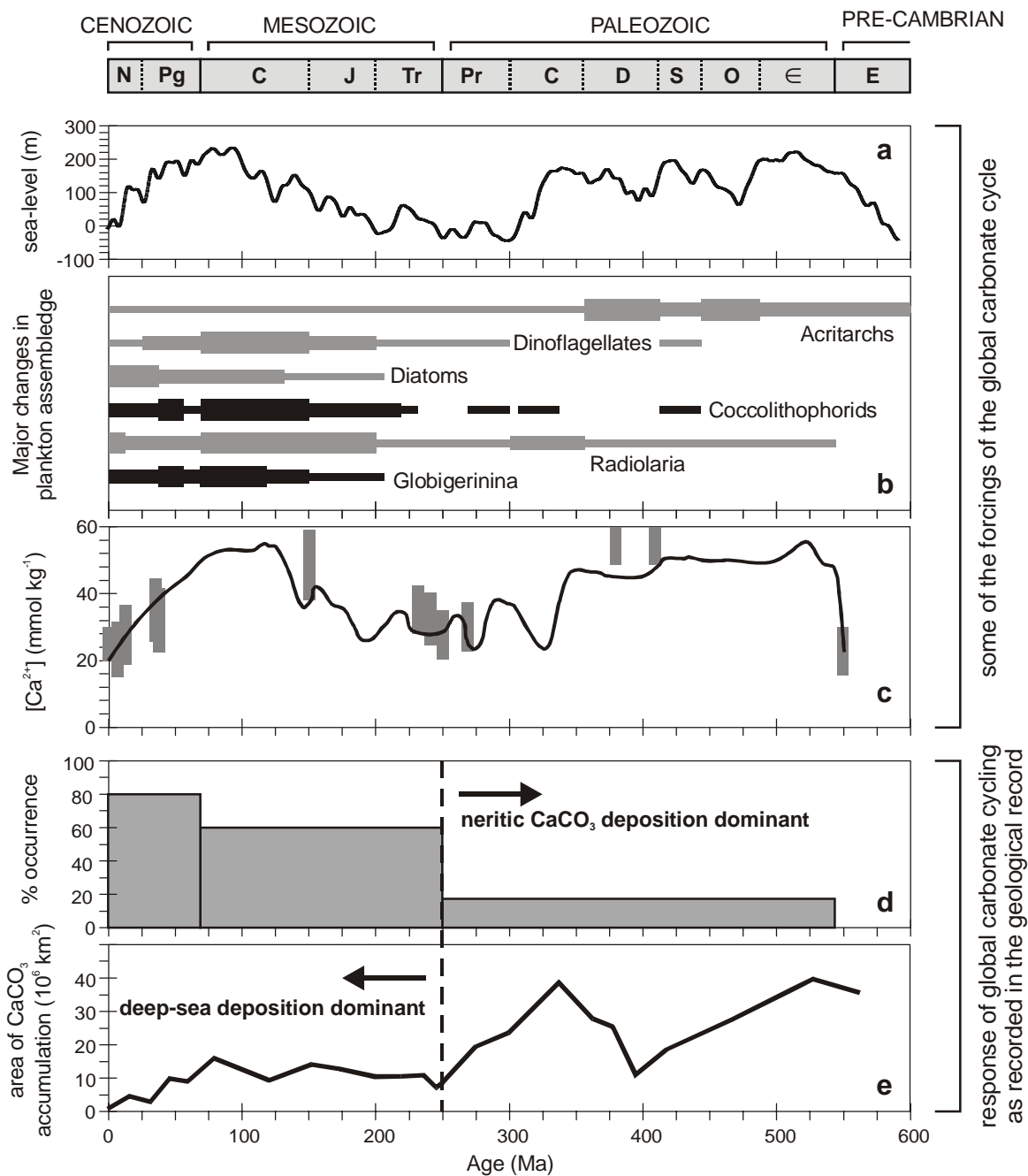
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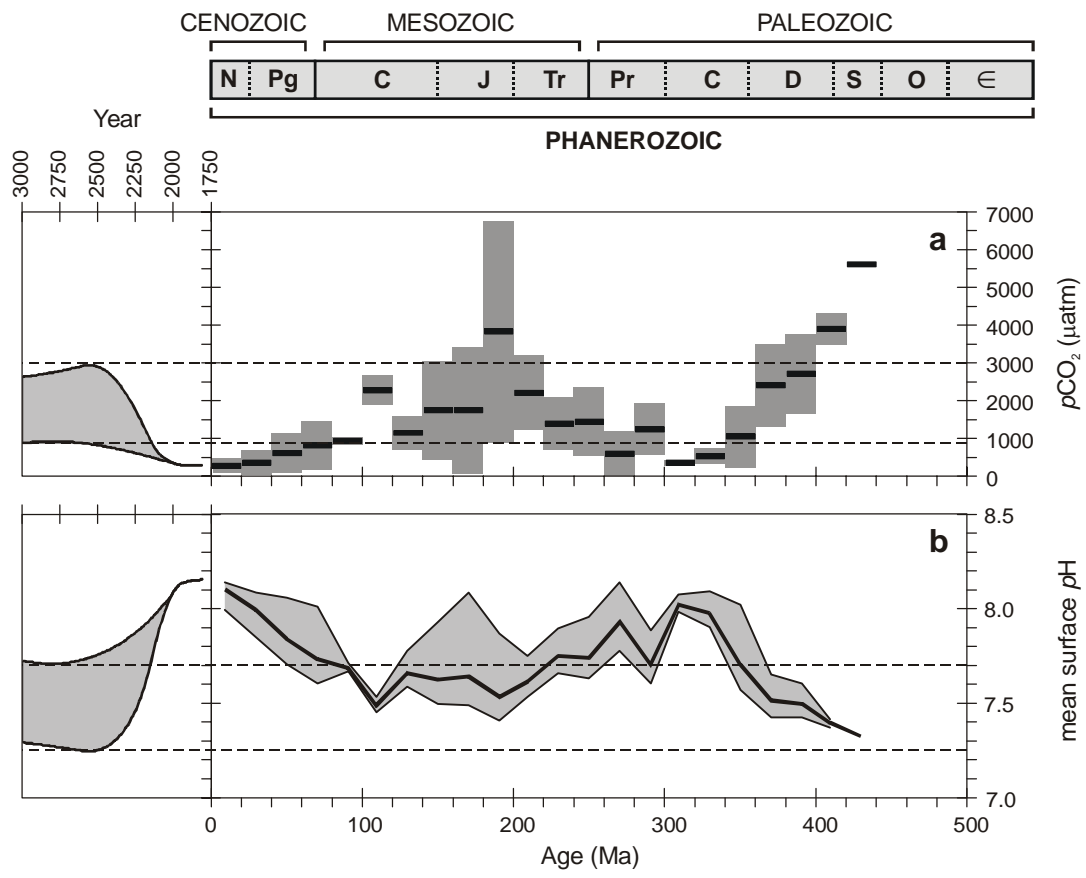
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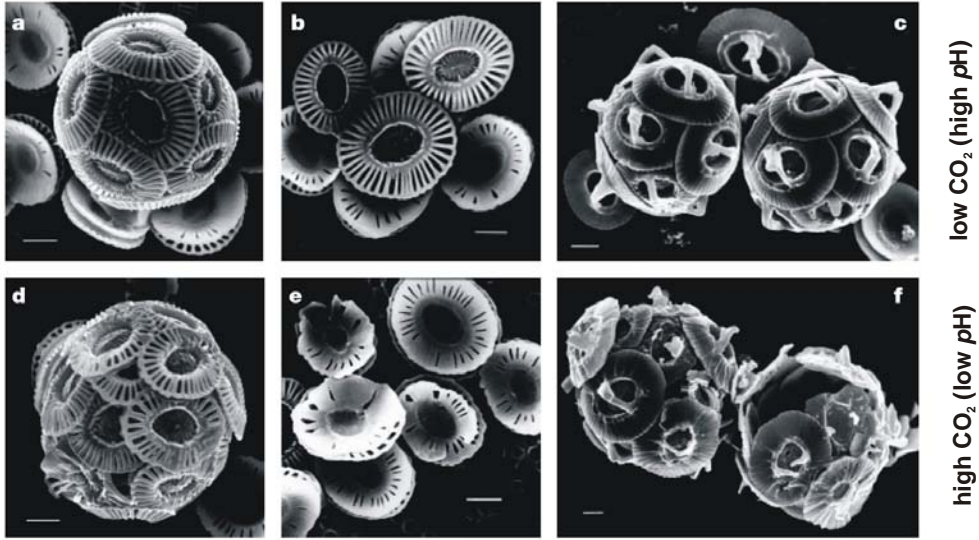
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