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CHAPTER 5

Skeletons and ocean chemistry: the long view

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5.1 Introduction

In the present day seas, animals, algae, and protozoans are threatened by ocean acidification, amplified in many regions by seawater warming and hypoxia (Doney *et al*. 2009). Many species may be affected adversely by 21st century environmental change, but a decade of research suggests that the hypercalcifying animals responsible for reef accretion may be especially vulnerable to acidity-driven decrease in the saturation state (Ω, see Zeebe and Gattuso, Box 1.1, this volume) of surface seawater with respect to calcite and aragonite.

The geologic record reveals that natural changes in the marine carbonate system have impacted the evolution and abundance of calcifying organisms throughout the Phanerozoic Eon [542 million years (Myr) ago to the present]. This being the case, we can use our understanding of the dynamic behaviour of the carbon cycle and the stratigraphic comings and goings of reef-building organisms to inform what, if any, lessons can be drawn from the long-term past and applied to our near term future.

5.2 A record of atmospheric pCO_2 and past global change

If there is one fact that geology makes clear it is that the Earth and its biota are continually in a state of change. Because of its relationship to climate, the partial pressure of CO_2 (pCO_2) in the atmosphere has been of particular interest to geologists and geochemists, but direct measurement of ancient CO_2 levels is impossible for intervals older than those recorded in glacial ice preserved today near the poles and at high altitude (Petit *et al.* 1999). Therefore, deep time estimates of pCO_2 rely on models, broadly constrained by geochemical proxy data. For example, the widely applied models of Berner and colleagues (e.g., GEOCARB III; Berner and Kothavala 2001; Berner 2006; Fig. 5.1C) estimate fluxes of carbon from one reservoir to another, based on geochemical proxies (mainly isotope ratios and abundances of sedimentary carbonate and organic carbon), and then calculate successive steady-states of the system through time. Additional parameters are considered, including estimates of carbon fluxes due to erosion, river runoff, plant evolution, volcanic weathering, global CO_2 degassing, and land area; these also influence the model results.

These models suggest that atmospheric pCO_2 was not wildly different from pre-industrial modern levels back into Miocene time (23 to 5 Myr ago), but was moderately higher earlier in the Cenozoic, and higher yet – perhaps five to eight times the present atmospheric level (PAL) - during the warmest parts of the largely unglaciated Mesozoic

Era (252-65 Myr ago). Modelled $p\mathrm{CO}_2$ during the Late Paleozoic ice age is, as might be predicted, low, but earlier Paleozoic estimates exceed ten times PAL, with values in some iterations (Berner and Kothavala 2001) spiking as high as 25 times PAL during the later Cambrian Period (ca. 500 Myr ago; Fig. 5.1). An independent biogeochemical model (COPSE; Bergman *et al*. 2004) suggests a similar history, but with less extreme late Paleozoic and Mesozoic values. Geochemical proxies for ancient $p\mathrm{CO}_2$ (the C-isotopic composition of alkenones, soil carbonates, and organic matter; the distribution of stomata in the epidermis of fossil leaves; and the stable isotope ratios of boron) come with their own interpretational challenges (e.g., Royer *et al*. 2001), but generally support model-based hypotheses for Phanerozoic environmental history.

The amount of CO_2 in the atmosphere has clearly varied through geological time, and was often considerably higher than values seen in the atmosphere today. However, when considered alone, estimates of past atmospheric $p\mathrm{CO}_2$ do a poor job in predicting the evolutionary history of skeletal biotas (Fig. 5.1). For example, during the Cambrian and Ordovician periods, when $p\mathrm{CO}_2$ was at its Phanerozoic maximum, skeletal biotas were radiating throughout the oceans (e.g., Knoll 2003). Clearly, then, $p\mathrm{CO}_2$ is not, in and of itself, a parameter that tracks hypercalcifier evolution. To understand the history of biomineralization, we must place it in the broader context of the expected behaviour of the fluid Earth carbonate system as a whole.

Over long timescales (≥10 000 years) the marine carbonate system operates in a dynamic equilibrium due to feedbacks among fundamental processes operating in the carbon cycle. The carbonate system has six parameters, but because of interdependencies can be reduced to two dimensions (Zeebe and Ridgwell, Chapter 2, this volume); here we consider those processes that affect total alkalinity (A_T), total dissolved inorganic carbon (C_T), or both simultaneously. Figure 5.2 depicts one such solution for the marine carbonate system. Given a range of plausible A_T and C_T values, functions of equal saturation state (here calculated for calcite, but a similar reasoning applies to aragonite and magnesian calcite) can be drawn. Three primary processes control the fluid Earth carbonate system over long timescales. 1) CO_2 produced from solid Earth sources (volcanoes and metamorphism) and the weathering of sedimentary rocks increases C_T, but does not affect A_T. This process works to lower **Ω** in seawater and will slow the rate of carbonate precipitation or even begin to promote dissolution of carbonate sediments. 2) Chemical weathering of silicate minerals consumes protons (derived from CO_2 via carbonic acid) and increases A_T, but not C_T. This process serves to raise **Ω** in seawater and both increases the rate of carbonate precipitation and promotes precipitation and preservation of carbonate minerals in areas of the oceans previously undersaturated. 3) Finally, carbonate mineral precipitation provides the mathematical complement to CO_2 outgassing and silicate weathering by consuming A_T and C_T with a slope of -2.

It is not by chance that these fundamental processes have a $\Delta A_T:\Delta C_T$ vector sum that equals zero: they do not operate independently of one another. CO_2 outgassing and silicate weathering are connected via the silicate weathering feedback (e.g. Walker *et al.* 1981), and because the global oceans have a finite and stable water volume, they produce carbonate minerals to alleviate inputs of dissolved inorganic carbon and total alkalinity. This forms the basis for a set of negative, or stabilizing, feedbacks on **Ω** in seawater (a form of 'carbonate compensation'). The result is that, over long timescales, the $CaCO_3$ saturation state of seawater globally is both stable and close to that predicted by thermodynamic equilibrium (Ω ~ 1), despite tropical surface waters being strongly supersaturated. For example, if CO_2 outgassing were to increase, so too would silicate weathering (due to increased temperature). At the same time, the rate of carbonate precipitation from seawater would decrease due to carbonate compensation (lowering Ω) and the system would arrive at a new steady-state with a higher atmospheric CO_2, but a similar Ω.

This thought experiment illustrates two important concepts. One, it explains why, in times past, CO_2 can have been far higher than today, and yet seawater Ω remained at levels adequate for calcification. And two, if we are concerned about ocean acidification events in Earth history, we need to look for transient departures from long-term dynamic equilibrium. Global deviations in Ω in seawater cannot last long, in geological terms. Given enough time (> 10 000 years), carbonate compensation and silicate weathering will work to balance CO_2 outgassing (and inputs of acidity in general). Zeebe and Ridgwell (Chapter 2, this volume) provide a detailed discussion of the mechanisms involved.

It is the rapidity of $p\mathrm{CO}_2$ increase in present day oceans that is outstripping the buffering capacity of the Earth system and, potentially, the genetic ability of populations to adapt. Thus, if we seek to understand the lessons of the past for our future, we need to identify brief intervals in the past when carbon dioxide is inferred to have risen too rapidly for the Earth system to remain in equilibrium (e.g., Hoegh-Guldberg *et al*. 2007; Knoll *et al*. 2007; Zeebe and Ridgwell, Section 2.5.3, this volume). The geologic record does indeed contain several such events, and reveals that perturbations to the marine carbonate system can have complex, and in some cases devastating, effects on populations of calcifying organisms. In addition to these, however, the rock record contains intervals in which the patterns of biological calcification exhibit signal features of stress like those of ocean acidification, but sustained over timescales far longer than those expected from our understanding of ocean acidification and the marine carbonate system (e.g. Knoll *et al*. 2007). These observations highlight an important gap in our understanding and require an additional class of hypotheses for processes responsible for controlling **Ω** in surface seawater. The mechanisms of interest are discussed in section 5.3.3.

5.2.1 The Paleocene-Eocene Thermal Maximum

Because their calibration depends on assumptions of equilibrium, models such as GEOCARB and COPSE integrate over long intervals of time and cannot be used to identify times of geologically rapid $p\mathrm{CO}_2$ increase in the geologic record. We need to find high resolution geologic records in which geochemical data suggest rapid environmental change. Perhaps the best studied example is the so-called Paleocene-Eocene Thermal Maximum, or PETM, a brief interval of pronounced global warming about 55 Myr ago (Kennett and Stott 1991; Zachos *et al*. 1993).

Warming of 5 to 8°C, with larger increases at high latitudes, has been inferred from a sharp excursion of about -1.7‰ in the oxygen isotopic composition of carbonate skeletons (Zachos *et al*. 2003). Other geochemical proxies for sea surface temperature (Mg/Ca, the relative abundance of unsaturated alkenones, and the structures of archaeal lipids) are consistent with this estimate, as are biogeographic changes among both corals and land plants (reviewed by Scheibner and Speijer 2008). A -2.5 to -3‰ shift in the C-isotopic composition of carbonate skeletons coincides with the temperature excursion, suggesting that increased atmospheric CO_2 supplied from an isotopically light source drove climate change. It has been hypothesized that catastrophic release of methane from shelf/slope clathrate hydrates was involved in the PETM event (Dickens *et al*. 1995), but the inability of clathrate release to supply the quantity of carbon needed to account for recorded C-isotopic change (Zachos *et al*. 2005) suggests that other mechanisms, including thermogenic methane release associated with end-Paleocene flood basalts, may have played a role (Svensen *et al*. 2004; Higgins and Schrag 2006). In any event, high-resolution stratigraphic and geochemical data indicate that the PETM perturbation was rapid and transient; the decrease in C-isotope values occurred largely in two bursts, each less than 1000 years in duration, and the system returned to its background state within about 100 000 years (Rohl *et al*. 2000; Nunes and Norris 2006). Shoaling of the calcite compensation depth by as much as two kilometers provides empirical evidence of ocean acidification (Zachos *et al*. 2005).

Parallels to the present prompt the question of how Earth's biota fared across the PETM event. On land, vascular plants record pronounced but transient species migrations, with only limited extinction (Wing *et al*. 2005). Paleocene mammals suffered extinctions, but new taxa appeared, including many modern mammalian orders, most at initially small size – marking the PETM as a time of pronounced mammalian *turnover* rather than diversity decline (Gingerich 2006).

Many marine taxa also display a pattern of pronounced turnover but limited extinction (Scheibner and Speijer 2008), with corals (Kiessling 2001) and various microplankton groups (Scheibner and Speijer 2008) showing transient range expansion toward the poles. Major extinction depleted the diversity of deep sea benthic foraminiferans (Thomas 2007), but corals – a group considered especially vulnerable to present day ocean acidification (Kleypas *et al*. 1999; Hoegh-Guldberg *et al.* 2007) – show little diversity change. Diversity, however, does not tell the whole story. In a comprehensive review of carbonate platforms along the Paleogene margins of the Tethyan Ocean, Scheibner and Speijer (2008) demonstrated that shelf margin reefs built by colonial corals and calcareous algae declined markedly at the PETM. Solitary (but not colonial) scleractinians occur in basal Eocene carbonates, but contribute relatively little to carbonate accumulation. Across the same boundary, larger benthic foraminifera expand dramatically.

Thus, combined warming and ocean acidification 55 Myr ago made only a limited long-term mark on the marine biota. While acidification expanded the volume of undersaturated deep-sea waters, skeleton formers persisted on the shelves. This persistence, however, does not imply strict ecological continuity. Coral reef ecosystems declined widely and did not recover for hundreds of thousands of years – a geological instant but almost impossibly long by the standards of human civilization. Migration may have played an important role in taxonomic persistence on land and in the ocean, but this required corridors for migration, no longer unimpeded on land or, perhaps, in the sea. In summary, then, the PETM record may be reassuring on an evolutionary timescale, but it raises concerns on the ecological scales relevant to humans. Persistence of coral species, perhaps in isolated populations with little or no calcification (e.g., Fine and Tchernov 2007) may not ensure the continual accretion of reefs, with their attendant ecosystem services.

5.2.2. End-Permian mass extinction

An earlier event interpreted in terms of ocean acidification occurred 252 million years ago, at the end of the Permian Period. Estimates of $p\mathrm{CO}_2$ change and global warming coincide broadly with those for the PETM, but the biological consequences were starkly different. On land, a poorly resolved record of vertebrate evolution suggests migration and increased taxonomic turnover across the Permian-Triassic boundary (Smith and Botha 2005), and land plants show both poleward migration and regionally distinct patterns of extinction, most pronounced in high southern latitudes (Rees 2002; Abu Hamad *et al.* 2008). Marine ecosystems, however, were devastated – species loss is estimated at 90% or more, while metazoan reefs and other ecosystems that had long dominated the seafloor disappeared (Erwin 2006).

A reasonable scenario for end-Permian mass extinction invokes rapid, massive influx of CO_2 into the atmosphere and oceans, in association with one of the largest eruptions of flood basalts known from the geologic record. At least 1.2×10^6 km^3 of basaltic volcanic rocks were deposited over what is now western Siberia, largely accumulating in a million years or less (Reichow *et al*. 2007). Comparison with modern volcanoes, such as those in Hawaii, suggests that this event might have released 10^{17} to 10^{19} mol CO_2 (equivalent to 10 to 1000 times the amount of carbon dioxide estimated for the latest Permian atmosphere; Wignall 2001), although integrated into an active carbon cycle over a million years, this would increase atmospheric levels by only two-fold or less (Knoll *et al.* 2007). Comparisons with Hawaiian volcanism, however, probably underestimate carbon dioxide release from Siberian trap volcanism, very likely by a wide margin. The Siberian magmas ascended through thick carbonate and evaporate deposits, adding CO_2 from contact heating and decarbonation (and sulfur dioxide, a second source of acidity; e.g., Knoll *et al.* 2007; Ganino and Arndt 2009; Iacono-Marziano *et al*. 2009). Today, as much as 10% of all CO_2 released from mid-ocean ridges, volcanoes, and convergent plat margins can be attributed to Mount Etna, a volcano developed on extensive platform carbonates (Marty and Tolstikhin 1998). Moreover, Siberian Trap magmas and lavas intruded into and extruded onto extensive late Paleozoic peat and brown coal deposits, generating large additional fluxes of CO_2 and thermogenic methane (CH_4) to the atmosphere (Retallack and Jahren 2008). Thus, both massive volcanism and the geologic context of the volcanism contributed to rapid CO_2 (and SO_2) increase, driving global warming and ocean acidification.

End-Permian extinctions in the oceans were extensive but not random. Knoll *et al*. (1996) documented a strong pattern of selectivity with respect to fundamental physiological and ecological features of the biota. Hypercalcifiers and other animal and algal groups with limited capacity to pump ions across membranes show nearly complete extinction, but groups better able to modulate the composition of fluids from which carbonate skeletons were precipitated survived differentially well. Further, taxa characterized by high rates of exercise metabolism and well developed respiratory and circulatory systems survived better than anatomically simple hypometabolic taxa, and infauna survived better than epifauna. In 1996, the term ‘ocean acidification’ was not a part of paleontology’s vocabulary, but an extensive physiological literature suggested that observed patterns of extinction and survival matched predictions made on the basis of organismic tolerance to and compensation for hypercapnia (elevated CO_2 in internal fluids).

Stimulated by environmental concerns, a large body of research on marine organisms has accumulated during that past fourteen years, prompting a number of general statements about vulnerability to hypercapnia and increasingly acidic seawater. For example, Widdicombe and Spicer (2008, p. 194) wrote:

> *'We conclude that there is clear potential for the chemical changes associated with ocean acidification to impact on individuals at a physiological level particularly through disruption of extracellular acid-base balance. There is some weak evidence that the severity of this impact could be related to an organism's phylogeny suggesting that both species and taxonomic measures of biodiversity could be reduced. However, there is also evidence that potential species extinctions will be more strongly governed by factors related to an organism's lifestyle and activity (e.g. infaunal v epifaunal, deep v shallow, deposit feeder v suspension feeder, large v small) than by its phylogeny. There is also huge uncertainty as to what extent organism adaptation or acclimation will mitigate the long term effects of ocean acidification.'*

And, in a comparison of marine animals more and less tolerant of hypercapnia, Melzner *et al*. (2009) proposed that '*All more tolerant taxa are characterized by high (specific) metabolic rates and high levels of mobility/activity*.' These conclusions about the present recall observed patterns of end-Permian extinction.

In light of new experimental results, especially those on ocean acidification and calcification, Knoll *et al*. (2007) returned to the Permian-Triassic data, focusing largely on inferred differences in the physiology of skeleton formation. This exercise requires physiological inference from fossil remains. From fossils we can establish the lifestyles of ancient organisms and, to the extent that phylogeny is a good predictor of anatomy and physiology, those can be inferred, as well. Widdicombe and Spicer (2008) reasonably stress that strict phylogenetic focus in ocean acidification research may be limiting. Nonetheless, in terms of broad physiological attributes important to assessing hypercapnia and ocean acidification, many species within marine classes and phyla share fundamental features of metabolism and (key to interpreting fossils) skeletal biosynthesis. Thus, while individual species may respond variably to increased CO_2 load, groups like corals will have a statistical tendency to respond coherently - and differently than, say, mollusks. And what the fossil record provides is a statistical digest of extinction and survival.

Knoll *et al*.'s (2007) focus on skeletal physiology once again showed evidence of dramatic variations in extinction probability (Fig. 5.3). Hypercalcifiers (corals and massively calcifying sponges) and other groups with minimal capacity to buffer calcifying fluids (e.g., lophophorates and crinoids) lost 86% of their genera during the extinction, whereas genera of animals and protists that made skeletons of materials other than $CaCO_3$ exhibit extinction rates of only about 5% - comparable to or less than background extinction rates for the preceding 50 Myr. Calcifying organisms better able to modulate internal fluids (mostly mollusks and arthropods) show intermediate levels of genera loss (54%), and within this category, groups predicted to be relatively vulnerable to hypercapnic stress based on ecology or anatomy disappeared at rates twice those of groups deemed less vulnerable. Also, for a series of animal, protozoan, and algal taxa, genera characterized by carbonate skeletons showed much higher rates of extinction than close non-calcifying relatives, providing some control on physiological variability among taxa. All of these observations are consistent with a prominent role for hypercapnia/ocean acidification in generating the selectivity associated with end-Permian mass extinction.

5.2.3 Why the difference?

Clearly, end-Permian fossils record environmental catastrophe more dire than the PETM, but why did the marine biota respond so differently in the two events? Possibly, end-Permian environmental disruption was simply more pronounced. Certainly, the carbon isotopic excursion across the Permian-Triassic boundary is double that at the PETM. But there is more to the story. In fact, in our summary of environmental triggers for end-Permian mass extinction, we revealed only half the story – the other half may be what ensured the unusual severity of this largest mass extinction.

In some ways, the late Permian world into which the Siberian traps erupted was almost maximally different from the Earth we experience today. Continental masses were aggregated into the supercontinent Pangea, resulting in a Panthalassic ocean more than a hemisphere in extent. With the mid-Permian decay of late Paleozoic continental ice sheets and climate warming, physical circulation in this ocean may have been relatively sluggish, promoting extensive subsurface hypoxia (e.g., Meyer *et al*. 2008). Both deep sea black shales, preserved in obducted slivers of late Permian seafloor (Isozaki 1997) and biomarker lipids that document anoxygenic photosynthetic bacteria in latest Permian seas (Cao *et al*. 2009) record oxygen depletion in subsurface water masses. Global warming associated with volatile release from Siberian volcanism appears to have tipped the oceans into a state of widespread anoxia beneath the mixed layer (Wignall and Twitchett 1996), generating additional fluxes of CO_2 from upwelling waters (Knoll *et al*. 1996). In short, as observed at some level today, the end-Permian extinction was not a crisis fomented by hypercapnia/ocean acidification, global warming *or* subsurface anoxia, it was a crisis in which all three occurred simultaneously (Knoll *et al.* 2007). Given the interconnected nature of the Earth system, it could hardly be otherwise.

Subsurface anoxia would have impacted the biota in several ways. Most obviously, shoaling of the oxycline would have stressed benthic populations, much as it does in seafloor ‘dead zones’ today. Secondly, the physiological effects of warming, hypercapnia, and hypoxia are not independent, but rather are synergistic, amplifying physiological stress (Pörtner 2008; Pörtner *et al.*, Chapter 9, this volume). Many organisms in end-Permian oceans probably died of asphyxiation; nonetheless, end-Permian skeletons suggest marked selectivity consistent with the physiological effects of hypercapnia/ocean acidification.

Recently, Higgins *et al*. (2009) explored the consequences of widespread subsurface anoxia for the carbonate system. As discussed in more detail below, anaerobic heterotrophs generate total alkalinity as they remineralize organic matter. Thus, in oceans with widespread subsurface anoxia, subsurface water masses should be expected to have higher Ω than at present, while the Ω of overlying surface waters should be reduced. Reduction of surface water Ω should, in turn, make skeleton formation by hypercalcifiers more difficult (e.g., Gattuso *et al*. 1999), increasing the physiological stress on latest Permian corals, hypercalcifying sponges, and other organisms with limited ability to modulate internal fluid composition.

The punchline for end-Permian extinction, then, is that the ability of marine organisms to precipitate calcium carbonate skeletons was impeded by *two* circumstances. Expanding subsurface anoxia and rapidly rising $p\mathrm{CO}_2$ would both have lowered Ω in the surface ocean; operating in tandem, they appear to have depressed Ω strongly for a biologically protracted interval of time. To the extent that this is correct, it suggests that the end-Permian extinction can inform current research in terms of taxonomic, ecological, and physiological vulnerability to 21st century global change. Perhaps mercifully, however, the extent of the end-Permian catastrophe appears to rely on concatenated factors only partially in play today.

5.3 Is there a more general historical pattern?

Reefs are a striking component of the carbonate sediments through geologic time, and the record of biological calcification is well written in the fossil composition of ancient reefs. The preceding sections examined two historical events wherein ocean acidification occurred due to rapid influx of CO_2 from the solid Earth; the effects of these events on the biota were variable, but in one case, at least, devastating for marine hypercalcifiers. Using historical metrics, one can ask a set of broader questions about the processes that have controlled the abundance and diversity of reef-building organisms through time. What conditions are responsible for observed long-term patterns in the evolution of hypercalcifiers? And how might these trends reflect long-term changes in the nature and behaviour of the marine carbonate system that extend beyond short-term ocean acidification events?

5.3.1 Skeletons and surface water Ω

A large body of experimental research supports the hypothesis that the cost and effectiveness of carbonate skeleton formation vary inversely with Ω (Gattuso *et al.* 1999; Langdon and Atkinson 2005, and references therein). Skeletal responses to ocean acidification, however, vary across taxa, as might be predicted from basic features of skeletal physiology. Because hypercalcifiers have only limited physiological capacity to pump ions across membranes to modify the composition of fluids from which skeletal minerals are precipitated, they are particularly vulnerable to decreasing Ω in ambient waters. Ries *et al*. (2009) grew a variety of skeletal invertebrates and algae at a range of Ω. Not surprisingly, a majority of the experimental species showed a decline in skeleton formation with decreasing Ω. Three arthropods, however, actually increased skeletal mass with decreasing Ω, and red and green algae, as well as a limpet and a sea urchin showed initial increase in calcification followed by decline as Ω decreased beyond a threshold value. Gooding *et al*. (2009) also observed an increase in skeletal mass in the sea urchin *Pisaster ochraceus* grown at elevated $p\mathrm{CO}_2$ and temperature. These responses are consistent with the pattern of extinction and survival across the Permian-Triassic boundary, and expectations for vulnerability to decreasing Ω. We note, however, that changing calcification rate is only one of many potential physiological responses to ocean acidification – in some cases, skeletal compensation is accompanied by decreased performance in other important aspects of growth or metabolism (Pörtner 2008, Barry *et al.*, Chapter 10, this volume).

5. 3.2 Hypercalcification through time

Paleontologists have long understood that neither the abundance nor the taxonomic composition of reefs has remained constant through time, prompting the generalization that six to eight successive reef biotas have flourished in Phanerozoic oceans, separated by stratigraphic gaps during which metazoans contributed little to reef accretion (e.g., Wood 1999; Copper 2002a; Kiessling 2002; Ezaki 2009). In a recent compilation of reef abundance and diversity, Kiessling (2009) has refined this view.

Perhaps surprisingly, Kiessling's data show that widespread reef development, common from early Neogene time through today, is not generally characteristic of Phanerozoic oceans (Fig. 5.1A).

Reefs can be defined as discrete rigid carbonate structures formed by *in situ* or bound components that develop topographic relief upon the sea floor (Wood 1999). Structures that fit this definition have existed since the evolution of benthic microbial communities more than three billion years ago (Grotzinger and Knoll 1999; Allwood *et al*. 2009). With the late Neoproterozoic emergence of complex multicellularity, both animals and algae began to participate in reef accretion, and through the Phanerozoic Eon (the past 542 Myr), a number of major taxa have contributed to reef formation. Kiessling's (2009) compilation highlights several first order stratigraphic patterns in the composition of reef biotas (Fig. 5.1B). First, microbial accretion did not cease with the evolution of hypercalcifying metazoans, but rather declined slowly and fitfully through time, ceasing to be quantitatively important only in the Cretaceous Period. Second, bryozoans, bivalves, calcareous algae, and other groups have contributed a moderate volume of reef carbonate through time, with calcareous algae peaking in the late Carboniferous and early Permian periods and again in the Neogene, and rudist bivalves playing a major role in Cretaceous reefs (to the extent that rudist deposits fit Wood's definition of a reef; Gili *et al*. 1995). Throughout the Phanerozoic Eon, however, peaks in reef abundance correspond to times of widespread and diverse hypercalcifying animals, mainly massively calcifying sponges and cnidarians, and calcareous algae. It is principally the episodic waxing and waning of these organisms that gives rise to the widely applied concept of successive reef biotas. Insofar as hypercalcifiers should be sensitive to factors that control Ω, we can ask whether these factors were in play when successive reef biotas expanded and collapsed.

Archaeocyathids, an extinct group of calcareous sponges, were major contributors to reef accretion in Early Cambrian oceans, but a major extinction event near the Cambrian Stage 3-4 (Botomian-Toyonian) boundary essentially wiped out the group, beginning a nearly 50 Myr interval during which metazoans played only a minor role in reef accretion (Rowland and Shapiro 2002). As part of a broader radiation of well-skeletonized animals, sponges, rugose and tabulate corals, and bryozoans renewed metazoan reef accretion during the Ordovician Period (Harper 2006), and reefs constructed by these organisms persisted with varying abundance until the Frasnian-Famennian boundary in the late Devonian Period, some 370 Myr ago. At this time, hypercalcifying animals collapsed again, ushering in a brief interval of animal-poor microbial reefs (Copper 2002b). Animal-algal reefs occurred throughout the later Carboniferous and Permian periods, with hypercalcifying sponges once again playing a particularly important role in later Permian build-ups. Then, as discussed above, hypercalcifiers suffered differentially severe losses during end-Permian mass extinction.

Early Triassic reefs were microbial. Beginning in the Middle Triassic, however, reef abundance increased with the radiation of scleractinian corals and sponges. Many hypercalcifiers disappeared, once again, at the end of the Triassic, although enough species survived to fuel renewed reef expansion during the Jurassic Period (Lathuilière and Marchal 2009). Another decline toward the end of the Jurassic was followed by an extended interval dominated by rudist bivalves. Only after the end-Cretaceous mass extinction did modern reef ecosystems began to take shape.

5. 3.3 Mechanisms to explain the pattern of hypercalcification in reefs

Canonically recognized mass extinctions do not fully explain the stratigraphic pattern of hypercalcifier evolution (Kiessling 2009, Kiessling and Simpson 2010). Hypercalcifiers disappear completely during end-Permian mass extinction and decline markedly in diversity and extent during Late Devonian and Late Triassic extinctions. On the other hand, mass extinctions at the end of the Ordovician (Sheehan 2001) and Cretaceous periods do not show the preferential loss of hypercalcifiers observed for end-Permian collapse (Knoll *et al*. 2007); the proportional extinction of hypercalcifiers was modest during the end-Ordovician and end-Cretaceous mass extinctions, and the loss of metazoan-built reefs was transient.

Although there is good physiological reason to connect the abundance and evolutionary history of hypercalcifiers to state changes in Ω in ambient seawater (e.g. Veron 2008), the long ($>10^5$ years) timescales on which reef organisms have waxed and waned introduces a new class of problem. As discussed above, variables such as $p\text{CO}_2$ and temperature do not appear to explain the stratigraphic pattern of hypercalcifier evolution (Kiessling 2009). This should not be surprising, given the flexibility of these parameters within the dynamic equilibrium described in section 5.2. What we require is a mechanism that is congruent with this dynamic equilibrium, and yet can impact marine carbonate chemistry with a characteristic timescale greater than that expected for ocean acidification, bearing in mind the ever-present stabilizing feedbacks.

Hypercalcifying organisms residing in reefs experience the Ω of regional surface seawater. Global Ω is set by the overall marine carbonate system, but this value (which is close to thermodynamic equilibrium) represents a cumulative parameter integrated over the entire volume of global seawater. There are, in spite of this, large gradients in Ω. These gradients result in part from the hydrologic cycle (controlling salinity) and inorganic factors controlling the solubility of carbonate polymorphs (e.g. temperature and pressure). An underappreciated process promoting these gradients is the effect of the biological pump (Higgins *et al*. 2009). CO_2 fixed by primary producers in the surface ocean is aerobically respired in the deep, setting up a gradient in C_T that pushes Ω higher in surface seawater and lower in deep seawater (Fig. 5.4).

We can imagine how the geobiological behaviour of the biological pump differed in times past. The pump could be stronger or weaker. A stronger biological pump means larger gradients in C_T, and would translate into a world characterized by even larger gradients and a higher Ω in surface seawater than we observe today. We can also imagine a world with a reduced depth gradient in Ω, including lower surface seawater Ω, due to the impact of anaerobic metabolisms. In contrast to aerobic respiration, all anaerobic metabolisms significantly affect A_T in addition to C_T (Soetaert *et al*. 2007; Higgins *et al*. 2009). Anoxic environments characterized by anaerobic respiration tend to ameliorate depth gradients in Ω, while aerobic metabolisms tend to promote them. This means that a world in which a significant proportion of biological pump electrons pass through anaerobic metabolisms will tend to have subdued gradients in Ω, even though global seawater may not vary (Fig. 5.4). The ability of the marine carbonate system to accommodate this reorganization is, in principle, intimately tied to the processes that control the long-term and large-scale development of marine anoxia.

It is now possible to develop the logic for hypotheses to explain the abundance and diversity of marine hypercalcifying organisms through time, making reference to both short-term events of rapid CO_2 influx that cause Ω to deviate briefly (in geologic terms) from a dynamic equilibrium, and also long-term transitions due to the waxing and waning of ocean basin anoxia. Might multiple ancient reef crises be related to rapid decreases in Ω associated with ocean acidification, the expansion of subsurface anoxia, or both?

Recent radiometric determinations suggest that the Cambrian extinction of archaeocyathids may coincide with emplacement of the Kalkarindji Large Igneous Province, Australian flood basalts comparable in scale to the end-Permian Siberian traps (Evins *et al.* 2009). Citing the extensive deposition of black shales, Zhuravlev and Wood (1996) linked Cambrian hypercalcifer extinctions to the expansion of anoxic subsurface waters. In turn, Glass and Phillips (2006) and Hough *et al*. (2006) related anoxia and extinction to the Kalkarindji eruptions. In fact, the paleobiological particulars of this extinction suggest that we should focus on the modulation of Ω discussed in the previous section. Early Cambrian hypercalcifiers were widespread in shallow shelf and platform environments, and they disappeared despite the limited incursion of anoxic water masses into shallow marine environments. Trilobites, the dominant organisms recorded in Cambrian strata, suffered major extinctions, but because first appearances kept pace, the overall pattern is one of marked turnover, not diversity loss (Bambach *et al*. 2004). Small shelly fossils of phylogenetically diverse origins declined across this interval, but as their record is closely tied to preservational circumstances that also change, it is difficult to quantify their evolutionary pattern (Porter 2004). The renowned Burgess Shale in British

Columbia documents the persistence of diverse animal groups into mid-Cambrian oceans, but few of these made robust carbonate skeletons. In fact, in later Cambrian carbonates, skeletons account for only a few percent of known carbonate volume – more like the Early Triassic than any other time of Phanerozoic history (Pruss *et al*. 2010). As in the end-Permian example, massive basaltic volcanism appears to have been visited on a planet whose oceans were already characterized by subsurface hypoxia. Volcano-driven warming and expansion of subsurface anoxia caused mass mortality in deeper marine environments, but it may have been the associated decline in surface water Ω that selectively removed hypercalcifiers from shallow shelves and platforms.

Rapidly accumulating geochemical data (Hurtgen *et al*., 2009; Gill *et al.* 2010) suggest that the ensuing later Cambrian to earliest Ordovician oceans experienced persistent or recurring subsurface hypoxia, at least episodically expanding to widespread anoxia. Thus, the protracted post-extinction interval marked by limited skeletal contributions to accumulating carbonates, a dearth of hypercalcifiers, and few metazoan contributions to reefs may have been governed, at least in part, by the redox-modulated depression of Ω in surface seawater.

Depression of surface Ω may also explain hypercalcifier loss at the boundary between the Frasnian and Famennian stages of the Devonian Period. Although commonly included as one of the ‘big five’ mass extinctions, extinction rates are not unusually high during this event. Rather origination rates declined, resulting in a ‘mass depletion’ of standing diversity (Bambach *et al*. 2004). In fact, the Frasnian-Fammenian loss of reef building hypercalcifers, especially calcareous sponges, sits in the middle of a protracted interval of diversity decline. As discussed earlier for Permian and Cambrian hypercalcifier extinctions, this entire mid-Devonian to basal Carboniferous interval is characterized by widespread black shales as well as high taxonomic turnover. Once again, then, anoxia at depth may have influenced diversity through a protracted interval, with the Fransian-Famennian boundary representing an extreme perturbation that exceeded the capacity of hypercalcifiers to respond.

Thus, a case can be made that the three Paleozoic intervals marked by hypercalcifer extinction and subsequent gaps in metazoan reef accretion may share the environmental circumstance of marked reduction of Ω in surface waters. Although in need of geochemical testing, this hypothesis can account for both the timing and taxonomic/physiological selectivity of extinctions at these moments in time.

Transient ocean acidification triggered by eruption of the Central Atlantic Magmatic Province has been also argued as the trigger mechanism for pronounced extinctions at the end of the Triassic Period (200 Myr ago; Hautmann 2004; Hautmann *et al*. 2008a). Coral diversity declined strongly (Lathuilière and Marchal 2009), but not completely (Kiessling *et al.* 2009), so that relatively diverse communities, including reefs, became reestablished on a million year timescale (Hautmann *et al.* 2008b). Interestingly, flood basalts and transient subsurface anoxia recur about 17 million years later, at the Pliensbachian-Toarcian boundary of the early Jurassic Period; in this case, corals show elevated turnover rates, but not strong diversity decline (Lathuilière and Marchal 2009). Ocean acidification has been proposed to explain both Mesozoic events (Kiessling and Simpson 2010, and references therein). These events make it clear that while several episodes of hypercalcifier extinction coincide with large igneous eruptions (e.g., Courtillot and Olson 2007), large igneous provinces do not invariably result in mass extinction of reef-building metazoans (Wignall 2001). The hypothesis entertained here suggests that massive volcanism impacted hypercalcifiers most strongly when the redox state of the oceans was prone to subsurface anoxia (Fig. 5.1), facilitating a combined influence of ocean acidification and redox-driven redistribution of total alkalinity on surface water Ω. Of individually moderate effect, ocean acidification and subsurface anoxia in tandem provide a lethal cocktail for organisms with limited physiological capacity to buffer the fluids from which they precipitate carbonate skeletons.

Earth scientists commonly argue the merits of factors X *vs.* Y in affecting life's history; more realistic approximations may occur when we discuss the affects of X *and* Y, occurring together or in series. The point here is not to argue that saturation level was the sole influence on hypercalcifier evolution through time. Additional aspects of seawater chemistry (e.g. Mg/Ca), biological interactions, and other influences may well have affected hypercalcifier evolution (Kiessling 2009). But we do argue that emerging geochemical tools provide a means of exploring both short- and long-term changes in Ω through time and that results to date support the hypothesis that episodic declines in Ω have played a major role in governing the stratigraphic distribution of hypercalcifiers and, hence, metazoan reefs.

5.4 Summary, with lessons for the future

Several events in Earth history bear the fingerprints of ocean acidification. The two examples discussed here in detail (the Paleocene-Eocene Thermal Maximum and P-T mass extinction) reveal a complex, and sometimes devastating impact on the abundance, diversity, and evolution of calcifying organisms. More broadly, the geologic record indicates that calcifying organisms have been subject to episodically changing Ω throughout the past 542 Myr. Volcanism and associated thermal decomposition of organic matter have generated ocean acidification over intervals that were biologically long if geologically brief. Decreases in surface seawater Ω sustained for millions of years have also been associated with the expansion of anoxic subsurface waters and, hence, anaerobic heterotrophy. When ocean acidification and the expansion of anoxic waters occur in tandem, the result can be mass extinction that is differentially severe for hypercalcifiers and other animals with limited capacity to modulate the ionic composition of internal fluids. Our understanding of these events remains imperfect, but the perspective they offer can be used to better inform our expectations for the future of reefs during our current anthropogenic experiment.

Several generalities about the past seem relevant to our environmental future:

1. In assessing the vulnerability of the biota to decreasing Ω, *rate* is key. When rate of environmental change is fast, the probability of extinction is increased. Times of biological crisis in the past were times, like today, when pCO_2 increased rapidly, not when pCO_2 was high (see also Zeebe and Ridgwell, Chapter 2, this volume).

2. There is no clear reason to expect that the coming century will see a ‘sixth extinction’ comparable to those at the end of the Permian and Cretaceous periods. Nonetheless, the loss of vulnerable taxa from ocean ecosystems could affect ecological function for many millennia. The past tells us that there will be winners and losers in a changing ocean.

Corals, and therefore the coral reef communities that harbour so much of marine diversity, may well be among the losers.

3. In the past, extinction was more pronounced when several biological challenges were imposed at once. In similar fashion, the consequences of ocean acidification will be amplified by global warming, declining levels of dissolved oxygen (Brewer and Peltzer 2009), habitat loss, overfishing, and the impedance of routes for migration.

4. The timescale for recovery from ocean acidification is measured in geologic time. Thus, even assuming that inputs of CO_2 into the atmosphere and oceans are ameliorated, diversity loss will appear permanent on timescales relevant to the human population.

5. Physiological experiments and geologic history are mutually illuminating. Studies of the past can suggest relative biological vulnerabilities, highlighting candidates for physiological research. Physiology, in turn, provides an important lens through which paleontological research can be focused.

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Figure Captions

Figure 5.1. Phanerozoic distribution of reefs, reef builders, and environmental variables. A: Reef abundance through time, with intervals of widespread subsurface anoxia in yellow. B: Proportional contribution of reef building organisms to total reef mass as a function of time. The data are coloured to highlight to comings and going of hypercalcifying taxa (in red). C: Atmospheric $p\mathrm{CO}_2$ estimates and intervals marked by continental ice sheets, as inferred from geological observations, geochemical data, and numerical models. Initials indicate the periods of the Phanerozoic Eon: Cm = Cambrian, O = Ordovician, S = Silurian, D = Devonian, C = Carboniferous, P = Permian, Tr = Triassic, J = Jurassic, K = Cretaceous, Pg = Paleogene, and N = Neogene. Data in A and B from Kiessling (2009).

Figure 5.2. Three fundamental processes that control the marine carbonate system and influence the saturation state of calcite (Ω_c) of seawater on geological timescales. See text for details.

Figure 5.3. Selective extinction during the end-Permian crisis (data from Knoll *et al.* 2007). Hypercalcifers and other animals that have a limited capacity to buffer internal fluids lost 86% of known genera; groups with carbonate skeletons but well developed physiological mechanisms for buffering internal fluids lost 54% of genera; and groups that use carbonate minerals sparingly or not at all in skeleton formation lost 5% of genera. Grey-scale coding for individual taxa shows how they align along a gradient of increasing extinction severity. The distribution of taxa along this gradient can be predicted from expected variations in vulnerability of these different groups to hypercapnia and ocean acidification as deduced from physiological experiments. See text for discussion and references.

Figure 5.4. Schematic cross-section of gradients in Ω in seawater under different scenarios. Global seawater tends to arrange gradients around a mean value controlled by carbonate compensation ($\Omega \sim 1$). Today, large gradients exist with depth due to the biological pump and aerobic respiration. Surface seawater is strongly supersaturated and deep seawater is undersaturated. A world without a biological pump would still have gradients in Ω in seawater due to the effects of temperature, pressure, and salinity. An idealized world with a biological pump, but anaerobic metabolisms at depth, will have subdued gradients in Ω, due to metabolic gradients in total alkalinity.

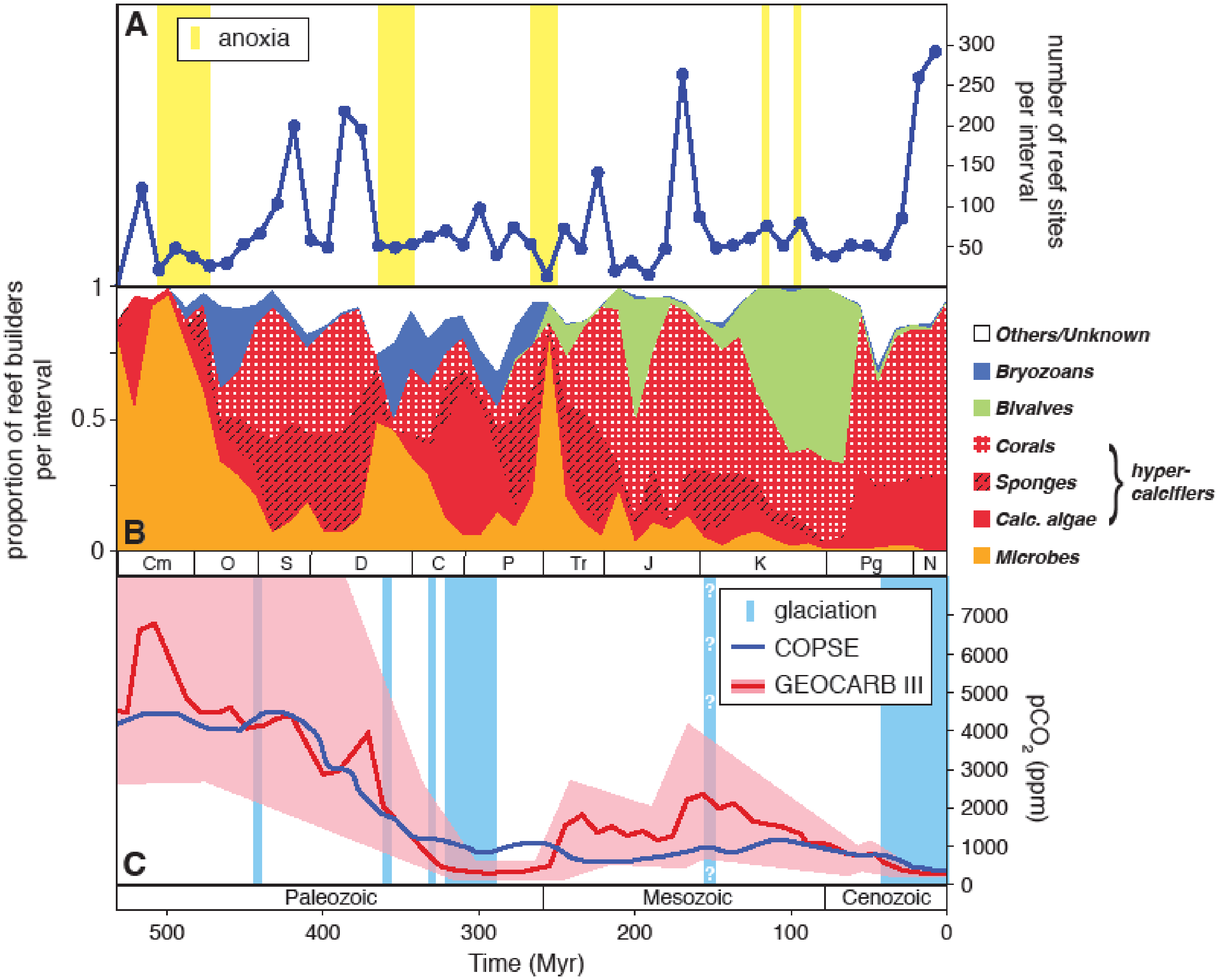
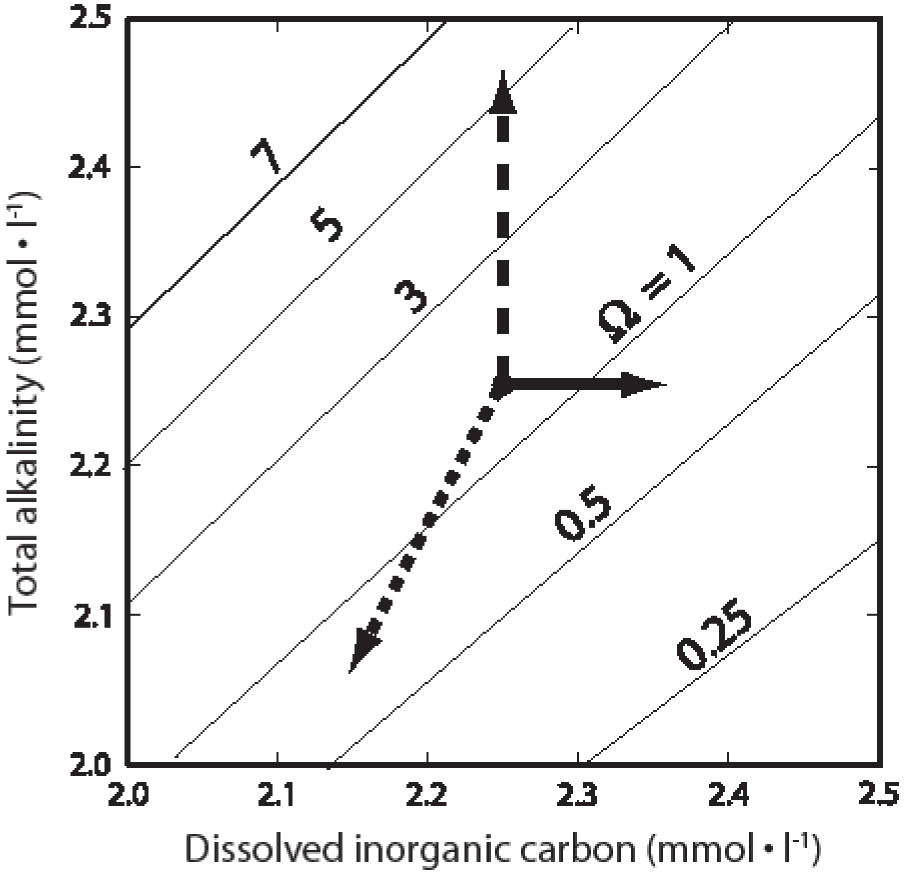

A
anoxia
300
250
200
150
100
50
number of reef sites per interval
1
0.5
0
proportion of reef builders per interval
B
Others/Unknown
Bryozoans
Bivalves
Corals
Sponges
Calc. algae
Microbes
hyper-calcifiers
Cm
O
S
D
C
P
Tr
J
K
Pg
N
C
glaciation
COPSE
GEOCARB III
?
7000
6000
5000
4000
3000
2000
1000
0
pCO₂ (ppm)
Paleozoic
Mesozoic
Cenozoic
500
400
300
200
100
0
Time (Myr)

Fig. 1



Process	$\Delta A_T : \Delta C_T$
▬▬ CO_2 outgassing	0 : 1
▬ ▬ ▬ Silicate weathering $CaSiO_3 + 2CO_2 + H_2O \Rightarrow Ca^{2+} + 2HCO_3^- + SiO_2$	2 : 0
▪▪▪▪▪ Carbonate precipitation $Ca^{2+} + CO_3^{2-} \Rightarrow CaCO_3$	-2 : -1
vector sum	0 : 0

Fig. 2

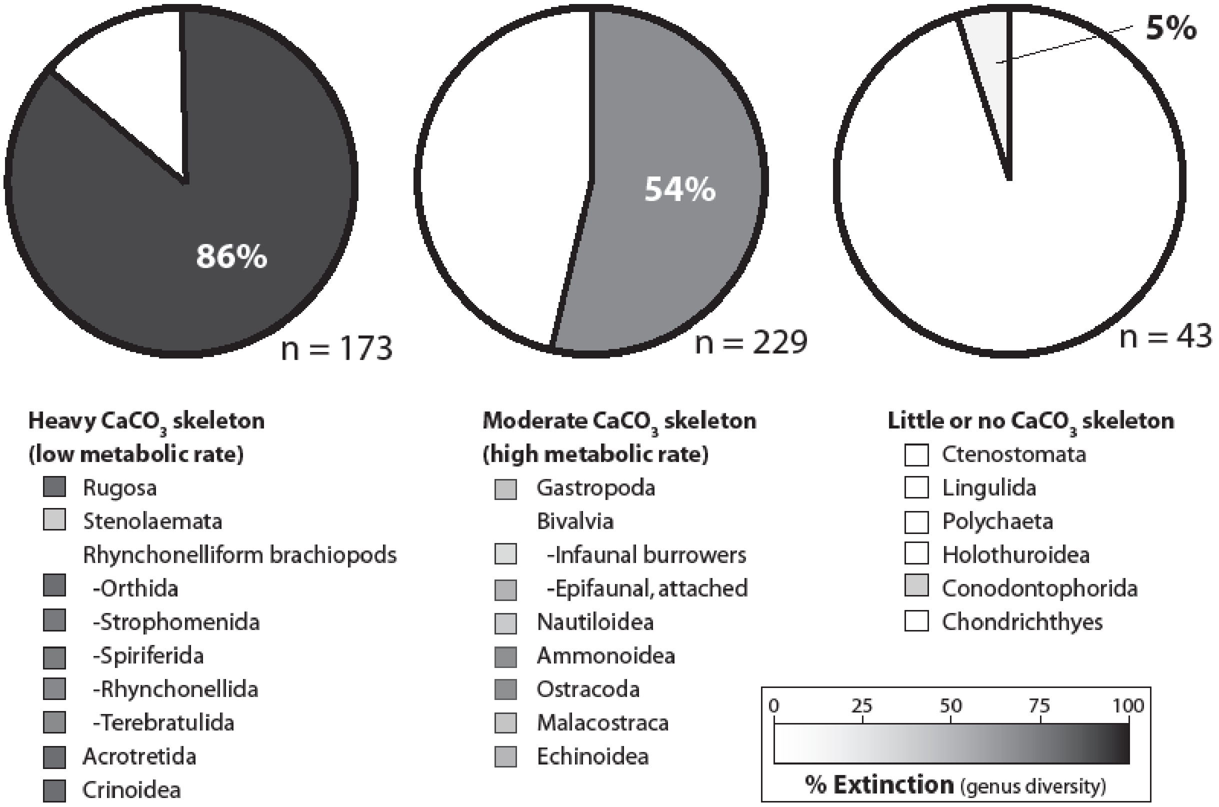

86%
n = 173
54%
n = 229
5%
n = 43
Heavy $CaCO_3$ skeleton
(low metabolic rate)
Rugosa
Stenolaemata
Rhynchonelliform brachiopods
-Orthida
-Strophomenida
-Spiriferida
-Rhynchonellida
-Terebratulida
Acrotretida
Crinoidea
Moderate $CaCO_3$ skeleton
(high metabolic rate)
Gastropoda
Bivalvia
-Infaunal burrowers
-Epifaunal, attached
Nautiloidea
Ammonoidea
Ostracoda
Malacostraca
Echinoidea
Little or no $CaCO_3$ skeleton
Ctenostomata
Lingulida
Polychaeta
Holothuroidea
Conodontophorida
Chondrichthyes
0
25
50
75
100
% Extinction (genus diversity)

Fig. 3

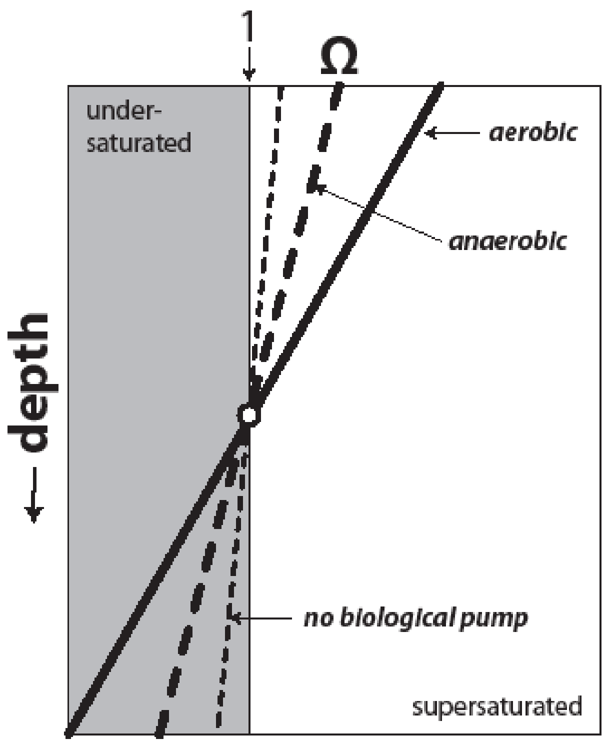

1
Ω
under-
saturated
aerobic
anaerobic
depth
no biological pump
supersaturated

Fig. 4