REPORT

Mass extinctions and ocean acidification: biological constraints on geological dilemmas

J. E. N. Veron

Abstract The five mass extinction events that the earth has so far experienced have impacted coral reefs as much or more than any other major ecosystem. Each has left the Earth without living reefs for at least four million years, intervals so great that they are commonly referred to as 'reef gaps' (geological intervals where there are no remnants of what might have been living reefs). The causes attributed to each mass extinction are reviewed and summarised. When these causes and the reef gaps that follow them are examined in the light of the biology of extant corals and their Pleistocene history, most can be discarded. Causes are divided into (1) those which are independent of the carbon cycle: direct physical destruction from bolides, 'nuclear winters' induced by dust clouds, sea-level changes, loss of area during sea-level regressions, loss of biodiversity, low and high temperatures, salinity, diseases and toxins and extraterrestrial events and (2) those linked to the carbon cycle: acid rain, hydrogen sulphide, oxygen and anoxia, methane, carbon dioxide, changes in ocean chemistry and pH. By process of elimination, primary causes of mass extinctions are linked in various ways to the carbon cycle in general and ocean chemistry in particular with clear association with atmospheric carbon dioxide levels. The prospect of ocean acidification is potentially the most serious of all predicted outcomes of anthropogenic carbon dioxide increase. This study concludes that acidification has the potential to trigger a sixth mass extinction event and to do so independently of anthropogenic extinctions that are currently taking place.

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Introduction

The five great mass extinction events that have greatly influenced paths of evolution of life on Earth have attracted a wide range of speculation about original causes and ultimate effects. In this context, reefs are among the most widely studied of marine communities, partly because carbonate platforms are so enduring, but also because the fossil record of corals is relatively well-known in terms of abundance and distribution. There is no doubt that reefs have been particularly impacted in mass extinctions. In each case they have taken many millions of years to recover, intervals of time known as 'reef gaps'. Many authors have speculated on the causes of mass extinctions and reef gaps (Wood 1999; Stanley 2001; Kiessling 2001; Veron 2008), the outcome being a wide array of hypotheses involving climatic upheavals of both terrestrial and extraterrestrial origin.

Past reviews of these hypotheses are generally based on the palaeoclimates and fossil records of specific extinction events. This is understandable given the vast amount of time separating mass extinctions and the very different suits of biota that were affected. During these intervals, ecosystems dominated by calcifying taxa may have been replaced by highly productive non-calcifying systems, leaving the geological remnants of reefs to become highly erosional through CO_2-enhanced dissolution (Berner 1993) and bioerosion. However, there are common elements in

mass extinctions, not the least being that tropical marine biota has been the most impacted in all cases.

When all proposed causes of mass extinctions are examined in the light of the biology of modern corals and their Pleistocene history, it becomes clear that most proposed causes of mass extinction can be dismissed. By process of elimination, we are left with some form of disruption to the carbon cycle for viable explanations. Importantly, none of the five mass extinction 'events' are events at all, rather they are due to cumulating effects of many causes acting in synergy over hundreds of thousands to millions of years. However, in all cases, some form of perturbation of the carbon cycle, and by inference its fast-acting currency, CO_2, is implicated (Veron 2008).

Mass extinctions, reefs and reef gaps

Mass extinction events are characterised by fundamental changes in plant and animal diversity as many high-level taxonomic groups go extinct over the same geological time interval. They are also characterised by very slow recovery, led by the evolution of new species rather than recolonisation by survivors.

The five great mass extinction events occurred at widely spaced intervals, each at or near the end of major divisions in Earth history. Of these, one at the end of the Permian and one at the end of the Cretaceous were so profound that they, respectively, mark the end of the Palaeozoic and Mesozoic eras (Fig. 1). However, interest in mass extinctions is not in their geological timing, but rather because they show beyond a doubt what can happen when the environment undergoes a massive upheaval. Mass extinction events in this context represent worst-case scenarios.

Mass extinctions are usually perceived as dramatic catastrophes inflicted on an otherwise peaceful Earth, but this is not the case. There were actually many minor or background extinction events at other times that left clear marks in the fossil record—no fewer than 27, according to a particularly detailed study (Raup and Sepkoski 1986; Sepkowski 1995) and data compilation (Kiessling 2001). Although not global, some background extinctions were just as catastrophic as mass extinctions for particular ecosystems or particular places, and many had major impacts on coral reefs. Reefs, more than any other major type of ecosystem, leave a geological record that tracks such events (e.g. Sepkowski 1995; Wood 1999; Stanley 2001). On an Earth history scale, this record does not show a process of gradual evolutionary development or improvement, but rather a stop-start response to a succession of environmental upheavals. This vulnerability of reefs to these upheavals is demonstrated many times in the fossil record, although the palaeoclimatic record provides only uncertain glimpses of it—narrow windows separated by immense intervals of time.

The end Ordovician mass extinction, 434 mya

The first great mass extinction 'event' took place at the end of the Ordovician, a time when, according to the fossil record, 26% of all families and 60% of all genera of both terrestrial and marine life worldwide were exterminated (Hallam and Wignall 1997). This extinction occurred at the end of a period of high mean global temperatures, probably caused by global greenhouse stability (Copper 2002), a condition that seems to have prevailed since the end of Cambrian 70 million years earlier. The extinction, however, was not just one 'event'. It took place over a very long time span, perhaps several million years, and appears
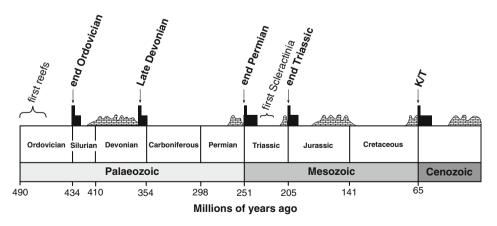

Fig. 1 Timeline of mass extinction events. The five named vertical bars indicate mass extinction events. Black rectangles (drawn to scale) represent global reef gaps and brick-pattern shapes show times of prolific reef growth. At other times reef growth appears to have been between these extremes, although there were many gaps not associated with mass extinctions and there were intervals of prolific growth in limited geographic regions not indicated here (after Veron 2008)

to have been the cumulative outcome of a succession of disasters. Possible causes that have been suggested include major fluctuations in sea level, multiple short-lived polar glaciations, and changes in ocean temperature, circulation and chemistry. The extinction was particularly disastrous and long lasting for reefs (Webby 1992; Copper 2001). Extreme levels of CO_2 have been recently implicated (Berner 2006).

Although some individual rugose and tabulate coral taxa survived, living reefs disappeared from the face of the Earth and did not reappear for another 4–6 million years, long after the climate had returned to pre-extinction conditions. This is the first true 'reef gap', meaning a gap in the geological record of reefs (Fig. 1).

The Late Devonian mass extinction, 360 mya

The Late Silurian to Late Devonian period—75 million years or so of more or less global greenhouse conditions with high temperatures set between ice ages—probably included all-time peaks of Palaeozoic reef development (Copper 2002). Sea levels were mostly high, so that seas flooded extensive areas of continents, forming epicontinental seas. However, despite the apparent proliferation of reefs, their development was intermittent, with major periods of worldwide expansion, especially during the Middle Silurian to Late Devonian interspersed with periods of apparent collapse (Copper 1994).

The world's Devonian reefs may have been every bit as well-formed and biologically diverse as today's reefs and, with an estimated area of 5×10^6 km^2 (including inter-reef areas), may have been as much as twice as extensive (Copper 1994). However, during the Late Devonian the environment that had clearly nurtured reefs for at least 13 million years turned hostile and the world plunged into the second mass extinction event. The Late Devonian mass extinction, like that at the end of the Ordovician, has been linked to multiple causes. A bolide may have struck around this time (McLaren and Goodfellow 1990), although most palaeontologists no longer seriously consider this to be a likely cause of the extinction. A precipitous drop in atmospheric CO_2 owing to uptake by vascular plants, low global temperatures and wildly fluctuating sea levels have all been blamed (Copper 2001). The extinctions appear to have varied geographically, although they primarily affected marine life: reef development ceased almost completely. Some corals and stromatoporoid sponges lived on, but there was no recovery of the vast coral-sponge reef-building communities anywhere in the world (Copper 1994, 2002; Wood 1999).

Reefs—although still not structures comparable to today's coral reefs—existed sporadically during much of the Carboniferous and Permian—through times of

oscillating temperatures and sea levels, including the periodic development of polar ice caps. Some of these reefs, especially those of the Late Permian, were very extensive. Their fossil content indicates that they were exceptionally diverse relative to their forebears, for they contained extensive arrays of all of the major marine groups, especially molluscs, echinoderms and crustaceans, as well as rugose and tabulate corals (reviewed by Copper 2001).

The end Permian mass extinction, 251 mya

The fossil record of the end Permian mass extinction reveals a staggering loss of life: 82% of all genera and perhaps 80–95% of all marine species went extinct (Sepkowski 1995, 2002; Erwin 2006). All rugose and tabulate corals and most other calcifying organisms ceased to exist. Why? This was one of the foremost questions in palaeontology a century ago, and it remains so today. At one point or another, wildly fluctuating temperatures in response to sharp increases in atmospheric CO_2, acid rain and lack of oxygen in shallow waters after protracted times of plenty have all been held responsible. The oceans are widely believed to have turned anoxic and to have contained free hydrogen sulphide (Wood 1999). Another study suggests that a sudden release of methane occurred at this time (Ryskin 2003; Erwin 2006). Recently, a comprehensive palaeophysiological study clearly implicates CO_2 (Knoll et al. 2007), perhaps associated with the Siberian Traps, the biggest volcanic outpouring of all time. Whatever the cause (reviewed by Knoll et al. 2007), the impact on reefs was sudden by geological standards and devastating. Some members of most marine phyla survived, yet reefs did not reappear for about 10 million years, the greatest hiatus in reef building in all of Earth history. What emerged in the Middle Triassic was the Scleractinia in place of their Palaeozoic predecessors. There is much in common between the ancient reefs of the mid-Palaeozoic and the first scleractinian reefs that took their place, not so much in the animals that built them, but in the stop-start nature of their intervals of growth, their biodiversity, and the sheer size of the structures they formed.

The end Triassic mass extinction, 205 mya

For 20 million years Triassic scleractinian corals, in concert with calcifying sponges and algae, went on to build some of the most spectacular reefs of all time. There was another substantial extinction of corals early in the Late Triassic, followed by a brief interval of dramatic recovery. Then, once again, the Earth plunged into a full-scale mass extinction. The end Triassic mass extinction (Stanley 1988, 2001)—the fourth in the history of reefs—is estimated to

have claimed about half of all marine invertebrates. The main taxa affected were conodonts (all), ammonites (almost all) and bivalves and gastropods (over half of all species). One-third of all scleractinian families went extinct and fewer than 25% of all genera are known to have survived (Beauvais 1984). Nevertheless, this mass extinction, like its predecessors, was not only marine; perhaps 80% of all land quadrupeds also went extinct. The cause, again, has been much debated without a clear outcome (Wood 1999; Flügel and Senowbari-Daryan 2001). Atmospheric CO_2 reached extreme levels for the Mesozoic (at least eight times today's level) (Hautmann 2004), and high greenhouse temperatures certainly resulted. Short-term sea-level fluctuations and various changes in ocean chemistry have been implicated by several palaeontologists, although none gives convincing evidence. The extinction was relatively abrupt (in geological time), making the reason for it particularly obscure. Whatever the cause, reefs again remained rare or absent throughout the world for a vast amount of time, perhaps 6–8 million years.
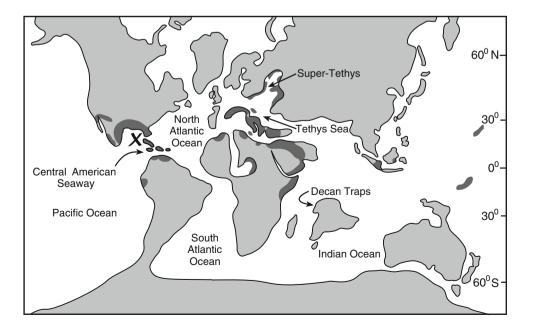
The end Cretaceous mass extinction (K/T), 65 mya

K/T has been extensively studied because of its indelible association with the demise of the dinosaurs. However, many well-known animal groups besides the dinosaurs went extinct at the K/T boundary. Virtually no large land animals survived. Plants were also greatly affected, although this is less clearly documented. Once again tropical marine life was decimated, including an extraordinarily high proportion of calcifying organisms. All remaining ammonites and belemnites went extinct, as did a high percentage of bivalves, gastropods and echinoids, as well as almost all Foraminifera. Many other unicellular organisms including radiolarians were also severely affected. Curiously, most other major taxa—including freshwater fish, amphibians, turtles, crocodiles, snakes and lizards—appear to have been almost unaffected, as were placental mammals.

Scleractinian corals appear to have just barely survived: some 33% of all families and 70% of all genera went completely extinct. Of the extant families, one (the Faviidae) retained six of its original sixteen genera; the others survived with only one or two. At least that is what the fossil record says (Veron 1995). However, that record is poor (Rosen and Turnšek 1989; Kiessling 2001) partly because sea levels were high during most of the Cretaceous and reefs were eroded away as the seas receded. Importantly, no branching corals appear to have survived, thus the habitats maintained by branching corals—those that provide shelter for algae-grazing fish—would have completely disappeared. Crucially, azooxanthellate corals were affected to the same degree as zooxanthellate corals. The most diverse azooxanthellate family (Caryophylliidae) lost half of its 27 genera; another family (Rhizangiidae) survived by three, and each of the other thirteen families survived by only one or two (Veron 1995).

Yet it was not the great diversity of the reefs of the Jurassic that was finally destroyed by K/T, for corals had been declining in abundance, and perhaps diversity, throughout the Early to Middle Cretaceous (summarised by Veron 1995). The Middle Cretaceous was a time of great environmental upheaval. Sea levels reached over 300 m above present levels, an all-time high for the Mesozoic so that the oceans flooded up to 40% of the continents, leaving only 18% of the Earth's surface as land (compared with 28% today) (Fig. 2).

Fig. 2 Positions of the continents during the Late Cretaceous, showing surviving reef limestone. Epicontinental seas were extensive during this time, especially over Europe and North Africa. X marks the impact site of the K/T bolide in the Gulf of Mexico. Note that South America was still connected to Antarctica and thus there was no Antarctic Circumpolar Current to drive the major circulation patterns that dominate climate patterns today (after Veron 2008)

Globally averaged atmospheric temperatures at the time of K/T have been estimated to be 6–14°C higher than at present (Barron 1983), ranging from a few degrees' difference at the equator to as much as 20–40°C at the poles (Barron and Washington 1985). Just what that would have meant for reefs is uncertain, as the surface temperature of the largest oceans would have been limited by the Thermal Cap of ~31°C, widely believed to be the highest temperature large oceans can reach (Kleypas et al. 2008). Estimates of CO_2 levels vary greatly, however the data for K/T are more reliable than those for more ancient extinctions. By the end Cretaceous CO_2 levels were at least five times, and perhaps as much as 10 times, those of today (Berner 1994; Tajika 1999; Gale 2000; Johnson et al. 2002).

A bolide hitting the Earth near the Yucatán Peninsula of southeast Mexico is widely thought to have caused the K/T extinctions. This historic discovery (Alvarez et al. 1980) conjures up images of unbridled devastation—of a 'nuclear winter'. This theory, however, is highly controversial: over 2,000 books and articles were published about it within a decade of the original publication (Glen 1990), the consensus now being that the bolide was not the primary cause of the extinction (Briggs 1991 and many others).

There is no doubt that the bolide impact would have sent shock waves around the Earth, creating tsunamis of immense size and triggering widespread volcanic activity. The impact itself and the outpourings of the shock-induced volcanoes are widely believed to have created a stratospheric dust cloud that would have plunged the whole of the Earth into a cold, interminable night. Certainly acid rain (including nitric acid generated from heat-induced fusion of nitrogen and oxygen), high levels of CO_2 released from the impact site and from volcanic eruptions everywhere, and high concentrations of methane released from continental slopes would have combined to create intense greenhouse warming. However, the timing of the ultimate extinction of different animal groups, the time taken for many to go extinct, and the age of the bolide debris do not correlate well (Keller et al. 2004). Some animal taxa became extinct within an apparently brief period, whereas others, including the dinosaurs, took hundreds of thousands of years, and their decline started long before the bolide's impact. The debate goes on, yet the tide has turned against the idea that the bolide was the main cause of K/T (MacLeod et al. 1997).

Some corals survived K/T, yet the hiatus in reef growth was so long that extensive reefs, comparable to those of the Cretaceous before the extinction, did not appear again until the Middle to Late Eocene, at least 10 million years later. Even then all reefs had a low level of diversity although the fossil record for the corals of this recovery period is poor and few details been gleaned from it (Rosen 2000).

Causes of mass extinctions

The causes of mass extinctions are divisible into two classes; those that do not involve the carbon cycle and those that do (Veron 2008). The former group are considered here, the second below.

Causes that are independent of the carbon cycle

Extrapolations from today's knowledge of coral biology to past environments must, of course, be cautiously made, especially as the Scleractinia of today have been in existence for only the past two mass extinctions (the end Triassic, and K/T). However, physiological processes, while they may vary in detail over time, would in general have been applicable to the Scleractinia throughout their existence.

What conditions in today's world could lead to a reef gap, major extinction of reef-building species, and simultaneous extinction of azooxanthellate species? Reef development has three prerequisites: (1) corals (and/or other calcifying organisms) must exist in environments that are favourable for calcification, (2) the resulting calcium carbonate must be consolidated into reefs, and (3) the rate of erosion must be less than the rate of accretion. Reef gaps, then, might occur whenever calcification is decreased, or there is a breakdown in the mechanisms of consolidation, or there are factors that increase the erosion or dissolution of calcium carbonate. Furthermore, to explain the simultaneous extinction of both zooxanthellate and azooxanthellate coral species, we must be looking for global-scale changes in conditions that span wide depth ranges as well as broad spatial scales.

The following is a summary of proposed causes of mass extinctions and reef gaps not attributable to a disruption of the carbon cycle. For good reasons each can be conclusively dismissed.

Direct physical destruction from bolides

A bolide many kilometres across could possibly cause massive destruction of reefs along the exposed side of an area the size of a continent; however, it beggars belief that such an effect, from a single point source, could envelop the whole Earth (Toon et al. 1997). Nor is there any way that azooxanthellate species would be equally affected or that surviving reef corals would take millions of years to recommence reef building. Be that as it may, the Earth has several large and well-known craters (13 of which date to the early Mesozoic or later) (Jablonski 1986), and many studies, motivated by the discovery of the K/T bolide, have sought to establish these as the primary cause of extinction events. Yet credible links have not emerged (Rothschild

and Lister 2003). Indirect effects of bolides are another matter.

'Nuclear winter' induced by dust clouds

Bolides are certainly capable of creating dust clouds in the order of magnitude greater than humans have ever witnessed—dense clouds that may have enveloped the Earth for weeks or months, creating devastating darkness and cold.

Survival estimates for corals under conditions of very low light vary from death in just a few weeks to survival of at least parts of colonies for six months or more (personal observation). It is significant, however, that (except for two or three species) no extant reef-building corals are found naturally in such conditions (such as in caves, under overhangs, or at depths where human vision is diminished). This strongly suggests that, if today's reef-building species were suddenly subjected to conditions of very low light for periods of years rather than weeks or months, 99% of species would go extinct. No such extinction happened; at least some representatives of two-thirds of families survived (Veron 1995). The proportion of zooxanthellate corals that went extinct at K/T is not on its own sufficient to explain the end of reef building or the reef gap that followed: (1) Many taxa that survived, including members of the Poritidae and Faviidae, are among the best reef builders (Veron 1995). (2) Azooxanthellate taxa, indicated above, fared no better than zooxanthellate taxa. (3) The K/T mass extinction caused a much higher rate of extinction in corals than in many other photosynthetic organisms, notably terrestrial vascular plants, which would have been more vulnerable to prolonged darkness.

From a biological point of view, it can be concluded that very low light, even if maintained for months, is exceedingly unlikely to have been the principal cause of the K/T mass extinction event.

The dust cloud created by the K/T bolide would also have caused atmospheric temperatures to plunge, but only for as long as the cloud persisted. The thermal inertia of the oceans would have protected marine environments from significant temperature change.

Sea-level changes

The major sea-level changes throughout Earth's history have been due to plate tectonics. These are very different from the sea-level changes that occurred during the ice ages, primarily in being much slower and of immensely longer duration.

We have specific data on this subject from the last glacial cycle, when the sea dropped 130 m (Lambeck and Chappell 2001; Siddall et al. 2003). Importantly, this fall is more than the depth range of all but a few deepwater zooxanthellate corals, which means that almost all corals had to relocate. During the ice ages, such falls were repeated many times, yet only about 10% of all corals went extinct over this entire interval (Veron and Kelly 1988). This is no more than a background extinction rate. Thus sea-level changes of any kind, let alone those resulting from tectonic movements, can be discounted as a primary cause of coral species extinctions.

Loss of area during sea-level regression

Loss of reef area during sea-level changes of the past has been suggested as a cause of coral extinctions, but the Pleistocene history of modern corals offers a number of reasons why this would not be so. There were major losses of reef area during the last glacial cycles, including most of the area of the Great Barrier Reef and the Philippine/Indonesian island archipelagos, the two most extensive reef areas on Earth. These great changes left no significant mark on today's coral diversity. At the opposite extreme, small areas may have most of the species complement of an entire province. The great dispersal capabilities of corals would ensure that recolonisation would take place swiftly from surviving niches. Area loss is thus highly unlikely to have been a primary cause of any extinction. Furthermore, azooxanthellate species would have been unaffected by a loss of reef area.

Loss of biodiversity as a cause of reef gaps

Reef building does not depend on high species diversity. Many of the corals that survived K/T belonged to genera well able to build reefs in the absence of any other coral species. We can therefore discount loss of biodiversity as a primary cause of reef gaps.

It has also been suggested that reefs do not re-establish until peak evolution rates of new species are reached (Jablonski 1986). Although this may have been true after some mass extinctions (there is no evidence either way), it was certainly not the case after K/T as coral diversity remained low long after widespread reef building had re-established.

Low temperatures

Conceptually, low temperatures could explain reef gaps and coral extinctions, but the data available for global temperatures give no credence to this. During the K/T extinction, ocean temperatures were at or above, rather than below, present levels. Furthermore, the suite of reef-building genera that survived indicates no selection for cold tolerance. Nor does low temperature explain why

azooxanthellate species were lost. In fact, even during a full glacial cycle, the world's oceans cool only around 6°C, and less than this at the equator. Although temperature reductions of this extent would be enough to contract the latitudinal range of species today, such a decrease could not have initiated extinctions in equatorial regions on the scale of any mass extinction.

High temperatures

Elevated temperatures can cause mass bleaching of corals, creating widespread devastation when reef ecosystems become so degraded that they are taken over by macroalgae and bacterial slime. However, even in a warmer world there would have been safe havens. Deep ocean temperatures would have remained well below surface temperatures in past geological times just as they do today and there would inevitably have been regions of upwelling. Deeper reef slopes of outer reefs would be exposed to mixing from oceanic water, and the temperature maximum of the Pacific of the past, and the Panthalassa before then, would have been subject to a Thermal Cap similar to that of today. This is an equatorial maximum; a mass extinction would have required that such temperatures extend to high latitudes. This would never have been possible, even under the most extreme conditions. Even supposing this did happen, under such a temperature regime we would expect surviving taxa to be biased towards those that thrive in relatively deep water, especially those exposed to deep oceanic water. In fact, the taxa that survived K/T are rarely, if ever, found in such regions. They are shallow-water species (typically occurring down to 20 m), most commonly occurring in sheltered habitats.

Through bleaching and general stress effects, elevated temperatures could have significant impact on reef development, including regional extinction of reef-building species. Even so, high temperatures cannot explain the extent or global nature of mass extinction events, nor can they account for the species that survived K/T, nor the loss of azooxanthellate taxa.

Salinity

Corals, and by extension reefs, are adversely affected by low salinity and low salinity may well have been a major cause of regional extinctions at various times, especially in partly landlocked regions such as the epicontinental seas of the Super-Tethys and North Africa during the Cretaceous (Fig. 2). However, it is inconceivable that any continental landmass could hold enough fresh water to cause a global mass extinction. High-salinity crises, such as occurred when the Mediterranean and Red seas became landlocked during protracted intervals of low sea-level, could cause

total regional extinctions, but again these could not be a significant cause of a global extinction.

Disease and toxins

There is strong evidence today that stresses such as mass bleaching, hyposaline influxes and a wide range of other ecological imbalances can greatly increase the incidence of diseases in corals (Rosenberg and Ben-Haim 2002; Selig et al. 2006). Combinations of stresses from high temperature, high light levels, and disease might lead to major regional losses of corals for as long as those stresses persist. However, azooxanthellate corals would not have been similarly affected, nor is disease attributable to the particular suite of zooxanthellate corals that survived K/T. The same arguments apply to toxins. These would have to be very widespread and affect deepwater and nearshore corals equally. The Earth has no toxins in such quantities, nor any that can exist both on land and in the oceans.

There is no credible case that supports the argument that mass extinctions had a biological cause. A rampant virus, far beyond anything known to science, might conceivably have caused the loss of life at the end Permian mass extinction, which was so extreme that all life on Earth came close to extermination. However, that was not true for any other mass extinction event, for none had anywhere near the same severity, or the same uniformity across all forms of life, both marine and terrestrial.

Extraterrestrial events

Extraterrestrial events apart from bolides have commonly been suggested as causal factors in extinctions. Episodes of ultraviolet or cosmic radiation from solar flares or supernovas (which may be capable of stripping away the ozone layer, allowing high levels of ultraviolet radiation to reach terrestrial life) can be discounted as causes of mass extinctions because the deep ocean would have shielded bottom-dwelling communities, and these were not shielded. Then there is the often-mentioned finding that extinctions follow a 26-million-year periodicity, implying an overriding extraterrestrial 'supercycle' of unknown origin. The database of fossils referred to above presents an avalanche of statistics in support of this conclusion (Raup and Sepkoski 1986); nevertheless, although this long periodicity does not look entirely random, it does not look distinctly cyclical either, so this concept remains enigmatic and without a plausible mechanism.

Links between mass extinctions and the carbon cycle

If the above causes of mass extinctions and reef gaps are discounted as primary factors we are left with an array of

further possibilities that have one aspect in common: they are either part of the carbon cycle or closely linked to it. This is hardly surprising: of all the great matter cycles of the Earth, only the carbon cycle is capable of inflicting mass destruction on all life, both terrestrial and marine, simultaneously.

The chemical cycles discussed here are all directly or indirectly linked to the carbon cycle. Several may be secondary outcomes of bolide impacts, traps, and supervolcanoes. However, the slower processes mentioned above—the vast quantities of gases released from volcanic chains as a result of seafloor spreading and other tectonic movements—might also be potential causes of relatively abrupt mass extinction events through cumulative outcomes and synergies.

It is now clear that small changes in the concentration of gases in the atmosphere can lead to major changes in global environments, potentially affecting both marine and terrestrial life. These gases include major components of our atmosphere, notably oxygen and water vapour, as well as those that are present only in trace amounts. The latter include a few that are critically important as climate regulators, with an influence far out of proportion to their concentrations. These are the gases that control the atmosphere's greenhouse warming, CO_2 and methane being the most important. Peripheral links to the carbon cycle are considered here first.

Acid rain

High levels of atmospheric CO_2 produce carbonic acid, and high levels of sulphur dioxide produce sulphuric acid. These substances, together with nitrous oxide from industry and the draining of tropical marshlands, are the main sources of acid rain today. Carbon dioxide and sulphur dioxide are released in massive amounts from some volcanoes, traps (notably the Deccan Traps of India at the time of K/T, see Fig. 2) and other sources, both terrestrial and marine, which are ultimately neutralised by ocean buffers. Although sulphur dioxide and nitrous oxide do not contain carbon, by the time their products reach the oceans they do, and thus they are inextricably linked to the carbon cycle. It is not quantitatively possible for acid rain to be a primary cause of an extinction event; however, acid rain may well have acted in synergy with other causes to create extreme environmental degradation.

Hydrogen sulphide

Hydrogen sulphide is another gas released in large quantity into the oceans and atmosphere from volcanoes or from sulphur-rich geysers and the like. It also has biological origins, which is why it regularly occurs in anoxic waters

of all types, ranging from aquaria to atoll lagoons. As with sulphur dioxide, although it does not contain carbon, it is inextricably linked to the carbon cycle and could, in terms of quantity, have been a significant contributor to an environmental upheaval in synergy with other gases.

Oxygen and anoxia

In a nitrogen-dominated atmosphere, oxygen and CO_2 have an additive relationship, an increase or decrease of the one creating a parallel effect in the other, all else being equal. However, all else may sometimes not be equal, and there may have been conditions, perhaps the end Permian and K/T, where ocean anoxia may have been created by primary productivity decrease (through phytoplankton depletion) as a result of acidification. By this simple mechanism, high atmospheric CO_2 can work synergistically with low levels of atmospheric oxygen to create ocean anoxia. Whether or not this has actually happened is not known.

Methane

Methane from geological sources, plant respiration and some animal life exists in minute amounts in the atmosphere (currently 1.8 ppm). However, it occurs in much greater quantities in permafrost, in tropical marshlands and in vast quantities as icelike solids (clathrates and hydrates) that are stable only under pressure and at low temperatures on continental shelves. The volume of these solids is unknown, although it is of the same order of magnitude as the Earth's total quantity of fossil fuels. Methane leaks into the ocean and atmosphere naturally, for example, as marsh gas. However, if it were released into the atmosphere in substantial quantities, perhaps induced by a bolide impact or a buoyancy change in the methane ice (for which there are many possible causes), there could be serious consequences. It would have a major greenhouse effect (methane has 22 times the potency of an equal volume of CO_2) and would also be converted to CO_2 by microbes and chemical oxidisation, causing the same adverse effects characteristic of high levels of CO_2. As far as the oceans are concerned, methane need not reach the atmosphere; if dissolved in shallow water it will oxidise to CO_2 and attack carbonate buffers directly.

Carbon dioxide

Both increasing and decreasing CO_2 levels have been proposed as major contributors to mass extinction events in the past. Over geological time scales, CO_2 has varied from levels much lower than the 375 ppm of today up to perhaps ten times today's level (depending on the reliability of studies of a small number of fossil soils and whether or not

results from single points in time are representative of longer time intervals) (Fig. 3). The effects of high levels of atmospheric CO_2 are pursued below.

Ocean chemistry and pH

In a geological perspective, Phanerozoic oceans have been divided into three intervals of 'aragonite oceans' and two of 'calcite oceans' which are characterised by secular shifts in the Mg/Ca ratio and Ca^{2+} of seawater. These changes, presumably the outcome of tectonically released CO_2, correlate with changes in calcifying biota, especially those of the Cretaceous-Tertiary acidification interval spanning K/T, and potentially the end Permian mass extinction (Stanley and Hardie 1998).

Increased atmospheric CO_2 leads to greater amounts of the gas dissolving in the oceans, which directly reduces pH. This, in turn, alters the proportions of different forms of inorganic carbon (CO_2, H_2CO_3, HCO_3^- and CO_3^{2-}) in the ocean (Buddemeier et al. 2004; Kleypas and Langdon 2006). Increasing the concentration of CO_2 in the ocean alters the proportion of the other three forms of carbon. Calcifying organisms use carbonate and/or bicarbonate ions to build skeletons, and thus a decrease in their availability slows the calcification process (Gattuso et al. 1999). The proportions of each of these carbon components are sensitive to temperature and pressure, and thus to latitude and depth.
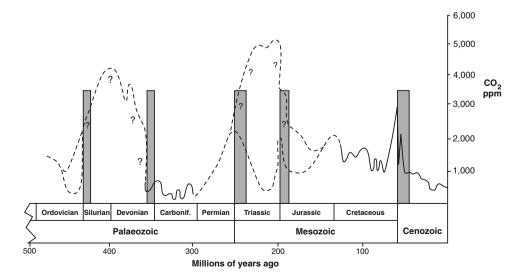
In the current context, it is important to consider the interactions between acidification of surface waters where zooxanthellate corals occur and the deep ocean where most azooxanthellate corals occur. The former are sensitive to acidification of surface waters by CO_2 directly; the latter are potentially sensitive to having their depth range reduced by shallowing of, or decrease in $\Omega_{aragonite}$. These surface and deep layers directly influence each other at high latitudes where ocean temperatures are uniform and mixing occurs relatively easily. They are, however, well separated in the warm tropics, especially at the thermocline, and interact primarily via the sinking of carbonate skeletons of surface-dwelling plankton.

Shallow oceans are currently supersaturated with carbonates, allowing zooxanthellate corals to calcify. However, as $\Omega_{aragonite}$ decreases, the process requires increasing amounts of energy. The same applies to azooxanthellate corals, although here the process depends on the depth of the aragonite saturation horizon, which, in turn, varies with temperature as well as chemistry (Guinotte et al. 2003): as changes in water temperature and chemistry cause the horizon to rise, the depth range of azooxanthellate corals shallows.

Acidification

What will happen to reefs if calcification mechanisms are diminished by changing pH? The dependence of calcareous algae on high-magnesium calcite, the most soluble of all calcium carbonate skeletons, would make them early casualties of decreasing pH. Since these algae are critical to reef consolidation, their demise would seriously threaten net accretion of reefs, even before reduced calcification became a significant ecological issue for Scleractinia. With further decrease in pH, aragonitic organisms including Scleractinia would become increasingly affected, further tipping the balance in favour of reef erosion. Since acidification from elevated atmospheric CO_2 affects oceans on a global scale, the effects on reefs would be worldwide, although influences from temperature and surface water mixing would create local variations both spatially and with depth. In equatorial regions, adverse changes in carbonate/bicarbonate ion availability as a result of decreasing pH would be exacerbated by lack of mixing among the warm, shallow, CO_2-enhanced surface layers and the

Fig. 3 Atmospheric CO_2 levels in parts per million (ppm) over the time of the existence of reefs. The vertical bars are the intervals of reef gaps following the five great mass extinction events. Broken lines indicate doubtful reconstructions. All reef gaps, with the exception of the Late Devonian, are probably associated with rapidly increasing or high CO_2 levels (after Veron 2008)

buffers of cool, deeper ocean water. Acidification could thus have a devastating effect on reef development, leading initially to widespread inhibition of reef growth and eventually to reef erosion and dissolution.

As far as corals are concerned, the first impact will be on azooxanthellate taxa, which will become increasingly displaced from deeper oceans as the $\Omega_{aragonite}$ horizon shallows, particularly at high latitudes (Guinotte et al. 2003; Turley et al. 2007).

Just what form the specific influence on skeletal structure would take for both azooxanthellate and zooxanthellate corals is far from clear. Lowered calcification rates might result in slower-growing yet similarly dense skeletons, or they might result in more lightly calcified, weaker skeletons growing at normal rates. To some extent these differences would be taxon specific, dependent on the ability of the species to actively control the calcification process. As inhibition of calcification progressed, most corals would become increasingly fragile and more readily broken by wave action. Eventually these changes would significantly affect the rate at which the corals grow and would lower their resistance to predators and disease, as well as their capacity to make three-dimensional habitats for other reef organisms. Fast-growing branching species (especially *Acropora* and its ecological equivalents) would likely be most affected. These are the very species that currently make reefs so resilient to physical damage by recovering rapidly from tropical cyclones or damage from Crown-of-Thorns starfish.

The corals likely to resist the effects of acidification the longest would probably have some or all of the following characteristics: (1) Have massive (or low-profile) growth forms that could remain relatively resistant to wave action even when skeletal density fell. (2) Be long-lived as these taxa would already be tolerant of environmental variations over life spans of centuries. (3) Have relatively well-developed, active control of calcification. (4) Be less likely to live in habitats where synergistic stresses could exacerbate the effects of acidification.

Is this what happened at K/T? The principle that skeletal growth is affected by carbonate ion concentration has been well established (Marubini et al. 2002). In addition to the evidence presented above, recent studies point towards acidification as the primary cause of coral extinctions and the reef gaps, despite deficiencies in the fossil record. (1) Late Cretaceous azooxanthellate corals of the caryophylliid genus *Coelosmilia* has been found to have calcitic skeletons rather than skeletons of the more soluble aragonite as have today's Scleractinia (Stolarski et al. 2007). (2) Two Mediterranean corals, *Oculina patagonica* and *Madracis pharensis* which were placed in acidified aquaria gradually lost their skeletons, and then re-grew them after being returned to normal seawater (Fine and Tchernov 2007). (3)

Three common zooxanthellate species produced calcite in artificial Cretaceous seawater (Ries et al. 2006).

Unlike the alternative causes of extinctions noted above, acidification can explain why both azooxanthellate and zooxanthellate species were affected. It can also explain the loss of reefs both locally and globally, as well as account for the existence of long-lasting reef gaps. Although acidification may be difficult to initiate because of ocean buffers, once achieved it will persist as long as atmospheric CO_2 remains high. Furthermore, the oceans would remain acidified for tens of thousand years after CO_2 levels had declined, that being the time required for normal alkalinity to be restored (Archer 2005). This may be an interval long enough for corals to initiate an evolutionary recovery. Under such a recovery sequence, reef gaps in the past millions of years would be a plausible consequence, depending primarily on the endurance of atmospheric CO_2 and the rate of evolutionary accommodation to it.

Low levels of carbon dioxide

Low levels of CO_2 may result in low levels of photosynthesis, leading to low levels of oxygen and eventually ocean anoxia. This might have triggered the Late Devonian mass extinction event; the evidence is inconclusive.

Reefs during carbon dioxide highs?

The foregoing discussion argues that acidification as a mechanism explains mass extinctions better than other mechanisms that have been offered. However, studies of ancient environments also suggest that similar atmospheric CO_2 levels may have occurred at times when reefs actually proliferated rather than declined. Can these two observations be reconciled?

One explanation may lie in the interpretation of information from such ancient times. Fig 3 shows that CO_2 data are very uncertain for most of geological time, the data being based on a small number of point samples from widely different geological intervals. When this diagram is compared to those for shorter geological intervals (Fig. 4, and then ice core records), it is obvious that substantial variability is present at progressively finer scales, variation that is masked at large scales. Two possibilities present themselves: (1) Reefs may not have proliferated at all during CO_2 highs; they may just appear to have survived because they were able to resume growth when levels fell. (2) The high apparent CO_2 levels of ancient times may be an artefact of a lack of data and measuring method.

Further explanation is based on the non-linear relationship between acidification and atmospheric CO_2. The longer time frame of gradual increases in CO_2 allows mixing and buffering of surface layers by deep ocean sinks
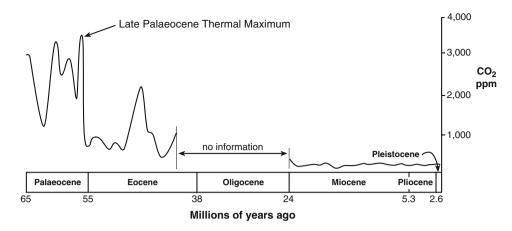
Fig. 4 Global CO_2 levels (in ppm) of the Cenozoic. The major peaks of the Paleocene and Eocene, especially their duration, are based on little solid information. Very high levels at these times do not necessarily mean that the oceans were as acidic as today's predictions suggest, because the accumulation of high levels of CO_2 was not rapid (in a geological sense). As a result, surface ocean waters would have been buffered by deep-ocean water and carbonate rock. Furthermore, high CO_2 levels over prolonged intervals dissolve terrestrial limestone, a process that would have raised ocean alkalinity (after Veron 2008)

as well as adaptation to new environmental conditions by marine organisms. In contrast, when atmospheric CO_2 increases abruptly, its effects are intensified in shallow waters owing to a lack of mixing. It also gives marine life little time for evolutionary adaptation. The degree of ocean mixing has altered over geological time. The physical surface of the Earth—the geographic positions of the continents, prevailing climate regimes, and the pathways of ocean currents—is such that it is not possible to compare widely separated periods of the Earth's history. Threshold conditions for acidification may have varied with tectonic changes and associated variability in current patterns and deep ocean exchange. The last prolonged interval of very high CO_2 levels (Fig. 4) pre-dates the formation of the Antarctic Circumpolar Current in the Early Oligocene, and thus pre-dates the main driver to today's climate patterns.

Reef proliferation in the distant past during periods when atmospheric CO_2 may have been high could mean that the reef builders and consolidators were better adapted to these conditions and could exploit the enhanced calcification and photosynthesis promoted by warmer sea surface temperatures without adverse effects. Many organisms in the ancient oceans would have been more tolerant to acidification through their dependence on calcitic skeletons rather than aragonite or high-magnesium calcite. There may have been other aspects of coral biology that allowed ancient corals to tolerate water chemistries that are lethal to today's Scleractinia. If so, it would be more than interesting to know what those physiological mechanisms were.

Synergies, spikes and last straws

Although these deliberations about possible causes of mass extinction events have highlighted acidification as by far the most probable cause of both coral extinctions and reef gaps, it would be misleading to consider this the only cause. Indeed, all mass extinctions appear to be the outcome of several different influences acting synergistically. Acidification may well have been a primary mechanism by which marine ecosystems were affected; however, low light, bleaching, deteriorating water quality owing to acid rain or anoxia, mechanical damage and disease would all have played their parts. Although the time frames of bolides do not always fit the facts as a singular cause of extinction, bolides or traps or volcanic chains may have created severely adverse conditions that became the straw that broke the camel's back.

The future

If acidification was in fact a major cause of mass extinctions and reef gaps as the above discussion suggests, prospects for the future are frightening, not because of any immediate impact on corals, but because of commitment. Commitment embodies the concept of unstoppable inevitability, according to which the nature and health of future environments will be determined, not by our actions at some future date but by what is happening now. The oceans, including the ocean depths, respond slowly to atmospheric conditions, whether a temperature increase or a CO_2 build-up, which means that the full effects of acidification will take decades to centuries to develop. Nevertheless, this is only a delay: the factors causing acidification will have irretrievably committed the Earth to the process long before its effects become anywhere near as obvious as those of mass bleaching today.

About half of all CO_2 from anthropogenic sources still remains in the atmosphere. Of the remainder, most has been taken up by the ocean (Raven et al. 2005), a process that has now used up about one-third of the total storage capacity of the ocean surface (Sabine et al. 2004). The rest has been taken up by terrestrial life (Feely et al. 2004).

It is clear that, without uptake of anthropogenic CO_2 by the oceans, atmospheric levels would be about 55 ppm higher than at present (IPCC 2007). The pre-industrial levels of carbonate ions in seawater were about 85% HCO_3^- and 15% CO_3^{2-}; doubling atmospheric CO_2 will alter this ratio to about 90% HCO_3^- and 10% CO_3^{2-}. On time scales of decades to centuries, if dissolved ocean surface CO_2 continues to increase in proportion to atmospheric CO_2, a doubling of the latter from pre-industrial levels will result in a 30% decrease in carbonate ion concentration and a 60% increase in hydrogen ion concentration in surface waters. These changes will increasingly diminish the ocean's capacity to absorb CO_2 from the atmosphere—the proportional net rate of ocean extraction from the atmosphere declining in a self-reinforcing cycle, even though the physical rate of exchange of CO_2 between atmosphere and ocean will remain approximately constant.

If CO_2 levels are allowed to increase to 650–700 ppm, as is projected to occur later this century, a return to twice the pre-industrial level of 560 ppm will take disproportionately longer (hundreds of years) owing to this slowing of the rate of uptake by the oceans. It is generally unappreciated just how long it will take to bring CO_2 concentrations back down to normal levels (Raven et al. 2005). If we continue to produce CO_2 at the present rate, we can expect the atmosphere to retain significant effects from it for between 30,000 and 35,000 years, which, when modelled, means that 17–33% of the excess CO_2 currently in the atmosphere will still be there a thousand years from now. The acidification effect caused by increasing atmospheric CO_2 will initially be buffered by bicarbonate–carbonate ion exchange, but once the buffers are overwhelmed (depending on as yet unpredicted depth effects) it will change relatively abruptly. Unlike enhanced greenhouse temperature increase, the acidification effect of CO_2 will not bounce back to a benign level if atmospheric CO_2 returns to normal; the oceans will remain acidified until they are neutralised by the dissolving of marine carbonate rocks and the weathering of rocks on land, a hugely protracted process.

When CO_2 levels increase to 560 ppm, the Southern Ocean surface waters will be undersaturated with respect to aragonite, and the pH will be reduced by about 0.24 units—from almost 8.2 today to a little more than 7.9. At the present rate of acidification, all reef waters will have a $\Omega_{aragonite}$ of 3.5 or less by the middle of this century

(Guinotte et al. 2003). Should CO_2 levels reach 800 ppm later this century, the decrease will be 0.4 units (Riebesell et al. 2000; Caldeira and Wickett 2003) and dissolved carbonate ion concentration will have decreased by almost 60%. At that point all the reefs of the world will be eroding relics.

The levels of CO_2 and pH predicted by the end of this century may not have occurred since the Middle Eocene, but the all-important rate of change we are currently experiencing has no known precedent. There can be no evolutionary solution for such a rate of change.

Ultimately—and here we are looking at centuries rather than millennia—the ocean pH will drop to a point at which a host of other chemical changes, including anoxia, would be expected. If this happens, the state of the oceans at the end of K/T, or something like it, will become a reality and the Earth will enter the sixth mass extinction. Another 1–3 decades like our last will see the Earth committed to a trajectory from which there will be no escape.

References

Alvarez L, Alvarez W, Asaro F, Michel HV (1980) Extraterrestrial cause for the Cretaceous-Tertiary extinction: experimental results and theoretical interpretation. Science 208:1095–1108

Archer D (2005) Fate of fossil fuel CO_2 in geological time. J Geophys Res 111:C09S05. doi:10.1029/2004JC002625

Barron EJ (1983) A warm, equable Cretaceous: the nature of the problem. Earth Sci Rev 19:305–338

Barron EJ, Washington WM (1985) Warm cretaceous climates: high atmospheric CO_2 as a plausible mechanism. In: Sundquist ET, Broecker WS (eds) The carbon cycle and atmospheric CO_2: natural variations, Archaean to Present. Geophys Monogr 32:546–553

Beauvais L (1984) Evolution and diversification of Jurassic Scleractinia. Palaeontogr Am 54:219–224

Berner RA (1993) Weathering and its effect on atmospheric CO_2 over Phanerozoic time. Chem Geol 107:373–374

Berner RA (1994) GEOCARB II: a revised model of atmospheric CO_2 over Phanerozoic time. Am J Sci 294:56–91

Berner RA (2006) Inclusion of the weathering of volcanic rocks in the GEOCARBSULF model. Am J Sci 306:295–302

Briggs JC (1991) A Cretaceous-Tertiary mass extinction? Bioscience 41:619–624

Buddemeier RW, Kleypas JA, Aronson RB (2004) Coral reefs and global climate change: potential contributions of climate change to stresses on coral reef ecosystems. Pew Center on Global Climate Change, Arlington

Caldeira K, Wickett ME (2003) Anthropogenic carbon and ocean pH. Nature 425:365

Copper P (1994) Ancient reef ecosystem expansion and collapse. Coral Reefs 13:3–11

Copper P (2001) Evolution, radiations, and extinctions in Proterozoic to Mid-Paleozoic reefs. In: Stanley GD Jr (ed) The history and sedimentology of ancient reef systems. Academic/Plenum Publishers, New York, pp 89–119

Copper P (2002) Silurian and Devonian reefs: 80 million years of global greenhouse between two ice ages. In: Kiessling W, Flügel E, Galonka J (eds) Phanerozoic Reef Patterns. SEPM (Soc Sediment Geol) Spec Publ 72:181–238

Erwin DH (2006) Extinction: how life on earth nearly ended 250 million years ago. Princeton University Press, Princeton

Feely RA, Sabine CL, Lee K, Berelson W, Kleypas JV, Fabry J, Millero FJ (2004) Impact of anthropogenic CO_2 on the CaCO3 system in the oceans. Science 305:362–366

Fine M, Tchernov D (2007) Scleractinian coral species survive and recover from decalcification. Science 315:1811

Flügel E, Senowbari-Daryan B (2001) Triassic reefs of the Tethys. In: Stanley GD Jr (ed) The history and sedimentology of ancient reef systems. Academic/Plenum Publishers, New York, pp 217–249

Gale A (2000) The Cretaceous world. In: Culver SJ, Rawson PF (eds) Biotic response to global change: the last 145 million years. Cambridge University Press, Cambridge, pp 4–19

Gattuso J-P, Allemand D, Frankignoulle M (1999) Photosynthesis and calcification at cellular, organismal and community levels in coral reefs: a review on interactions and control by carbonate chemistry. Am Zool 39:160–183

Glen W (1990) What killed the dinosaurs? Am Sci 78:354–370

Guinotte JM, Buddemeier RW, Kleypas JA (2003) Future coral reef habitat marginality: temporal and spatial effects of climate change in the Pacific basin. Coral Reefs 22:551–558

Hallam A, Wignall PB (1997) Mass extinctions and their aftermath. Oxford University Press, Oxford

Hautmann M (2004) Effect of End-Triassic CO_2 maximum on carbonate sedimentation and marine mass extinction. Facies 50:257–261

IPCC (2007) Summary for Policymakers. In: Solomon S, Quin D, Manning M, Chen Z, Marquis M, Averyt KB, Tignor M, Miller HL (eds) Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University press, Cambridge, pp 1–18

Jablonski D (1986) Mass extinctions: new answers, new questions. In: Kaufman L, Mallory K (eds) The last extinction. MIT Press, Cambridge, pp 43–61

Johnson CC, Sanders D, Kauffman EG, Hay WW (2002) Patterns and processes influencing Upper Cretaceous reefs. In: Kiessling W, Flügel E, Galonka J (eds) Phanerozoic reef patterns. SEPM (Soc Sediment Geol) Spec Publ 72:549–585

Keller G, Adatte T, Stinnesbeck W, Stüben D, Berner Z, Kramer U, Harting M (2004) More evidence that the Chicxulub impact predates the K/T mass extinction. Meteoritics Planet Sci 39:1127–1144

Kiessling W (2001) Phanerozoic reef trends based on the Paleoreef database. In: Stanley GD Jr (ed) The history and sedimentology of ancient reef systems. Academic/Plenum Publishers, New York, pp 41–88

Kleypas JA, Langdon C (2006) Coral reefs and changing seawater carbonate chemistry. In: Phinney JT, Hoegh-Guldberg O, Kleypas JA, Skirving W, Strong A (eds) Coral reefs and climate change: science and management. Coast Estuar Stud 61:73–110

Kleypas JA, Danabasoglu G, Lough JM (2008) Potential role of the ocean thermostat in determining regional differences in coral reef bleaching events. Geophys Res Lett 35:L03613. doi: 10.1029/2007GL032257

Knoll AH, Bambach RK, Payne JL, Pruss S, Fischer WW (2007) Paleophysiology and end-Permian mass extinction. Earth Planet Sci Lett 256:295–313

Lambeck K, Chappell J (2001) Sea level change through the last glacial cycle. Science 292:679–686

MacLeod N, Rawson N, Forey PF, Banner FT, Boudagher-Fadel MK, Brown PR, Burnett JA, Chambers P, Culver S, Evans SE, Jeffery C, Kaminski MA, Lord AR, Milner AC, Milner AR, Morris N, Owen E, Rosen BR, Smith AB, Taylor PD, Urquhart E, Young JR (1997) The Cretaceous-Tertiary biotic transition. Journal of the Geological Society, London 154:265–292

Marubini F, Ferrier-Pages C, Cuif J-P (2002) Suppression of skeletal growth in scleractinian corals by decreasing ambient carbonate-ion concentration: a cross-family comparison. Proc R Soc Lond B Biol Sci 270:179–184

McLaren DJ, Goodfellow WD (1990) Geological and biological consequences of giant impacts. Annu Rev Earth Planet Sci 18:123–171

Raup DM, Sepkoski JJ Jr (1986) Periodic extinction of families and genera. Science 231:833–836

Raven J, Caldeira K, Elderfield H, Hoegh-Guldberg O, Liss P, Riebesell U, Shepherd J, Turley C, Watson A (2005) Ocean acidification due to increasing atmospheric carbon dioxide. Policy Document 12/05, Royal Society, London

Riebesell U, Zondervan I, Rost B, Tortell PD, Zeebe RE, Morel FMM (2000) Reduced calcification of marine plankton in response to increased atmospheric CO_2. Nature 407:364–367

Ries JB, Stanley SM, Hardie LA (2006) Scleractinian corals produce calcite, and grow more slowly, in artificial Cretaceous seawater. Geology 34:525–528

Rosen BR (2000) Algal symbiosis and the collapse and recovery of reef communities: Lazarus corals across the Cretaceous/Tertiary boundary. In: Culver SJ, Rawson PF (eds) Biotic response to global change: the last 145 million years. Cambridge University Press, Cambridge, pp 164–180

Rosen BR, Turnšek D (1989) Extinction patterns and biogeography of scleractinian corals across the Cretaceous/Tertiary boundary. Memoir of the Association of Australasian Palaeontologists 8:355–370

Rosenberg E, Ben-Haim Y (2002) Microbial diseases in corals and global warming. Environ Microbiol 4:318–326

Rothschild LJ, Lister AM (eds) (2003) Evolution on planet earth: the impact of the physical environment. Academic Press, London

Ryskin G (2003) Methane-driven oceanic eruptions and mass extinctions. Geology 31:741–744

Sabine CL, Feely RA, Gruber N, Key RM, Lee K, Bullister JL, Wanninkhof R, Wong CS, Wallace DWR, Tilbrook B, Millero FJ, Peng T-H, Kozyr A, Ono T, Rios AF (2004) The oceanic sink for anthropogenic CO_2. Science 305:367–371

Selig ER, Drew Harvell C, Bruno JF, Willis BL, Page CA, Casey KS, Sweatman H (2006) Analysis and relationship between ocean temperature anomalies and coral disease outbreaks at broad spatial scales. In: Phinney JT, Hoegh-Guldberg O, Kleypas J, Skirving W, Strong A (eds) Coral reefs and climate change: science and management. Coast Estuar Stud 61:111–128

Sepkowski JJ Jr (1995) Patterns of Phanerozoic extinction: a perspective from global databases. In: Walliser OH (ed) Global events and event stratigraphy. Springer-Verlag, Berlin, pp 35–51

Sepkowski JJ Jr (2002) A compendium of fossil marine animal genera. Bull Am Paleontol 363:1–563

Siddall M, Siddall EJ, Rohling A, Almogi-Labin C, Hemleben D, Meischner I, Schmelzer I, Smeed DA (2003) Sea-level fluctuations during the last glacial cycle. Nature 423:853–858

Stanley GD Jr (1988) The history of early Mesozoic reef communities: a three-step process. Palaios 3:170–183

Stanley GD Jr (2001) Introduction to reef ecosystems and their evolution. In: Stanley GD Jr (ed) The history and sedimentology of ancient reef systems. Academic/Plenum Publishers, New York, pp 1–39

Stanley SM, Hardie LA (1998) Secular oscillations in the carbonate mineralogy of reef-building and sediment-producing organisms driven by tectonically forced shifts in seawater chemistry. Palaeogeogr Palaeoclimatol Palaeoecol 144:3–19

Stolarski J, Meibom A, Przenioslo R, Mazur M (2007) A Cretaceous scleractinian coral with a calcitic skeleton. Science 318:92–94

Tajika E (1999) Carbon cycle and climate change during the Cretaceous inferred from a biogeochemical carbon cycle model. The Island Arc 8:293–303

Toon OB, Zahnle K, Morrison D, Turco RP, Covey C (1997) Environmental perturbations caused by the impacts of asteroids and comets. Rev Geophys 35:41–78

Turley CM, Roberts JM, Guinotte JM (2007) Corals in deep-water: will the unseen hand of ocean acidification destroy cold-water ecosystems? Coral Reefs 26:445–448

Veron JEN (1995) Corals in space and time: the biogeography and evolution of the Scleractinia. University of New South Wales Press, Sydney

Veron JEN (2008) A reef in time: the Great Barrier Reef from beginning to end. Harvard University Press, Cambridge

Veron JEN, Kelly R (1988) Species stability in hermatypic corals of Papua New Guinea and the Indo-Pacific. Memoir of the Association of Australasian Palaeontologists 6:1–69

Webby BD (1992) Global biogeography of Ordovician corals and stromatoporoids. In: Webby B, Laurie JR (eds) Global perspectives on Ordovician geology 2. Balkema, Rotterdam, pp 261–276

Wood R (1999) Reef evolution. Oxford University Press, Oxford