Review

Ocean Acidification and Coral Reefs: An Emerging Big Picture

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Abstract: This article summarises the sometimes controversial contributions made by the different sciences to predict the path of ocean acidification impacts on the diversity of coral reefs during the present century. Although the seawater carbonate system has been known for a long time, the understanding of acidification impacts on marine biota is in its infancy. Most publications about ocean acidification are less than a decade old and over half are about coral reefs. Contributions from physiological studies, particularly of coral calcification, have covered such a wide spectrum of variables that no cohesive picture of the mechanisms involved has yet emerged. To date, these studies show that coral calcification varies with carbonate ion availability which, in turn controls aragonite saturation. They also reveal synergies between acidification and the better understood role of elevated temperature. Ecological studies are unlikely to reveal much detail except for the observations of the effects of carbon dioxide springs in reefs. Although ocean acidification events are not well constrained in the geological record, recent studies show that they are clearly linked to extinction events including four of the five greatest crises in the history of coral reefs. However, as ocean acidification is now occurring faster than at any know time in the past, future predictions based on past events are in unchartered waters. Pooled evidence to date indicates that ocean acidification will be severely affecting reefs by mid century and will have reduced them to ecologically collapsed carbonate platforms by the century's end. This review concludes that most impacts will be synergistic and that the primary outcome will be a progressive reduction of species diversity correlated with habitat loss and widespread extinctions in most metazoan phyla.

Keywords: ocean acidification; coral reefs; climate change; coral

1. Introduction

There are now several hundred publications concerning the history, causes and possible effects of ocean acidification (OA) and how it may progress during the 21st century and beyond. Chemical aspects were described [1–7] long before impacts on marine ecosystems were recognised [8]. However over half of all publications about OA now refer to reefs, or are specifically about reefs and most of these have been published in the last 10 years. Because reefs are both geological and biological structures, OA has now come to span a range of sciences that are almost the equal of climate change, yet OA is only tangentially an aspect of climate change, linked by a common cause (anthropogenic CO_2) together with impacts on biodiversity that are predicted to act in synergy with global temperature increase.

Like climate change, OA has moved from a purely scientific subject to one of wider public interest. This move has been slow and recent, primarily because OA is invisible and also because it unavoidably involves the use of chemical terms, an anathema to most non-scientists. This point is well illustrated by coral reefs: temperature-induced mass bleaching is dramatically destructive and well-known, whereas acidification impacts are almost entirely predictions which have no visible component. Nevertheless, public as well as scientific interest has been fuelled by the potential seriousness and irreversibility of OA. Science says humanity could be committing the Earth to a dire future on this basis alone, a prediction now attracting the sorts of attention that climate change originally did. At political levels, OA is usually put on the backburner as being even more remote from immediate imperatives than climate change; for scientists it has become a fertile field for research funding; for denialists it is ideal for indulging individual viewpoints and advertising books [9,10]; for the popular media it is becoming an attractive field for controversy. Certainly OA belongs in the domain of science, but what science: the equations of chemists, the experiments of physiologists, the field observations of ecologists, or the reconstructions of geologists? All have perspectives that make up the big picture.

This article summarises the sometimes controversial contributions made by the different sciences to predict the path of OA impacts on the diversity of coral reefs during the present century.

2. The Science

2.1. Ocean Chemistry

Dissolved inorganic carbon (DIC) is one of the most important chemical equilibria of the oceans and is largely responsible for controlling the pH of seawater [11–13]. DIC exists in seawater in four forms: CO_3^{2-}, HCO_3^-, aqueous CO_2 and carbonic acid (H_2CO_3). At a pH of 8.2, ~88% of DIC is in the form of HCO_3^- and ~11% in the form of CO_3^{2-}. Only ~0.5% is in the form of CO_2 and H_2CO_3. When CO_2 dissolves in seawater, the net effect is to increase the concentrations of H_2CO_3, HCO_3^- and H^+, and decrease the concentration of CO_3^{2-}, thereby lowering pH. Atmospheric CO_2 (pCO_2) today is ~100 ppm greater than the pre-industrial value of ~280 ppm causing the average ocean surface pH to drop by 0.1 pH unit, which represents a H^+ increase of ~30% [14]. This pH decrease may seem small; however it is a change in one of the most basic environmental norms of marine life to have occurred throughout the entire genetic history of most species.

The extent to which calcifying marine life is affected by such changes largely depends on the saturation state of $CaCO_3$ (Ω) the product of Ca^{2+} (estimated from salinity) and CO_3^{2-} (calculated from DIC and total alkalinity) divided by a solubility constant. Ω is different for the three forms of $CaCO_3$ produced by marine life: high magnesium calcite (secreted by coralline algae), aragonite (secreted by corals, macro-algae and some molluscs) and calcite (secreted by most molluscs, forams, also Palaeozoic corals). Saturation states of surface waters are highest in the tropics and lowest at high latitudes mainly because CO_2 is more soluble in colder waters, thus lowering the concentration of CO_3^{2-}. $CaCO_3$ solubility also increases with depth, the depth at which $CaCO_3$ becomes soluble being known as the saturation horizon. The depth of this horizon varies latitudinally and tends to shallow toward the poles, but also varies locally due to changes in ocean circulation patterns, such as in regions of upwelling. The depths of the saturation horizons for calcite, aragonite and high magnesium calcite are very different.

The aragonite saturation horizon (ASH) currently varies between ~100–800 m depth at the equator and [15] and has been estimated to be decreasing at a rate of ~1–2 m/yr [16]; however on the west coast of North America large areas of the continental shelf are now impacted by aragonite-undersaturated waters where upwelled water is further acidified by uptake of CO_2 from the atmosphere [17].

2.2. Physiology

Calcification by marine biota is not known in the detail of ocean chemistry [18,19] and it is also much more complicated, especially where it involves algal symbionts which respond to different environmental parameters. The list of actual or potential variables affecting physiological responses is indeed long: temperature, light, environmental history, acclimation, geographic location (temperate or tropical), respiration rate, photosynthesis, net productivity, reproductive effort, symbionts (type and density and growth rate) and form (massive or branching). Some of these variables acting in synergy are already known to cause different responses to change in pCO_2 and Ω_{arag}. For example, coral calcification has been found to decrease [18,20,21], increase [22], or be unaffected [20,23–26] by temperature at increased pCO_2 in different taxa in different experimental regimes. Other organisms, especially those who can utilize enhanced levels of HCO_3^-, have shown increased rates calcification created by increased pCO_2 [27–29].

In principle, OA can be accommodated by the same mechanisms that organisms use to counter metabolically produced H^+ and CO_2. These include passive buffering of intra- and extracellular fluids, control of ion exchange across semi-permeable membranes and physiological mechanisms to accommodate short-term metabolic spikes. However, corals do not have dedicated excretory organs as do many higher invertebrates and no marine life has the option of suppressing metabolic activity to wait out periods of OA. Similarly, none of the options for compensating short-term acidity such as dissolution of tests or shells are available over generational time spans. One review of short-term responses to acidified water [12] cites 39 studies indicating a range of deleterious impacts of OA on marine life. The same limitations potentially apply to freshwater habitats where the pH is much less buffered, and is commonly <7. Freshwater habitats with low pH exclude most calcifying invertebrates except molluscs and crustaceans which have compensating shell chemistries and elaborate excretory

organs. However, there are rare instances where such adaptation also occurs in the marine realm such as in mussels near hydrothermal vents [30].

The oceans permit marine life to construct carbonate exoskeletons and allow these skeletons to be consolidated into wave-resistent reef because they are supersaturated with carbonates—a physiological opportunity exploited by corals today and by other taxa in the geological past. Under natural conditions coral calcification is widely believed to be primarily dependent on Ω_{arag} [22–25,31–38], also Ca^{2+} [39] rather than pH. Deposition of this aragonite is an extracellular process where an organic matrix combined with minerals is precipitated in diurnal to seasonal bands by a single cell layer, the calicoblastic epithelium, adjacent to the skeleton. This layer facilitates transport of Ca^{2+} ions and DIC into a minute space filled with a chemically buffered fluid—the calicoblastic space—between the epithelium and the skeleton. The primary source of carbon is internal metabolic CO_2 which is in excess during daylight when skeletal formation is maximized. A secondary source is DIC in external seawater [40]. Either way, a cation exchanger precipitates aragonite at the skeleton surface.

There are a wide array of options available to corals for regulating skeleton formation, the most apparent being the physiological isolation of the calicoblastic space from the surrounding seawater by the actions of buffers, an extracellular control mechanism requiring increased energy expenditure [41]. It can also be regulated by controlling carbon exchange between corals and their zooxanthellae in zooxanthellate taxa exhibiting light-enhanced calcification, an intracellular control mechanism [42,43]. Potentially, OA can disrupt these mechanisms by decreasing CO_3^{2-} supply, decreasing pH, or by altering the buffering system [25].

In broader terms, the subject of coral calcification has remained a black box for over thirty years [44] and to a large extent it still is. Elucidation of the internal workings of this box will certainly shed light on the ways OA might affect corals and it may well be the case that different taxa have different control mechanisms. This would be hardly surprising given that that most scleractinian families diverged in the Mesozoic Era and that the enhancement of calcification by zooxanthellae has evolved independently several times [45]. It is even possible that different colonies of the same species can adopt different controls depending on the environment in which they occur. However, the external view of the box is clear enough: coral calcification usually varies with CO_3^{2-} availability and, given their physiological dependence on the properties of seawater, it is also dependent on adequate Ω_{arag}. Just how high Ω_{arag} must be for adequate calcification will be a sliding scale from a pre-industrial high of 3.6 at the equator to a range of numbers depending on taxon, habitat, depth and location. The bottom of the scale can be reasonably estimated to be ~2, which will occur in most reef regions this century (see below). However, given that Scleractinia characteristically have a wide range of strategies to deal with almost anything there will likely to be many exceptions to the norm; e.g., the finding that the Atlantic Ocean coral *Favia fragum* can still grow in seawater with $\Omega_{arag} = 0.22$, although with growth abnormalities [38].

2.3. Ecology

It is not yet possible to estimate the proportion of marine species occupying coral reefs; however as the diversity of most metazoan phyla peaks in reef habitats, that number is likely to be at least 25% of total marine biodiversity. Impacts on reef diversity are therefore of major global significance. Furthermore, because most reef habitats are of carbonate construction, any loss of coral diversity will have a major knock-on effect to all reef-dwelling taxa.

One natural impact of acidification on reef corals is via rainwater which commonly has a pH of 5.6 or less. Low salinity caused by rainwater can decimate reef flat corals, but those which survive are certainly tolerant of short-term acidity. Microatolls of *Porites* [46] are one such survivor. These have an outer rim of living colony surrounding a large central area which is usually excavated. This excavation may be due to bioerosion, but where water is regularly ponded for several hours each tidal cycle in areas of high rainfall it is likely to be enhanced by dissolution. Whether this is so or not, the living part of the colony shows a high resilience to repeated short-term acidity.

Extensive degradation of open-ocean coral communities in the vicinity of urban coastal developments is now common, especially in south-east Asia and the Indian Ocean perimeter. In most cases the primary cause (including sedimentation, salinity change, physical damage, mass bleaching and *Acanthaster* outbreaks) is visually evident; however clear-water impacts are seldom studied although many are potentially valuable sites for water quality assessments which incorporate local factors such as community metabolism, sediment dissolution, freshwater input and organic carbon cycling.

Natural CO_2 springs are widespread and clearly offer natural experiments of OA impacts. One such occurrence was a spring on the Italian coast where naturally occurring species with carbonate skeletons were displaced in favor of species without skeletons [47]. Similar occurrences in coral reefs have recently been observed in Indonesia (Komodo), not yet studied, and Papua New Guinea (Milne Bay) where detailed studies are currently underway [48]. The study demonstrated a wide range of tolerance among coral taxa, with *Porites* being the most tolerant and fast-growing and structurally complex corals such as branching *Acropora* the least. Down to pH 7.8, the primary impact of OA was therefore a reduction in biodiversity, structural complexity and coral juvenile densities rather than coral cover, as well as an increase in macroalgae and bioeroders. The study also showed that coral reef development ceased at a pH of less than 7.7 units.

Latitudinal sensitivity to OA will become an increasingly important issue during the 21st century as diversity changes resulting from the poleward migrations of tropical species are offset by predicted impacts of high latitude OA [8,49]. To date there no studies of tropical zooxanthellate corals demonstrating this, existing studies being confined to the temperate or azooxanthellate species *Cladocora caespitosa* [26] *Lophelia pertusa* [50] and *Oculina arbuscula* [51].

Sensitivity to depth is not relevant to reef corals, but it is to azooxanthellate taxa which have a similar diversity and which commonly occur to depths of >1000 m (but occasionally >6000 m), perhaps limited by the ASH, especially in the northern Pacific where the species diversity is low. The potential impact of the decreasing ASH [52] will occur over a wide latitudinal range, impacting the large bioherms of *Lophelia* found off the Scandinavian coast [53]. Presumably there will be a time-delay in the transmission of decreased Ω_{arag} from the surface to the depth where these corals

occur, however acidification impacts are likely to have already commenced and, irrespective of impacts on living corals, acidification will impact deep sea bioherms by compromising the structural integrity of the framework.

By far the most damaging ecological effects of OA are not on individual taxa but on the group of corals responsible for habitat construction. Coral reefs can only exist if macroalgae are kept in abeyance by herbivores, especially fish [54]. Most herbivores, especially herbivorous fish, need the protective three dimensional habitat provided by branching corals, especially *Acropora*, in larval as well as adult and phases of their life cycle. Should these corals cease to grow other corals and a high proportion of other life will follow as macroalgae become dominant.

2.4. Geology

Although many geologists are at the forefront of climate change science, some have expressed skepticism of predicted impacts of OA just as others are, or were, skeptical of the existence of anthropogenic CO_2-driven climate change. In cases where biological and geological sciences meet, there is great potential for misinterpreting concepts of time [55]. Biological changes on reefs in geological time exhibit a boom-to-bust existence where the same carbonate platform is repeatedly re-populated by the same or different suits of species over intervals as short as millennia. However, reefs as geological structures are more enduring than any other biologically-derived structures on Earth. For this reason, the geological history of a reef usually says little or nothing about biologically-significant impacts over the same time interval. In this context, palaeontological and chemostratigraphic records are scattered points which have scant relevance to the fragility of living reefs or the stability of geological platforms. This type of discrepancy is analogous to the reconstructions of pCO$_2$ from ice cores: the zig-zag nature of ice core records is not seen in other geological sources such as reef cores and ocean sediments, yet it is the ice core record that revealed the history of environment change that profoundly affected all ecosystems.

Geological indicators of pCO$_2$ (pCO$_{2paleo}$) have been referred to by several authors (in non peer-reviewed publications) as evidence that reefs will not be affected by today's increases in pCO$_2$. In the ice-core analogy above, these records are scatter points (derived from densities of leaf stomata; carbon isotope composition of fossil soils, boron isotope composition of marine carbonates and modeling) within geological history, points which may have nothing to do with the biological 'boom-to-bust' cycles of reef growth with which they are being correlated. Reefs accretion may in fact cease during intervals of high pCO$_{2paleo}$ without any record of this cessation being preserved. Although high pCO$_{2paleo}$ does not necessarily cause OA (because it is countered by the weathering of carbonate rock in geological time), some points of high pCO$_{2paleo}$ seem sufficiently well linked to intervals of reef development to indicate a tolerance for OA that exceeds any predicted to occur this century.

In broad perspective, the geological record appears to show that reefs have contracted or ceased development during geological intervals when pCO$_{2paleo}$ is both high and low, although the former is clearly dominant [56,57]. At least 27 extinction events involving reefs have been identified [58,59], the best known being the five great mass extinctions that obliterated a high proportion of the earth's marine and terrestrial life. The causes of mass extinctions have attracted a wealth of study culminating in many hypotheses [60]. However, when compared with each-other, and in the light of biological

knowledge, the most credible common cause is some sort of disruption of the carbon cycle, sometimes related to a slow geological process such as volcanism from sea-floor spreading, sometimes to an abrupt event such as a bolide impact. This strongly implicates OA and ocean anoxia as major drivers of mass extinctions [61] although direct geological evidence exists only for the end-Permian [62,63] and end-Triassic mass extinctions [64,65]. However, pCO_{2paleo} is clearly implicated in four of the five greatest reef crises (not necessarily mass extinctions) of all time [66]. The best studied among the latter is the Paleocene-Eocene Thermal Maximum (PETM), where a peak of pCO_{2paleo}, largely from methane [67], impacted the reefs of the Tethys [68], at that time the centre of coral diversity, causing a significant diversity reduction.

One long-term change in ocean carbonate chemistry with unclear relevance to OA is the alternation of 'calcite seas' (of low magnesium calcite) during greenhouse intervals with 'aragonite seas' (of high magnesium calcite and aragonite) during icehouse intervals. This change in the Mg^{2+}/Ca^{2+} ratio of seawater is correlated with high levels of pCO_{2paleo} as both are driven by changes in ocean crust production [69]. These secular changes in ocean carbonate chemistry correlate well with mass extinctions. During the end-Permian extinction, low magnesium calcite-secreting taxa (including all Palaeozoic corals) were replaced by aragonite-secreting taxa [57] among which were the first Scleractinia. During much of the Jurassic and on into the Cretaceous, seas again became calcitic and so did a significant proportion of the bivalve fauna of the time [70] including rudist bivalves (a major reef-builder of the mid-Cretaceous) and, curiously, at least one coral, *Coelosmilia* [71]. Indeed, two modern Mediterranean corals, *Oculina patagonica* and *Madracis pharensis* lose their skeletons when placed in highly acidified aquaria, then re-grow them when returned to normal seawater [72], a result in keeping with the intriguing 'naked coral hypothesis' where corals are proposed to live on, without skeletons, through geological intervals of OA [73].

3. Conclusions

The geological record leaves no doubt that OA has, in the past, devastated coral reefs. However, that record does not indicate what levels of Ω or pCO_2 were involved, nor does it indicate the importance of rate of increase of pCO_2 in the process. Furthermore, the fossil record does not indicate change in species diversity, the types of taxa most affected, or how these were affected.

OA impacts on coral reefs have been described as a sequence of degenerative changes within coral colonies or within coral communities and ecosystems [55,74–77]. Alternatively, impacts have been described in terms of a tipping point, when reef erosion exceeds reef accretion [78,79]. These views do not link closely with the reality of environmentally-driven change, dominated by synergies, and starting over a decade ago. Mass bleaching has seriously affected one-third of reefs worldwide, impacts that are mostly temporary for *Acropora*-dominated communities in otherwise healthy environments (as these have a return-time of a decade or less) but which are potentially permanent for communities dominated by slow-growing massive colonies. Increase in the frequency of mass bleaching events predicted to occur over the next 2–3 decades [75] will change this pattern: shallow-water communities will become populated by increasingly smaller colonies of the most rapidly recolonising species. These are changes in diversity, not abundance. Predicted increases in sea-level will probably have little effect on these communities other than to change zonation, but

increases in storm and flood damage almost certainly will. Within this scenario, impacts from OA will be additional to changes brought about by other forms of environmental deterioration. They will not occur in isolation, nor will they affect only corals. Impacts on crustose coralline algae, an essential component of reef accretion, are particularly significant as calcification is either inhibited when exposed to prolonged but mildly acidified seawater [80,81] or increases up to a pCO$_2$ of 600 ppm, then declines [28].

It is not possible to put a precise time-line of OA or identify the level of pCO$_2$ that will initiate reef degeneration on a geological scale. During the entire Pleistocene, pCO$_2$ remained <280 ppm giving the ocean surface a stable pH of 8.2. It now seems that OA, perhaps in synergy with temperature increase, may have been inhibiting coral growth since 1990 [82]. At a pCO$_2$ of ~450 ppm (due to occur by 2035 a present rate of increase) the southern ocean will be undersaturated with respect to aragonite [83] after which OA will be seriously impacting the tropics. This will decrease biodiversity and increase rates of extinction. A pCO$_2$ of ~560 ppm (due to occur around mid century) will cause a 20–60% decline in coral calcification [19,76,84] and most reefs will enter a state of net dissolution [37]. Should pCO$_2$ reach ~630 ppm (a realistic possibility as pCO$_2$ and methane release will not be controllable by this stage) reef growth will cease completely [85]. Should pCO$_2$ reach ~780 ppm, pH will have decreased by 0.3–0.4 pH units [86], the ASH will have reached the surface of all of the Southern Ocean south of ~60°S and the average saturation states of all CO$_3^{2-}$ in surface water globally will be half present levels [11,12]. Should pCO$_2$ reach 800 ppm (still within the 21st century) the decrease in ocean pH will have reached 0.4 units [87] and all reefs world-wide will be geological structures with none of the ecological characteristics we see today.

These changes, predicted to occur within a single century, are well in excess of any upheaval in any environmental parameter revealed during Pleistocene glacial cycles and are also in excess of any known geological event, even the PETM which occurred over a far longer time interval.

Fortunately, humanity appears to have moved on from crisis points like the political 'solution' of sequestration of CO$_2$ effluent in the ocean. However, we have not moved far. Several international committees and organisations, each claiming a cloak of knowledge and responsibility, continue to target a pCO$_2$ of 450 ppm as a safe level for a stable earth. The big picture of reef science, which must inevitably become an amalgam of temperature and OA, argues strongly against this. Whether or not it is still possible to bring the earth back to any specific pCO$_2$ level does not alter that science. A pCO$_2$ <350 ppm [88] is what is required if reefs are to be maintained free of atmospheric degradation for the foreseeable future.

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