Ocean acidification and coral reefs

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Acidification occurs when CO_2 dissolves in water forming carbonic acid. Given adequate time, carbonic acid is neutralised by the dissolving of carbonate rock and the weathering of silicate rocks. At the current rate of anthropogenic CO_2 production, increasing levels of dissolved CO_2 cannot be adequately neutralised by the much slower dissolution and weathering processes. As a result, the chemistry of seawater is altering in such a way that organisms like corals, which build their skeletons of aragonite, will do so with increasing difficulty. This process, however, neither starts nor ends with corals.

Taxa dependent on high magnesium calcite are the most susceptible to acidification. These and others with aragonite skeletons that live in cooler regions are likely to suffer early, before the effects move towards the equator. As acidification becomes more severe, it will then start affecting species in warmer waters, firstly those with high magnesium calcite skeletons, particularly the coralline algae that are so important for reef consolidation, then all organisms with aragonite skeletons including reef-building corals, molluscs such as giant clams, calcifying plants like Halimeda, and a range of planktonic organisms. Nor will it stop there; species with calcitic skeletons will only get a brief reprieve – in the end they too will suffer the same consequences. As far as corals themselves are concerned, there will be two largely independent effects; the shallowing of the aragonite compensation depth which will displace azooxanthellate (non-reef) corals from the deep habitats they now occupy, and the acidification of the ocean surface which will diminish the capacity of reef corals to build skeletons.

Non-specialists who are well aware of the role played by anthropogenic CO_2 in enhancing greenhouse warming are much less aware of its role in ocean acidification. This is partly because the effects of acidification are as yet not visible, but also because the subject has received much less coverage in both the popular and scientific press. So far the topic largely resides in humdrum chemical equations, in seemingly innocuous changes in ocean pH, and in computer models.

Carbonates in the ocean: the giant antacid tablet

The chemistry of CO_2 dissolved in seawater is generally understood, although it is not straightforward because the capacity of CO_2 to dissolve in the oceans is sensitive to atmospheric concentration as well as to water temperature. Increasing atmospheric concentration drives more CO_2 into the ocean, but rising ocean temperatures reduces the capacity of the ocean to absorb it. This temperature effect is significant: it reduces the capacity of the oceans to absorb CO_2, although, at least currently, not sufficiently to counter the effect of additional uptake due to increasing atmospheric concentration.

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, a process that has now used up about one-third of the total storage capacity of the ocean surface. The rest has been taken up by terrestrial life.

General points are:

- Without uptake of anthropogenic CO_2 by the oceans, atmospheric levels would be about 55 ppm higher than at present.
- The pre-industrial level of carbonate ions in seawater was 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 total carbonate ion concentration and a 60% increase in hydrogen ion concentration in surface waters. This will increasingly diminish the ocean's capacity to absorb CO_2 from the atmosphere.

- If CO_2 levels are allowed to increase to 650-700 ppm as is set 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 a slowing of the rate of uptake by the oceans (discussed below).
- When CO_2 levels reach 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 reefs waters will have an aragonite saturation state ($\Omega_{aragonite}$) of 3.5 or less by the middle of this century. Only a few reefs of the Pacific will have carbonate saturation adequate for uninhibited coral growth when this happens. When CO_2 levels reach 800 ppm later this century, the decrease will be 0.4 units and dissolved carbonate ion concentration will have decreased by almost 60%. At this point all reefs of the world will be affected.

Dissolution of calcium carbonate begins at pH 7.9 at which stage carbonate sediments on the ocean floor become a giant antacid tablet, making it virtually impossible for the oceans to actually turn acid, yet at the same time preventing living organisms from forming carbonate skeletons. The levels of CO_2 and pH predicted by the end of this century may not have occurred since the Middle Eocene (45 million years ago), however the all-important rate of change we are currently experiencing has no known precedent over any time scale. There can be no evolutionary solution for such a rate of change. Furthermore, as we have seen, the present buildup of CO_2 is a spike in geological time: any evolutionary changes made to accommodate it would, in evolutionary time, soon need to be reversed.

It is important to realise that, unlike enhanced greenhouse temperature increase, the acidification effect of CO_2 will not taper off. It will initially be buffered by bicarbonate/carbonate ion exchange and then (depending on as yet unpredicted depth effects) will change abruptly until it is neutralised by the dissolving of marine carbonate rocks and the weathering of rocks on land. It is also generally unappreciated just how long it will take these processes to bring CO_2 concentrations back down to normal levels. If we continue to produce CO_2 at the present rate, we may expect the atmosphere to retain significant effects from it for 30-35,000 years, which means that 17-33% of the excess CO_2 currently in the atmosphere will still be there 1,000 years from now. As the ocean surface water progressively loses its capacity to take up CO_2 as a result of increasing atmospheric concentrations, the proportional net rate of ocean extraction from the atmosphere will decline in a self-reinforcing cycle even though the physical rate of exchange of CO_2 between the atmosphere and ocean will remain approximately constant. Just what the long-term outlook might be is unpredictable. The protracted recovery times of reefs of the ancient world would have been greatly extended by prolonged high atmospheric CO_2 levels; just what happens when that CO_2 is a short-term spike is unknown, but will be in tens of thousands of years and of little relevance to any human world.

Coral calcification: the future outlook

The effect of doubling seawater CO_2 levels on coral calcification can be calculated, modelled, and experimentally tested.. Although there are varying opinions as to the short term future effects of decreased aragonite saturation on coral calcification in a greenhouse world, there can be no doubt that the medium and long-term consequences are likely to be dire as the buffering action of marine carbonates progressively fails.

There is a roughly direct relationship between aragonite saturation and the capacity of corals to calcify when temperatures are near optimum levels. In the longer term, when atmospheric CO_2 is doubled, calcification is set to be reduced by up to 50%. This production rate is well below that required to offset reef breakdown from bioerosion, which means that as this century progresses, reefs will erode, not grow.

Just what happens to corals, as opposed to reefs, under these conditions is unclear: will they simply grow slower, or will they grow at the same speed and have weaker (less calcified) skeletons – a sort of coralline osteoporosis? Will it increase their vulnerability to boring organisms and perhaps to pathogens? The study of such details is in its infancy. There will no doubt be considerable species-specific variability based on the degree to which different corals can actively control the calcification process as carbonate ions become scarcer. Their tolerance to other synergistic stresses, their growth forms and perhaps even their ability to alter the skeletal material they lay down, will vary among species.

There are many unknowns in this incredibly important matter. Despite a considerable amount of research over many decades, there remains much to be discovered about the biochemical mechanisms of coral calcification: the degree to which it is based on carbonate or bicarbonate ions, and its relationships to primary productivity, temperature, light, and (particularly) details of ocean chemistry.

Today, it can probably be claimed that no downturn in reef coral calcification has yet been conclusively observed in natural reef environments although the same cannot be said of some other calcifying organisms. Changes are now being observed in the aragonite compensation depth and measures in the pH of surface waters of the Southern Ocean. The aragonite compensation horizon has always limited the distribution of azooxanthellate corals; now as it shallows, it has begun excluding these from the ocean depths they have inhabited for millions of years. Phytoplankton, especially the coccoliths that create extensive blooms at the ocean surface, and which are responsible for the removal of a high proportion of carbonate derived from atmospheric CO_2 are already being adversely affected in the Southern Ocean.

The future of ocean acidification

Ocean acidification is a new area of science where data of all sorts are conspicuously wanting. To date there has also been relatively little cross-fertilisation among the different fields most relevant to it. Thus, for example, ocean carbon modellers use mild phrases like 'adverse biological consequences' to describe environmental conditions that would, in the long term, be absolutely catastrophic for reefs. There is also a general lack of awareness of the role of CO_2 in determining the fortunes (or rather misfortunes) of marine life in the remote past. Despite its importance, this subject does not come surrounded by a wealth of iron-clad science. Rather, it comes with a small number of solid scientific studies which must be heeded every bit as much as global warming now is. Fortunately the subject of acidification does not have anything like the number of variables as global warming does. Future trends in ocean pH and aragonite saturation are becoming predictable, at least in relation to atmospheric CO_2 levels. The general, far-reaching negative consequences of reduced calcification on marine ecosystems are also predictable. What is yet far from clear is exactly how these effects will manifest themselves – which will come first, which species will be most susceptible and what knock-on effects there will be for other dependent components of affected marine food webs. Nevertheless, these are details, however important, in a scenario which is now grounded in sound science.

The first widespread biological impact of acidification is likely to be on the phytoplankton of the Southern Ocean, the food source of krill, small shrimp-like animals that are the linchpin of virtually all Southern Ocean food webs. If krill are affected, there will be far-reaching implications for all the fauna of Antarctic waters. Deep sea (azooxanthellate) corals are likely to be next in line, with 70% of the area they now occupy becoming undersaturated with respect to aragonite by the middle of this century. Coral reefs will probably be next: at some point it will become obvious that acidification is diminishing the calcifying capacity of all organisms with aragonite skeletons. These impacts, like those of temperature, will at first be patchy in time as well as space because of the vagaries of ocean currents and short-term cycles to which they are linked. Ultimately – and we are looking at centuries rather than millennia – the ocean pH will drop to the point where a host of other chemical changes including lack of oxygen may kick in. This will be the onset of an extinction event the likes of which the Earth has not been seen in 65 million years. There is a little imagination but no fiction in this: we have set the stage for the sixth great mass extinction and another few decades like our last century will see the Earth committed to a trajectory from which there will be no escape.

This account of acidification may seem like a science-fiction horror story. Nevertheless, there is little evidence of fiction, either in the science on which it is based, or in the simplified interpretation of it given here. A continued business-as-usual scenario of CO_2 production will ultimately bring colossal destruction to marine life. It has happened before and it can happen again. Furthermore, CO_2 is far from the only source of carbon we need be concerned about. If some of the Earth's reserves of methane are also released either naturally, through mining, or via melting of the permafrost (which is already occurring) and the draining of tropical marshlands (also now occurring), undersaturation of both aragonite and calcite will ensue throughout all the oceans in an even shorter timeframe. The amount of methane sequestered on continental shelves is over 5,000 gigatonnes, more carbon than is stored as fossil fuel. If a small fraction of this methane were to be released (through buoyancy change allowing their ice-like slurries to float free of the substrate or simply by melting resulting from any regional temperature increase), it would accelerate both greenhouse warming and ocean acidification. Nothing comparable to this has occurred so rapidly at any time in the known geological record.

Coral reefs will not respond to acidification as rapidly, or as visibly, as they will to temperature stress. However, the response that will occur will be throughout all the oceans and will be permanent as far as humans are concerned. When both temperature stress and acidification are taken together the prognosis for corals is bleak indeed. The predicted rate of change is so great that there is no possibility that corals will be able to rely on genetic adaptation to respond to bleaching stress or reduced pH. Any adaptive advantage must already be present in today's gene pool for it to be effective. Even if temperature-tolerant symbiotic zooxanthellae exist which might allow a range of corals to tolerate the temperature extremes of the future, the species that might survive in an acidified ocean will be relatively vulnerable, certainly more-so than during previous extinction events where CO_2 build-up was more gradual, allowing time for adaptive change to take place. Surviving reef corals will probably be only non-branching species for they will have no skeletons and will grow only where they are protected from wave action. The myriad of grazing fish seen on healthy reefs today will, in consequence, be gone. Likewise, the wonderful diversity of life we enjoy on reefs will be replaced by algal and bacterial communities growing on rock, awash from a higher sea-level and pounded by waves from more frequent tropical storms.

Ocean acidification must be taken seriously and as a matter of urgency if the world's oceans are not to be committed to a future of unbridled destruction. It has happened before and it not only can happen again, *it will*, unless intergovernmental action moves on climate change *urgently*. It is one of the most serious if least well-understood of all predicted environmental changes on Earth, yet so far has attracted only superficial publicity and, as yet, only the beginnings of intergovernmental recognition. Preventative action is the same as for global warming, coral bleaching and all the other negative impacts of CO_2, but the time-frame and severity of acidification, as well as it's long-term consequences, have no equal. For those few scientists who understand what lurks ahead it must seem as though the Earth is being treated like a worn-out old car – taken past the mechanic to a car-wash for essential mechanical repairs.