Chapter 21

Ocean Acidification as an Indicator for Climate Change

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1. INTRODUCTION

1.1. Carbonate Chemistry

Oceans have the capacity to absorb large amounts of Carbon dioxide (CO_2) because CO_2 dissolves and reacts in seawater to form bicarbonate (HCO_3^-) and protons (H^+). About a quarter to a third of the CO_2 emitted into the

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atmosphere from the burning of fossil fuels, cement manufacturing and land use changes has been absorbed by the oceans [1]. Over thousands of years, the changes in pH have been buffered by bases, such as carbonate ions (CO_3^{2-}). However, the rate at which CO_2 is currently being absorbed into the oceans is too rapid to be buffered sufficiently to prevent substantial changes in ocean pH and CO_3^{2-}. As a consequence, the relative seawater concentrations of CO_2, HCO_3^-, CO_3^{2-} and pH have been altered. Since pre-industrial times the oceans pH has decreased by a global average of 0.1 (compare Fig. 1a and b). The

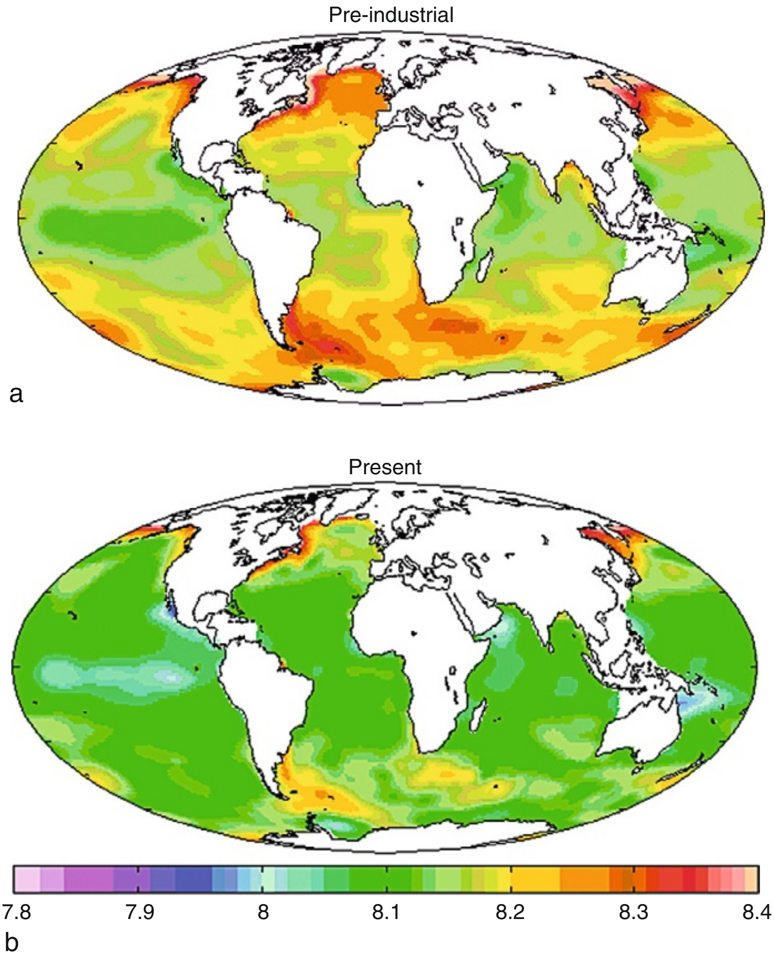

FIGURE 1 (a) Estimated pre-industrial (1700s) sea-surface pH and (b) present day (1990s) sea-surface pH, both mapped using data from the Global Ocean Data Analysis Project [5] and World Ocean Atlas climatologies; however, in the absence of estimated pre-industrial fields of temperature and salinity 1990s fields were used (although these contain a small signal from global warming). Note that GLODAP climatology is missing data in certain oceanic provinces (areas left white) including the Arctic Ocean, the Caribbean Sea, the Mediterranean Sea and the Malay Archipelago.

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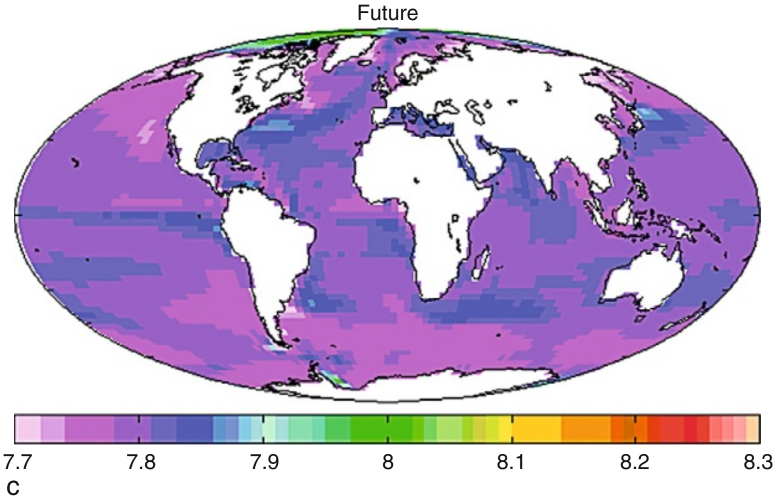

FIGURE 1 Cont'd (c) Predicted pH across the world's oceans for yr 2100 using the SOC model, which was part of the OCMIP-2 project [6] and used the IS92a CO_2 scenario. Note that the pH scale is different in (c). Courtesy of Andrew Yool (National Oceanography Centre, Southampton).

Intergovernmental Panel on Climate Change (IPCC) [2], using IS92 CO_2 emissions scenario, predicts that the pH of the surface ocean will decrease by as much as 0.4 by the year 2100 (Fig. 1c) and 0.77 by 2300 [3]. It will take tens of thousands of years for these changes in ocean chemistry to be buffered through neutralisation by calcium carbonate sediments and the level at which the ocean pH will eventually stabilise will be lower than it currently is [4].

The CO_3^{2-} concentration directly influences the saturation, and consequently the rate of dissolution, of calcium carbonate ($CaCO_3$) minerals in the ocean. The saturation state (Ω) is used to express the degree of $CaCO_3$ saturation in seawater:

$$\Omega = \left[Ca^{2+}\right]\left[CO_3^{2-}\right]/K_{sp}^*$$

where K_{sp}^* is the solubility product for $CaCO_3$ and $[Ca^{2+}]$ and $[CO_3^{2-}]$ are the *in situ* calcium and carbonate concentrations, respectively. When $\Omega > 1$, seawater is super-saturated with respect to mineral $CaCO_3$ and the larger this value the more suitable the environment will be for organisms that produce $CaCO_3$ (shells, liths and skeletons). When $\Omega < 1$, seawater is under-saturated and corrosive to $CaCO_3$. Currently, the vast majority of the surface ocean is super-saturated with respect to $CaCO_3$. The depth at which $\Omega = 1$ is known as the saturation horizon. The three main mineral forms of $CaCO_3$, in order of least soluble to most soluble, are calcite, aragonite and magnesium-calcite. Therefore, each mineral form has different saturation state profiles and saturation horizons with the aragonite saturation horizon (ASH) shallower than the calcite saturation horizon (CSH). Due to differences in ocean properties (salinity, temperature and pressure) both vary with latitude and ocean basin. The Southern Ocean has the lowest Ω, with $\Omega_{\text{aragonite}}$ currently reaching below 1.5. The depth of the ASH is 600 m or less in the North Pacific but can be over 2000 m deep in the North Atlantic. Increasing atmospheric CO_2 will cause Ω to decrease, as has already been occurring since pre-industrial times [6].

1.2. Combined Impacts of Ocean Acidification and Climate Change

Changes in climate resulting from anthropogenic influences will synchronously alter environmental conditions such as temperature, pH, salinity, wind strength and oxygen levels [7]. While seawater pH is sensitive to temperature, it is only a small contributing factor such that the predicted range for future temperatures will not make a significant difference to the pH decline [8]. However, organisms' responses may be different with increasing temperature depending on the level at which they adapted [9]. pH is also sensitive to changes in salinity, as a result of changes in total alkalinity and dissolved inorganic carbon, so organisms in coastal waters with riverine input, can experience larger variability in pH than in open oceans [10]. Both increasing temperature and decreasing salinity will also act to increase ocean stratification, which in turn will alter the nutrient supply that fuels primary production. A change in wind strength is also an important consideration for ocean acidification for two reasons. Firstly, wind strength determines the flux of CO_2 between the ocean and the atmosphere, so may reduce the ocean CO_2 sinks [11]. Secondly, wind strength drives ocean currents, mixes nutrients into the productive upper ocean and is particularly important for generating upwelling areas [12]. Upwelling areas, although rich in nutrients, are also rich in CO_2 and are therefore areas of natural low pH [13]. A reduction in oxygen (O_2), hypoxia, within the oceans occurs largely as a result of increased nutrient or organic matter input (e.g. caused by increased land-run off). An increase in nutrient load can substantially increase biological productivity and subsequent microbial decomposition of this excess productivity consumes large amounts of O_2 and releases CO_2 through respiration, causing hypoxia and low pH.

2. EVIDENCE FROM OBSERVATIONS

2.1. Evidence from Geological and Ice Core Records

Ice cores provide high resolution and accurate records of atmospheric CO_2 concentrations over the last 650 000 a and together with marine paleo-proxies (e.g. boron isotopes) serve to arrive at a reasonable estimate of ocean carbonate chemistry over millions of years [14].

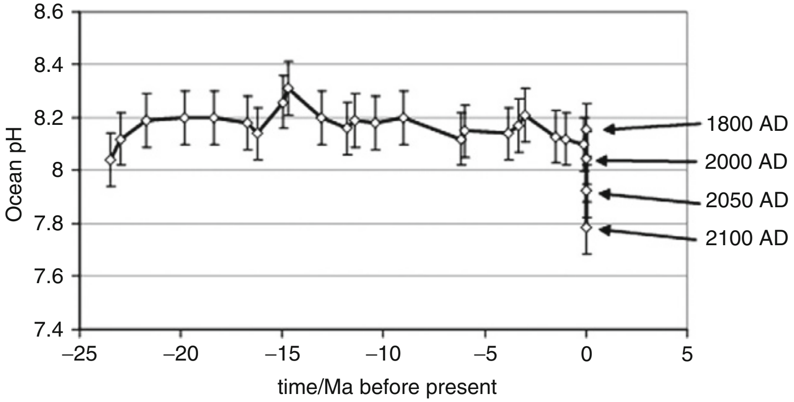

FIGURE 2 Past (white diamonds, data from Pearson and Palmer [14]) and contemporary variability of surface ocean pH (diamonds with dates). Future predictions are model-derived values based on IPCC mean scenarios. Adapted from Turley et al. [15].

Such measurements indicate no major undersaturation of the surface ocean for at least the last 65 Ma and that the current rate and magnitude of CO_2-induced chemical change occurring in the surface ocean are unprecedented for at least the past 25 Ma (Fig. 2).

Observations that CO_2 variations in the glacial and inter-glacial periods of the last 50 000 a correlated with the shell weights of fossil planktonic foraminifers [16] indicate that marine calcifiers are influenced by small fluctuations in atmospheric CO_2 values and those effects are likely to progressively intensify with increasing CO_2.

2.2. Evidence from Long-Term Oceanographic Time Series

The Pacific time-series station, off Hawaii (Hawaii Ocean Time-Series, HOTS), shows an increase in seawater CO_2 concurrent with the increase in atmospheric CO_2 recorded at Mauna Loa. The resultant decrease in surface ocean pH is $0.0019 \pm 0.00025\ a^{-1}$ (Fig. 3a) [17]. Aragonite and calcite saturation states also both show a decline over the last 20 a (Fig. 3b and c).

The other two major time series stations, the Bermuda Atlantic Time-Series (BATS) and the European Station for Time-Series in the Ocean at the Canary Islands (ESTOC), located either side of the North Atlantic, show a decrease in the seawater pH of around $0.0012 \pm 0.0006\ a^{-1}$ at BATS, and $0.0017 \pm 0.0004\ a^{-1}$ at ESTOC due to increased uptake of CO_2 [18]. These time-series data show that the Pacific and the subtropical gyre at both sites on the North Atlantic are becoming more acidic as predicted by ocean general-circulation models (OGCMs) (see below).

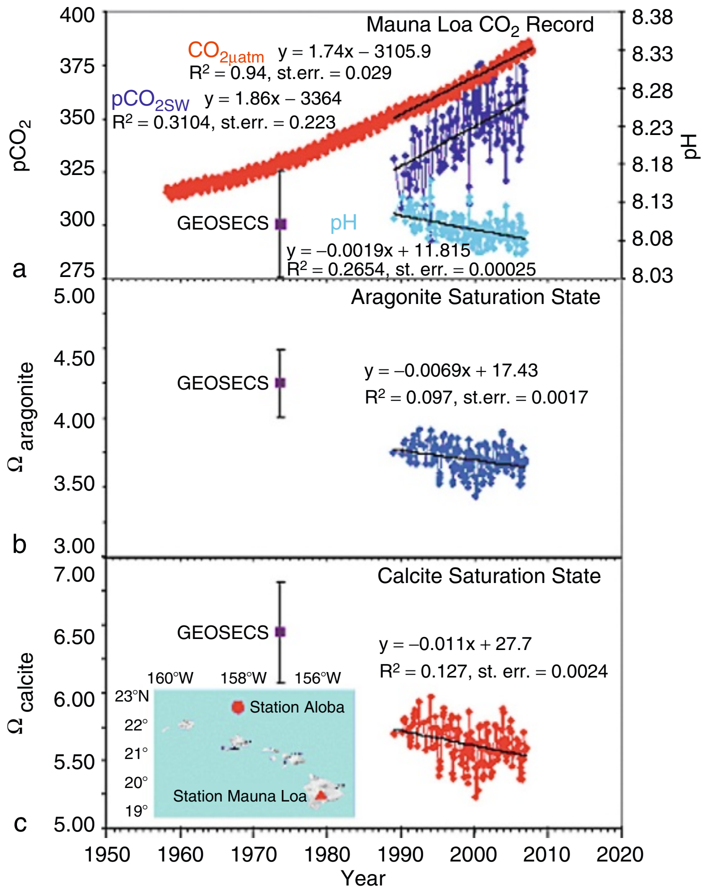

FIGURE 3 (a) The Mauna Loa records of atmospheric CO_2 over the last 50 a with the pCO_{2SW} and surface ocean pH recorder during the last two decades from the Hawaii Ocean Time-Series (HOTS) and the resultant changes to (b) Agaronite saturation state and (c) calcite saturation state over the same period. From Doney et al. [17].

2.3. Evidence from Oceanographic Cruises

Sabine and colleagues [1] used inorganic carbon measurements from an international survey effort in the 1990s, consisting of 9618 hydrographic stations collected on 95 cruises in different oceans (pH data is mapped in Fig. 1b). They estimated a global oceanic anthropogenic CO_2 sink for the period from 1800 to 1994 of 118 ± 19 Pg of carbon, accounting for about 48% of the total fossil-fuel and cement-manufacturing emissions.

A hydrographic survey along the western coast of North America, from central Canada to northern Mexico, revealed upwelling of seawater undersaturated with respect to aragonite and with low pH (<7.75) onto large portions

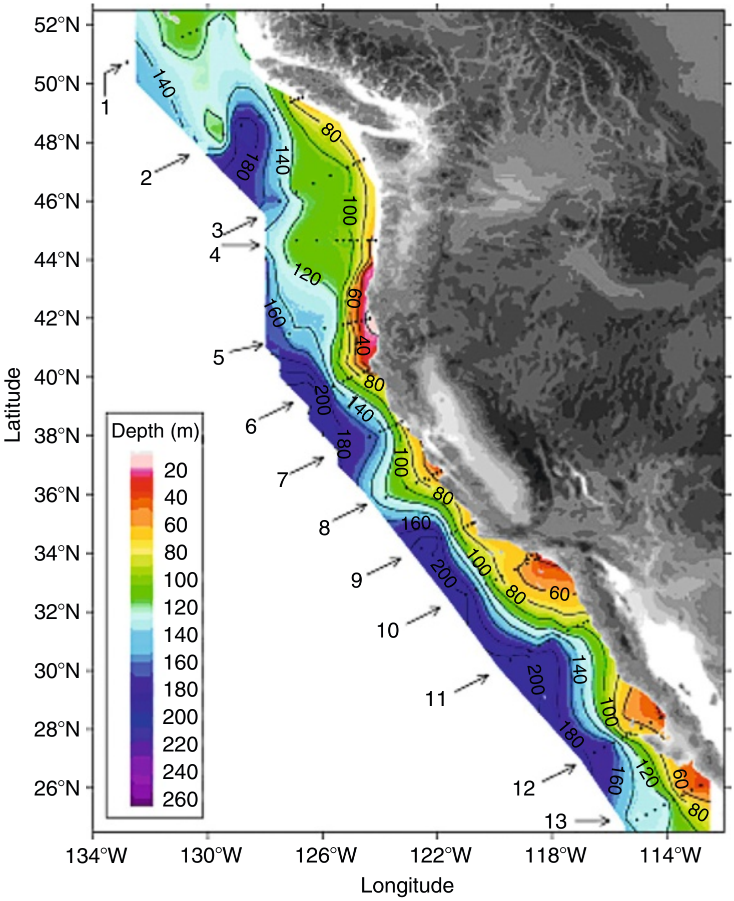

FIGURE 4 Distribution of the depths of the undersaturated water (aragonite saturation < 1.0; pH < 7.75) on the continental shelf of western North America from Queen Charlotte Sound, Canada to San Gregorio Baja California Sur, Mexico. On transect line 5 the corrosive water reaches all the way to the surface in the inshore waters near the coast. The black dots represent station locations. From Feely et al. [13].

of the continental shelf [13] (Fig. 4). The areal extent of this natural phenomenon has been increased by the ocean uptake of anthropogenic CO_2. They estimated that during pre-industrial days the ASH would have been about 50 m deeper with no undersaturated waters reaching the surface. With the additional anthropogenic CO_2 signal the ASH has shoaled by around 1 $m{\cdot}a^{-1}$ bringing increasingly corrosive conditions with pH as low as 7.6 not just to the deeper benthic communities but also, increasingly, to the productive, shallower continental shelf ecosystems. How these ecosystems respond to this seasonal inflow of undersaturated waters from February to August, during the growing season, has not yet been reported but these coastal ecosystems may well represent the first shallow sea ecosystems that experience rapid and nonlinear undersaturation due to uptake of anthropogenic CO_2. In CO_2-rich vent waters in the Mediterranean, useful ‘hot-spots’ of waters with a range of pH that offer a useful natural laboratory to study the response of marine organisms to long term exposure to reduced pH [19]. A seawater pH of around 7.8 seemed a critical threshold to the growth and survival of many of the local calcifiers and should organisms on the west coast of North America exhibit similar vulnerability then an ocean acidification ‘tipping point’ may well have been or soon be reached in these waters.

3. MODEL PREDICTIONS OF FUTURE CHANGE

OGCMs have been used to reconstruct, as well as predict, changes in climate. Forced by the physical dynamics of the ocean and atmosphere, and coupled together with biological models, OGCMs are able to reproduce biogeochemical cycling within the oceans that closely represents present and past observations. These models predict a global average decrease in pH of 0.4 by year 2100 in the surface ocean (Fig. 1c) and of 0.77 by year 2300 under the IPCC IS92 CO_2 scenario [3]. Introducing changes in temperature, weathering and sedimentation into these simulations only reduced this maximum decline by 10% [3]. More detailed predictions of both carbonate ion and CO_2 concentration for different oceans regions and across latitudinal gradients strongly imply that the polar and sub-polar oceans are particularly vulnerable to ocean acidification [6]. The carbonate ion concentration is already much lower in these regions so they are particularly vulnerable to a reduction in pH [20] such that they will become undersaturated with respect to both aragonite and calcite by 2100 under IS92 CO_2 scenarios [6]. Regional models are now being developed to assess the spatial and temporal variability in pH; for example, the future pH of the North Sea is predicted to undergo similar CO_2-induced changes to those predicted in the open oceans although coastal and shelf sea pelagic and benthic activities and riverine input are important factors in contributing to a greater variability [10]. Continued uptake of CO_2 by the oceans is predicted to cause some areas in the ocean to be completely outside their natural ranges by the year 2050 [10].

4. IMPACTS

4.1. Past Observations

There have been several ocean acidification events in Earth’s deep past, caused by massive input of carbon into the ocean, the best studied and most prominent of which occurred 55 Ma ago. The subsequent acidification led to the largest extinction of microscopic sea bed dwelling calcifiers [21]. In parts of the ocean, red clay instead of white carbonate was deposited for more than 100 000 a indicating the magnitude of the dissolution effect on global biogeochemical cycles and the duration of the recovery.

4.2. Current Observations

To date, there are limited observations of current changes in ocean biology as a result of ocean acidification. This is in part a result of a lack of chemical data with which observations can be correlated and a lack of research in this emerging area, but may also be an artefact of organisms' ability to cope with short-term variability in pH. Seawater pH in coastal and shelf sea water columns can fluctuate by up to 0.9 depending on time, season, position in water column and fresh water influence [10,22]. That is, there may be only short periods of low pH with the periods of high pH allowing the organisms to recover. Impacts may not become apparent until they are subjected to longer periods of lower pH or the whole pH range that they experience is reduced. In contrast, seasonal pH variation of open ocean surface waters is around 0.07 (Fig. 3a) which may make these regions more sensitive to current and future acidification. Indeed, the detected change in pH (-0.1) since the pre-industrial already exceeds the open ocean seasonal variation. Observed changes, for example, in species distribution which have been attributed to changes in climate, pollution, ecosystem detioration and so on, may have masked the role of ocean acidification. Further work at the international level needs to be carried out to explore current and future impacts of ocean acidification.

Observed differences in the cold-water coral ecosystems between the North Atlantic and the North Pacific may be indicative of biological responses to changes in ocean chemistry. Cold-water corals in the North Pacific are found living close to the ASH, as it is much shallower than in the North Atlantic; however, they do not flourish or form large structures, such as are found in the North Atlantic [23]. Only 10% of all known stylasterid corals produce calcite instead of aragonite, yet in the North Pacific six out of seven stylasterid corals used calcite to form their spicules and skeletons [24]. Near the ASH, it may be less costly for these corals to produce calcite thereby reducing the affects of dissolution.

Coral on the Great Barrier Reef (GBR), Australia, have shown a 21% decrease in net calcification and 30% decrease in growth over the period 1988–2003 [25]. Sea surface temperature does not appear correlated to this decline, as might be expected if increasing temperature was causing bleaching events or decreasing health of the corals. The change in carbonate chemistry observed in our oceans (Fig. 1a and b) could be impacting the growth and net calcification of corals, but as yet there is no chemical data directly from the GBR to confirm this. However, reefs in the Red Sea have shown correlated responses in net calcification rate to natural fluctuations in Ω and temperature [26], providing observational evidence of a response of corals to changes to today's carbonate conditions.

Spatial variation in sea bed organisms has been observed across a large pH range at natural marine volcanic CO_2 vent sites. A number of key ecosystem changes are apparent, for example, calcareous algae were replaced by non-calcareous algae and sea-grasses with the latter increasing their primary production. There was a large reduction in biodiversity, particularly a loss of calcifying organisms at low pH levels. A number of taxa appear to be more susceptible to acidification impacts than others, for example, echinoderms (particularly sea urchins) did not appear below pH 7.6, whereas molluscs (limpets) and crustaceans (barnacles) were present until pH 6.5 [19].

Coccolithophores, microscopic plants that secrete $CaCO_3$ platelets called liths, occur over a variety of environmental conditions throughout the worlds oceans yet they are excluded from certain locations, for example, the Baltic Sea. Areas known to have an extremely large seasonal cycle of calcite saturation states, with wintertime values declining to ≤ 1, appear to be areas where coccolithophores are absent [27] implying that the saturation state may have a large influence on their distribution, although low salinity or differences in the magnitude of the spring bloom will also contribute [27,28].

4.3. Experimental Observations

Experimental approaches have, so far, been carried out in controlled laboratory experiments on single organisms or in larger volume sediment or seawater mesocosms enriched with CO_2 containing mixed populations. There are many important biological processes within the lifecycle of an organism or even more so in an ecosystem. Therefore an impact on a process, be it at the cellular level or ecosystem level, may have a negative impact on the ultimate successful functioning of the ecosystem. An experimental approach is a key tool in determining the weak links in these processes.

4.3.1. Primary Production

The Royal Society [29] concluded that unlike land plants, most marine phytoplankton are thought to have mechanisms to actively concentrate CO_2 so that changes in seawater pH and CO_2 have little ($<10\%$) if any direct effect on their growth rate or their elemental composition. However, whilst taxon specific differences in CO_2 sensitivity have been observed in laboratory culture [30] it is currently unknown whether a reduction of the advantage of possessing a CO_2 concentrating mechanism will impact phytoplankton species diversity in the natural environment. This is a possibility and, should it occur, may impact the contribution of different functional groups, primary production, food web structure and marine biogeochemical cycles. The coccolithophore *Emiliania huxleyi* seem to be an exception to this generalisation, having low affinity for inorganic carbon such that it could be carbon limited in today's ocean, with increasing CO_2 resulting in increased productivity [31].

4.3.2. Calcification

Although there is variability amongst experiments, with some studies showing no change or even increased calcification [49,50], most calcifying species studied to date, representing the major marine calcifying groups (coccolithophores, pteropods, foraminifera, corals, calcareous macroalgae, mussels, oysters, echinoderms and crustacean), show reduced net calcification rates in response to elevated CO_2 [reviewed in Refs. 32-25]. For example, a mean decrease of 16% (double pre-industrial CO_2 concentration ($2\times\ CO_2$)) and 20% (triple pre-industrial CO_2 concentration ($3\times\ CO_2$)) for coccolithophores; 6% ($2\times\ CO_2$) and 9% ($3\times CO_2$) for foraminifera; 24% ($2\times\ CO_2$) and 41% ($3\times\ CO_2$) for Scleractinian corals; 25% ($2\times\ CO_2$) for coralline red algae; 25% ($2\times\ CO_2$) and 37% ($3\times\ CO_2$) for mussels; and 10% ($2\times\ CO_2$) and 15% ($3\times\ CO_2$) for oysters.

This variability between major groups of organisms may result primarily from the different mechanisms used to carry out calcification. Coccolithophores, for example, carry out calcification in an intracellular compartment which may be buffered against external changes by their own homeostatic mechanisms. Foraminifera and corals carry out calcification in an enclosed yet extracellular space, relying on membrane transporters to regulate conditions. In more complex multicellular organisms, such as crustaceans and molluscs, metabolic energy balance as well as whole animal acid-base regulation (see below) may be more important in determining the responses of calcification to decreased seawater pH. To maintain a calcified structure, when exposed to a more acidic environment for a short time, an organism may have to divert energy from other metabolic processes in order to compensate for dissolution. Other metabolic processes may also be impacted by CO_2 so this compensation may not always be possible over longer time periods. Evidence strongly indicates that dissolution rates will, over the timescale associated with ocean acidification, become greater than the rate at which organisms can grow and calcify, resulting in an inevitable reduction in biogenic $CaCO_3$.

4.3.3. Acid–Base Regulation and Internal Physiology

Much is known about the short-term effects of very high concentrations of CO_2 (higher than we will see due to ocean acidification) on respiration and acid–base balance in marine invertebrates and fish [9]. These early experiments were important in the discovery that CO_2 in seawater readily diffuses across animal surfaces, lowering the pH of internal fluids and that many animals have developed compensation mechanisms to regulate their internal pH. We now know that for normal function of an organism, internal pH must be kept within relatively narrow ranges because processes such as enzyme function, protein phosphorylation, chemical reactions and the carrying capacity of haemoglobin for O_2 are all influenced by pH and that these can be regulated for short periods of exposure to high CO_2. Evidence so far indicates that fish are tolerant to these short-term high CO_2 exposures but organisms such as squid, may be more vulnerable (reviewed in [9,33]). However, we do not yet know the impact of long term exposure to the relatively lower levels of CO_2 they will experience in the future from ocean acidification.

4.3.4. Fertilisation, Embryo Development, Larval Development and Settlement

Physiological impacts induced by lowered pH have the potential to affect an animal at any stage in its life cycle; however, adults tend to have more protection as well as better mechanisms to deal with a fluctuating environment with early life stages tending to be more vulnerable. Many benthic marine invertebrates produce free-swimming larvae, which spend time developing through several larval stages in the plankton before settling into the adult form (Fig. 5). Large numbers of larvae are often produced because of high rates of mortality, for example, coastal estuarine bivalves experience more than 98% mortality during settlement [36]. Oyster [37], echinoderm [38,39] and fish larvae [40] as well as barnacle, tube worm and copepod eggs [41, personal observation] have all been found to either be increasingly malformed or have slower rates of development at high CO_2. Barnacle settlement has also been affected [42].

Assuming that some larvae are still viable and go on to settle on the shore, delayed development could leave juveniles susceptible to additional stresses such as wave impact and temperature and salinity variations. In addition, if they settle later, they may miss their survival window.

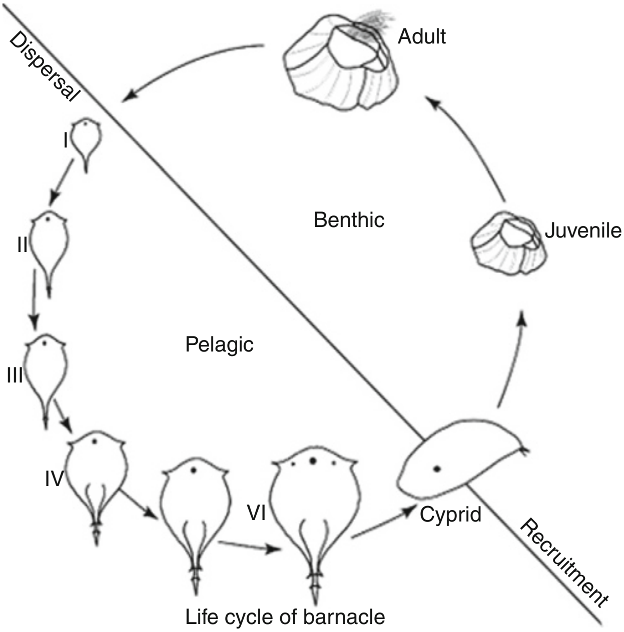

FIGURE 5 Barnacle life cycle, showing the pelagic larval stages I to VI, the cyprid larvae settling to become a benthic juvenile and finally an adult. From Desai and Anil [43].

4.3.5. Communication

Chemical cues are used for marine communication and can have strong influences on habitat selection and predator–prey interactions as well as courtship and mating, species recognition, and symbiotic relationships [44]. Some of these cues are known to be susceptible to changes in pH during formation and detection or within the seawater itself. Settlement of oyster larvae can be induced or inhibited by the presence of weak bases or acids, respectively, possibly as a mechanism for suitable habitat selection (e.g. [45–47]). Weakly acidic environments also impaired the ability of juvenile salmon to detect and respond to alarm cues [48]. The normal response to predators by littorinid snails on rocky shores is to thicken their shells. However, under CO_2-induced acidification the snails switched from thickening shells in the presence of predators to increased avoidance behaviour [49].

4.3.6. Interactions

The responses that occur within one individual can lead to changes in how it interacts with others and its environment. For example, burrowing brittlestars were found to have increased muscle wastage in their arms as compensation for increasing their calcified material under low pH conditions [50]. These brittlestars are important prey for commercial fish and aid nutrient and oxygen cycling between the sediment and the overlying water [51]. Reduced muscle may lead to reduced ability to feed themselves, lower quality of food for predators and reduce nutrient flow.

The importance of microbial and viral activity in the oceans is becoming ever more apparent; recent experiments show that bleaching of corals can be induced by increased viral activity [52], however, some evidence suggests that viral activity may decrease with increasing CO_2 [53]. The ability of a host to have an immune response to viral attack is critical for its health. Preliminary evidence suggests that at lowered pH mussels are unable to induce normal immune responses [54].

Organisms that occupy the same ecosystem space or function, may be outcompeted if they are less suited to surviving in a high CO_2 ocean. This may lead to an overall loss of biodiversity or even regime shift but may not lead to a complete breakdown in all functions of the ecosystem [19]. Changes to populations and their interactions within communities could well influence the relative composition, productivity, timing, location and predominance of the major functional groups and thereby impact the rest of the food web.

4.4. Coral Ecosystems and Their Services

Corals are the most studied organisms in relation to impacts of ocean acidification. Should these impacts occur in the natural environment they will have a large impact on the ecosystems they support. Corals are, therefore, a useful example of how ecosystems and their services may be impacted in the future.

4.4.1. Tropical Coral Reef Ecosystems

Tropical corals have adapted, over millions of years, to live in warm, sunlit waters highly saturated in aragonite. They are among the most diverse marine ecosystems, supporting about a quarter of all marine biodiversity. They are very important in local shore protection, important to tourism, and supply a critical level of subsistence protein as well as providing an income source in the developing world through fishing and tourism [7]. Unabated CO_2 emissions will result in suboptimal aragonite saturation states for coral growth by 2070 such that many reefs could be threatened resulting in reduced coral cover [6,32,55–57]. At this time erosion will outpace calcification so that reef structures will not be able to withstand the waves nor rebuild sufficiently after a storm.

Indeed, coral reefs in the waters off Panama and Galapagos, which live in a naturally more acidic and high CO_2 environment, suffer some of the highest erosion rates measured. They contain extremely low percentages of interskeletal pore cement to hold them in place compared to the coral reefs off the Bahamas that live in waters with less CO_2 and higher pH [58]. These reefs may be a vision into the future of reefs worldwide, since the Panama and Galapagos environments replicate the expected increased in acidity and CO_2.

4.4.2. Cold-Water Corals

Scleractinian cold-water corals, often referred to as deep-water or deep-sea corals, are long-lived (hundreds of years old), are found around 200–1000+ m depth throughout the worlds' oceans and can form large (100 km^2) reef frameworks that persist for millennia. They are biodiversity hotspots and play an important role as a refuge, feeding ground and nursery for deep-sea organisms, including commercial fish [23,59,60]. However, they may be the most vulnerable marine ecosystems to ocean acidification [23,61]. Future projections of global aragonite saturation state indicate that 70% of cold-water corals are likely to experience undersaturation this century through the shoaling of the ASH and in some instances this could be as early as 2020 [6,23,61]. It would seem unlikely that scleractinian cold-water corals would be able to calcify under these conditions; it would be more likely that aragonitic structures would experience dissolution in these corrosive waters. As yet there have been no experiments on their reaction at high CO_2 but if they respond in the same way as their warm-water cousins their calcification rates may decrease well before aragonite under-saturation occurs.

4.5. Combined Impacts

Temperature already provides limits to the survival of organisms; it alters many physiological processes by acting on the rates at which these processes occur (e.g. speeding up metabolism, enzyme activity, etc.). However, organisms are acclimatised to a certain temperature range. Acidification may act to narrow these ranges [9]. Increasing temperature will also drive many species polewards, either as a result of biogeographic range expansion (by temperate and tropical species) or as a result of contraction (by boreal and polar species). However, ocean acidification may act in the opposite direction, as the polar waters will be most affected by increasing CO_2 [6]. This could lead to a complete disappearance of boreal and polar species and may restrict the ability of temperate and tropical species to migrate.

Available oxygen is also a significant factor in controlling the distribution of organisms in marine environments. Eutrophication events and warming of waters decreases the oxygen content causing hypoxia. As mentioned previously, hypoxia is nearly always accompanied by an elevation of CO_2 (and thus a decrease in pH) and will compound the impacts [62].

Corals are again a good example of the effects of multiple stresses. They are affected by both ocean acidification and by warming of ocean surface waters leading to declining calcification and increase in bleaching [7,63]. Other climate change factors (sea-level rise, storm impact, aerosols, ultra-violet irradiation) and non-climate factors (over-fishing, invasion of non-native species, pollution, disease, nutrient and sediment load) add multiple impacts on coral reefs, increasing their vulnerability and reducing their resilience [7,32,63–65]. A recent report shows that about half of the coral reef ecosystem resources within the United States and Pacific Freely Associated States jurisdiction are considered by scientists to be in ‘poor’ or ‘fair’ condition and have declined over time due to several natural and anthropogenic threats [66]. Another consensus of opinion is that one-third of reef-building corals face elevated risk of extinction from climate change and local impacts and that the loss of reef ecosystems would lead to large-scale loss of global biodiversity [67].

5. BIOGEOCHEMICAL CYCLING AND FEEDBACK TO CLIMATE

5.1. Changes to the Ocean Carbon Cycle

Over several thousands of years, around 90% of the anthropogenic CO_2 emissions will end up in the ocean [4]. Because of the slow mixing time of the ocean the current oceanic uptake fraction is only about one-third of this value [1], without which atmospheric CO_2 would be about 55 ppm higher today than what is currently observed (385 ppm).

The Southern Ocean is estimated to account for around 25% of the anthropogenic CO_2 taken up by all the oceans while the North Atlantic is estimated to account for 40% [1]. Unlike the Southern Ocean which has a strong biological pump, the North Atlantic CO_2 sink is thought to be mainly due to the physical pump, with the ‘biological pump’ contributing only around 10% [68]. As the surface ocean CO_2 concentrations continue to increase the ocean’s ability to absorb more CO_2 from the atmosphere will slow down.

Whilst there were indications that this might be occurring in the analysis of 1990s oceanographic cruises by Sabine et al. [1], more recent analysis of CO_2 in the NE Atlantic [69] and Southern Ocean [11] show a decrease in CO_2 uptake over the last 1–2 decades. Whether this decrease in the efficiency of the ocean sink for anthropogenic CO_2 is decadal variation awaits further long time series study. If the ocean CO_2 sink is becoming less efficient then more CO_2 will remain in the atmosphere exacerbating global warming.

The 'biological pump' removes carbon from surface waters to the deep ocean via the organic or 'soft' tissue pump (which decreases CO_2 of surface water, increasing its ability to absorb atmospheric CO_2) while the inorganic or 'hard' $CaCO_3$ pump increases CO_2 of the surface water and decreases its ability to absorb atmospheric CO_2. Decreasing calcification and $CaCO_3$ export rates could therefore play a direct role in ameliorating future global change. However, decreasing primary production and export rates (the soft tissue pump) would have the opposite effect, resulting in less atmospheric CO_2 draw down by surface waters. To add to the complexity of these key mechanisms in the carbon cycle, there may be strong association between 'soft' and 'hard' pumps with a 'ballasting' of organic matter by carbonate particles, making the organic matter sink faster than it would on its own. A decrease in $CaCO_3$ production [70] would then lead to a reduction in the efficiency with which organic matter is transported to depth, weakening the biological pump and resulting in higher surface ocean CO_2. This would reduce fossil fuel CO_2 uptake by the ocean and exacerbate future climate change [71]. Although we have a poor understanding of the importance of these two mechanisms experiments looking at the calcification and primary production of coccolithophores in 27 m^3 seawater enclosures (mesocosms) found a shift in the ratio of organic carbon to calcium carbonate production and vertical flux with rising atmospheric CO_2 [72].

5.2. Changes to Ocean Nutrient Cycles

Another experiment maintaining natural plankton communities in mesocosms at 1× pre-industrial CO_2, 2× pre-industrial CO_2 and 3× pre-industrial CO_2 showed that primary productivity increased by as much as 39% under high CO_2 while nutrient uptake remained the same. This excess carbon consumption was associated with a more efficient biological pump and increasing C:N ratios [73]. If these findings were transferrable to the natural environment this could lead to an expansion of deep ocean oxygen minimum zones. Increasing C:N ratios would also lower the nutritional value of organic matter produced by primary producers thereby having further implications for marine ecosystem dynamics.

Nutrients such as nitrogen, phosphorus and iron often limit phytoplankton growth in major parts of the worlds' oceans. The lower pH expected over the next hundred years can theoretically impact the speciation of many elements

[15,29,74]. These include biologically important nutrients (nitrogen, phosphate and silica) and micronutrients (iron, cobalt, manganese, etc.). For instance, a decrease in pH of 0.3 could reduce the fraction of NH_3 by around 50% [75]. In addition, the key process of nitrification is sensitive to pH with rates reduced by ~50% at pH 7 [76]. This may result in a reduction of ammonia oxidation rates and the accumulation of ammonia instead of nitrate. Using this data to parameterise a shelf sea ecosystem model about a 20% decrease in pelagic nitrification by 2100 was predicted [10]. *Trichodesmium* cyanobacteria play a key role in sustaining primary production in the large low nutrient areas of the worlds' oceans through nitrogen fixation and show a >35% increase in rates of nitrogen fixation under elevated CO_2 of 750 ppm [77]. In addition, the proportion of soluble iron may increase which might be beneficial to the 10% of the oceans where iron is thought to limit primary production.

Depending on their nutrient requirements and uptake abilities, primary producers may respond differently to the effects of ocean acidification and nutrient speciation. Each response has the potential to impact the biodiversity and nutritional value of phytoplankton and the food webs and biogeochemical cycles that depend on them. Clearly, unravelling the combined impacts of declining pH on critical seawater constituents, such as nutrients and key biogeochemical processes such as nitrification, denitrification, nitrogen fixation and nutrient uptake will be a challenge.

5.3. Changes to Flux of Other Climate Reactive Gases from the Ocean

As well as their important role in calcification, coccolithophores are also major producers of dimethyl sulphide (DMS) which may have a role in climate regulation via the production of cloud condensation nuclei [78]. A reduction in the occurrence of coccolithophore blooms that occur in large areas of the global oceans, often as large as 10^5 km^2, could lead to a reduced flux of DMS from the oceans to the atmosphere and hence to further increases in global temperatures via cloud changes [78,79]. As the oceans, and organisms within them, are a major source of other atmosphere changing gases [80,81] changes to the biology could also alter their production and cycling.

6. ADAPTATION, RECOVERY AND MITIGATION

It is difficult to predict if marine organisms and ecosystem will adapt to or recover from the rapid changes to ocean carbonate chemistry. An optimistic view may be that for organisms with short generation times micro-evolutionary adaptation could be rapid and that species adversely affected by high CO_2 could be replaced by more CO_2-tolerant strains or species, with minimal impacts up the food chain. The less optimistic view is that CO_2-sensitive groups, such as the marine calcifiers, will be unable to compete ecologically, resulting in widespread extinctions with profound ramifications up the food chain.

6.1. Adaptation

There are periods within a coccolithophore life cycle that are non-calcifying. In addition, there are some species that appear to have lost the ability to form $CaCO_3$ liths [82]. This suggests that the biochemical pathways involved in calcification in coccolithophores can be turned on and off. Should coccolithophores struggle to form their coccoliths in future high CO_2 scenarios, as is suggested by experimental data, they may have the genetic diversity and capability to adapt. Indeed, this may have happened several times throughout the course of evolution [83] although they would have had more time to do this then than is available during the current acidification event.

Although tropical Scleractinian corals have adapted, over millions of years, to live in warm, sunlit waters highly saturated in aragonite they have survived, and even retained their algal symbionts and completed gametogenesis, for a year in experiments at pH 7.4 although in a ‘naked’, decalcified form [84]. When transferred back to ambient pH conditions of 8.2, the soft-bodied corals calcified and reformed colonies. However, it should be noted that if this occurred in the wild the naked corals would be prone to greater grazing and they could not build reef structures which create important biodiversity hotspots.

A fossil coral from $\sim$70 Ma ago had skeletal features identical to those observed in present-day Scleractinians but was made entirely of calcite rather than the aragonite of today’s Scleractinian coral skeletons [85]. This implies that in geological times, some corals may have been able to switch between different carbonate forms to make their skeletons. However, the estimated rate of change during even the largest of these previous acidification events was an order of magnitude lower (over several thousand years) than our predicted current change (over a few hundreds of years) [86] so current corals may not have sufficient time to adapt.

Tropical coral migration to higher latitudes with more optimal sea surface temperature is unlikely, due both to latitudinally decreasing aragonite concentrations and projected atmospheric CO_2 increases [6,57,87]. Coral migration is also limited by lack of available substrate.

It would therefore seem unlikely that coral reefs would be able to adapt to a high CO_2 ocean sufficiently quickly in this current rapid anthropogenic perturbation, neither through switching to another carbonate form nor through migration.

The changes in current ecosystem composition caused by a natural CO_2 vent systems emitted by a volcano have shown a lack of many calcifying organisms in the lower pH areas ($pH < 7.8$) and a shift to predominance of sea grass beds or invasive alien species [19]. This study demonstrates the inability of many calcifiers to adapt to longer term decline in pH and gives an unattractive *in situ* insight into future ecosystems in a high CO_2 ocean.

6.2. Recovery

Ocean carbon models and the sediment record both indicate that chemical recovery from projected CO_2 emissions will require thousands of years (chemical equilibration with carbonate minerals) to hundreds of thousands of years (equilibration with the carbonate-silicate cycle) [4]. This means that the chemical effects of CO_2 released from anthropogenic sources are not confined to a century time scale.

Diversity of the sea bed dwelling organisms after the acidification event 55 Ma ago took several hundreds of thousands of years to recover. In contrast, there is evidence that planktonic calcifiers tracked their habitat during this event (e.g. tropical species migrated towards the poles), thereby avoiding extinction [88]. The geological record also shows that Scleractinian corals have survived several mass extinction events, likely due to perturbations in the carbon cycle, but they took several millions of years to recover [89–91]. These lessons from the past indicate that should increasing ocean acidification lead to significant loss of biodiversity and even extinction, biological systems may not 'recover' to pre-industrial ecosystems, but rather may 'transition' to a new state.

6.3. Mitigation

As concerns over climate change grow there are increasing numbers of geoengineering solutions proposed. However, they often do not take into account or resolve the issue of ocean acidification (e.g. addition of sulphur dioxide into the stratosphere to deflect some of the sun's energy or ocean pumps of deep water rich in nutrients to increase productivity and drawdown CO_2) nor do they look at potential deleterious impacts on the marine environment (adding quicklime to the oceans to soak up CO_2, iron or urea fertilisation to increase ocean productivity and drawdown CO_2).

Currently, expert opinion is that the only method of reducing the impacts of ocean acidification on a global scale is through urgent and substantial reductions in anthropogenic CO_2 emissions [7,15,29]. A threshold of no more than a 0.2 pH decrease has been recommended to avoid aragonite undersaturation in surface waters [93]. In terms of atmospheric CO_2 concentration this would be just above the 450 ppm stabilisation scenario (Fig. 6). However some polar waters would experience aragonite undersaturation even at this stabilisation level.

7. CONCLUSION

The oceans have been buffering climate change by absorbing about a quarter to a third of the CO_2 emitted into the atmosphere from anthropogenic sources. This has resulted in the measurable alteration of surface ocean concentrations of CO_2, HCO_3^-, CO_3^{2-} and pH as well as the reduction of the

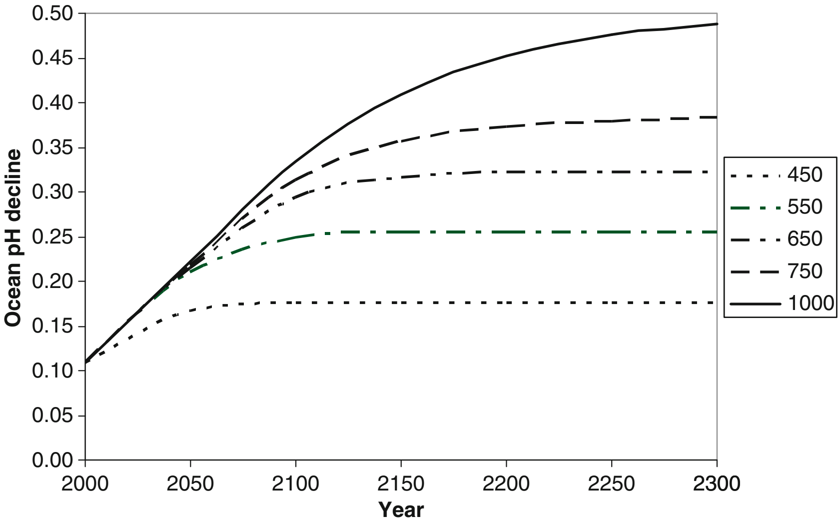

FIGURE 6 Trajectories for surface ocean pH decrease calculated for different atmospheric CO_2 concentration profiles leading to stabilisation from 450 to 1000 ppm. From Turley [92].

saturation state and shoaling of the saturation horizons of $CaCO_3$ minerals. Since pre-industrial times ocean pH has decreased by a global average of 0.1 and it has been estimated that unmitigated CO_2 emissions will cause ocean pH to decrease by as much as 0.4 by the year 2100 and 0.77 by 2300. These will be the most rapid and greatest changes in ocean carbonate chemistry experienced by marine organisms over the past tens of millions of years. Laboratory experiments, field observations of natural CO_2-rich seawater 'hot spots' and studies of previous ocean acidification events in Earth's history, indicate that these changes are a threat to the survival of many marine organisms but particularly organisms that use $CaCO_3$ to produce shells, tests and skeletons (e.g. coccolithophores, pteropods, foraminifera, corals, calcareous macroalgae, mussels, oysters, echinoderms and crustacean). The ASH is already shoaling, bringing increasingly corrosive waters to the productive, shallower shelf seas along the western coast of North America and models predict that polar and some sub polar waters will be undersaturated this century while saturation states in tropical surface oceans will be substantially reduced. Recent experiments reveal that other important biological processes (productivity, internal physiology, fertilisation, embryo development, larval settlement and communication) are also vulnerable to future changes in ocean chemistry. There could also be changes to ocean carbon and nutrient cycles but, because of their complexity, it is hard to predict what the implications of the changes to biology will be on marine food webs, ecosystems and the services they provide. However, examination of previous episodes in Earth's history indicates that unmitigated CO_2 emissions are likely to result in widespread extinctions. It will take tens of thousands of years for the changes in ocean chemistry to be buffered through neutralisation by calcium carbonate sediments and the level at which ocean pH will eventually stabilise will be lower than it currently is. The only way of reducing the impacts of ocean acidification on a global scale is through urgent and substantial reductions in anthropogenic CO_2 emissions. Ocean acidification is a key argument for united global societal action in future climate change negotiations.

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