Editorial

The societal challenge of ocean acidification

The carbonate chemistry of the world's oceans, including their pH, has been remarkably constant for hundreds of thousands of years (Pearson and Palmer, 2000), with typical surface ocean variations between ice ages and warm phases of no more than 0.2 pH units (Sanyal et al., 1995; Hönisch and Hemming, 2005; Foster, 2008). However, since the beginning of the industrial revolution, the oceans have taken up approximately 30% of the CO_2 produced from fossil fuel burning, cement manufacture and land use changes (Sabine et al., 2004). While the invasion of CO_2 into the ocean removes this greenhouse gas from the atmosphere and thereby dampens global warming, it forms carbonic acid in seawater and lowers ambient surface ocean pH (Broecker and Peng, 1982). Ocean acidification is the direct consequence of the excessive addition of CO_2 to seawater (Broecker and Takahashi, 1977) and is therefore inherently more predictable than temperature and precipitation changes due to rising CO_2 in the atmosphere. Changes are already measurable today (Bates, 2001; Bates et al., 2002; Takahashi et al., 2003; Keeling et al., 2004; Santana-Casiano et al., 2007) and will become more pronounced as humankind emits more CO_2 into the atmosphere, with surface ocean pH expected to decline by a further 0.3 pH units by the end of the century, corresponding to an approximately 100% increase in ocean acidity (hydrogen ion concentration [H^+]), on top of the ~0.1 pH unit decline to date (Caldeira and Wickett, 2003; Orr et al., 2005; Solomon et al., 2007) (Fig. 1). Such a rapid change in ocean pH has very likely not happened since the time the dinosaurs went extinct 65 million years ago (van der Burgh et al., 1993; Pearson and Palmer, 2000; Pagani et al., 2005). While the dissolution of carbonate sediments on the bottom of the ocean and the weathering of rocks on land coupled with mixing of surface and deeper waters will eventually restore ocean pH to its pre-industrial state, this process will take up to a million years to complete (Archer, 2005; Ridgwell and Zeebe, 2005).

With the progressive uptake of fossil fuel CO_2 by seawater, hydrogen ion concentration rises and pH, which is inversely related to hydrogen ion concentrations, declines. The relative abundance of dissolved CO_2 and bicarbonate (HCO_3^-) in seawater will increase while carbonate ions (CO_3^{2-}) will decrease. These chemical changes have direct implications for photosynthesis and physiological processes such as internal pH regulation in a wide range of organisms (e.g., Raven et al., 2005). The shells and skeletons of many marine organisms are made of calcite and/or aragonite, two different forms of the mineral calcium carbonate. Both minerals dissolve at low carbonate ion concentrations ('undersaturated' conditions), unless calcifying organisms have evolved mechanisms to prevent dissolution. Calcium carbonate becomes harder to precipitate even before undersaturation is reached. There is therefore growing concern about how ocean acidification may impact marine organisms at a range of levels, from molecular

processes within the organism, physiological and developmental processes, and competitive interactions among organisms to food web dynamics and hence global biogeochemical cycles, and climate.

It is important during the assessment of possible impacts to study the weakest link in an organism's physiology and life cycle. In order to survive, an animal has to carry out many functions including feeding, respiration, growth, cell maintenance, calcification, reproduction, defence, dispersal and settlement. A vulnerability to lower pH and carbonate saturation state in any of these functions at any life stage could result in loss of competitive fitness, narrowing of a species ecological niche or its demise. The majority of work up to now has been carried out on calcifiers. Therefore the focus of our review is on impacts on calcifying organisms which are directly linked to especially 'vulnerable' regions (Fig. 1).

While ocean acidification is a global-scale phenomenon (Fig. 1), there are areas which already naturally experience lower pH and carbonate ion concentrations than the global average – regions such as the high latitude oceans (Orr et al., 2005; McNeil and Matear, 2008), upwelling zones off the west coasts of the continents (Feely et al., 2008), and in the estuarine zones near river mouths (Salisbury et al., 2008). The organisms and ecosystems in these waters, which include globally important fishing grounds, will therefore be the first to be exposed to undersaturated conditions. Locations within the seasonal sea-ice zone of the polar oceans (Fig. 1) exhibit strong seasonality in aragonite and calcite saturation states in the surface layer due to CO_2 consumption and respiration by phytoplankton during their blooms and decay. Sea ice formation and melting, as well as changes in the wind direction and speed, further affect CO_2 uptake and release (McNeil and Matear, 2008). Upwelling of waters rich in CO_2 and with lower pH, both at the Equator and at continental margins is a seasonal process. For example, at the NE Pacific margin, shelf waters are supersaturated with respect to aragonite during weak upwelling (Feely et al., 2008) but as soon as upwelling intensifies, the deeper undersaturated water spills over the edge of the continental margin across the gently sloping, highly productive shelf. The area covered by undersaturated water is increasing due to shoaling of the aragonite saturation horizon by around 1 m each year caused by ocean acidification. Shelf seas (Blackford and Gilbert, 2007) and estuaries (Salisbury et al., 2008) are vulnerable regions because of inputs of freshwater, which changes the carbonate chemistry. Although surface waters of tropical areas are not expected to become undersaturated with respect to aragonite (Feely et al., 2004; Orr et al., 2005) (Fig. 1), the critical minimum concentration of carbonate ions limiting coral growth may be reached by the middle of this century (Cao and Caldeira, 2008). This is when the rate of erosion will outpace their calcification and hence impact
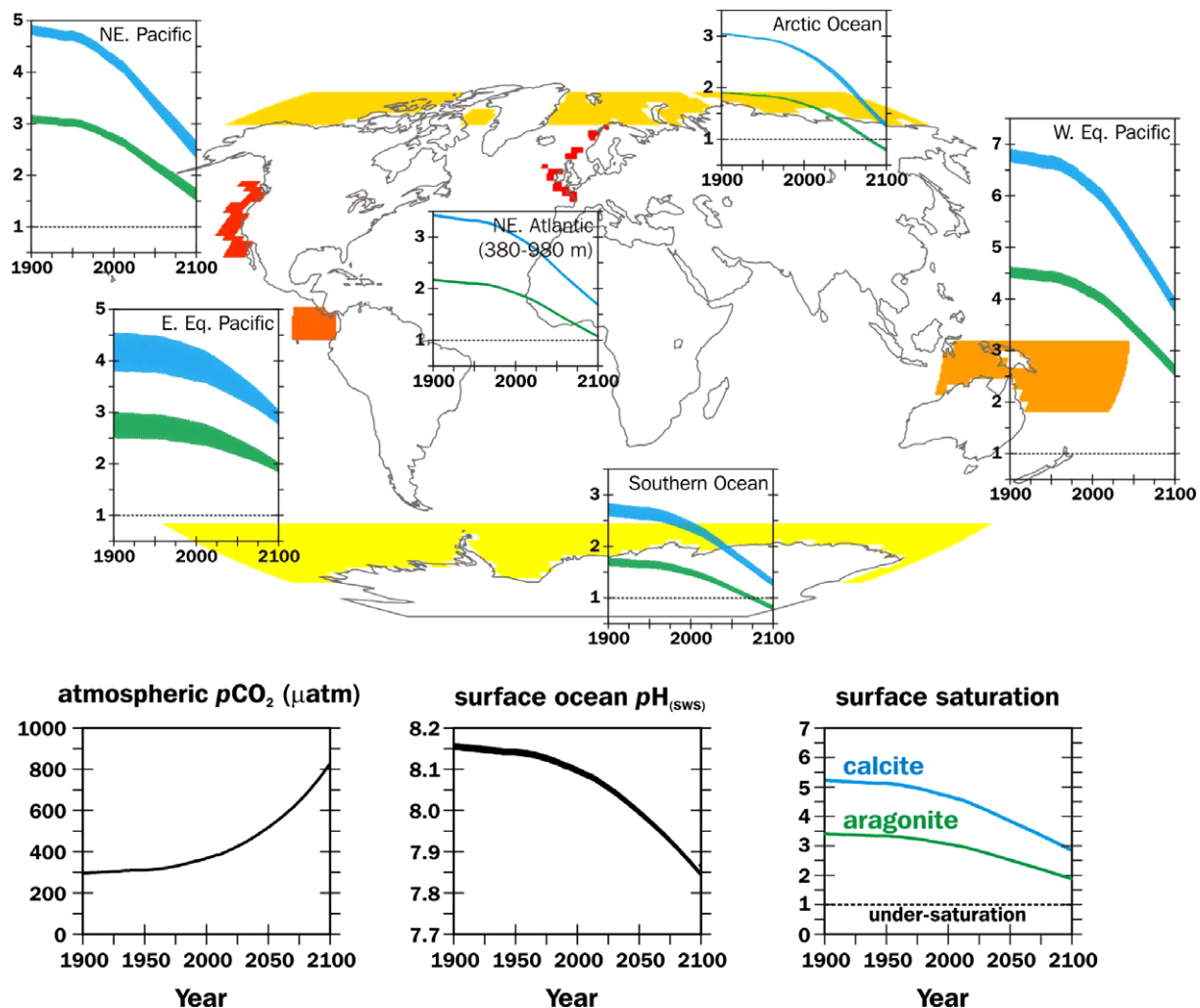
Fig. 1. Projected regional changes in ocean chemistry likely to be experienced by particularly vulnerable ecosystems and compared to global-scale surface ocean changes. The transient simulation of climate and carbonate chemistry was performed with the UVic Earth System Climate Model using observed historical boundary conditions to 2006 and the SRES A2 scenario to 2100 (Eby et al., 2009). For each of the six illustrative high risk marine ecosystems (Arctic Ocean, Southern Ocean, NE Pacific margin, intermediate depth NE Atlantic (500–1500 m), western equatorial Pacific, eastern equatorial Pacific) we have identified in this paper, the blue shaded band indicates the annual range in ocean saturation state with respect to aragonite, while the green shaded band indicates the range for calcite saturation. Area average surface ocean conditions are calculated for all regions with the exception of the NE Atlantic where area average benthic conditions between 380 and 980 m have been used. The thickness of the line indicates the seasonal range, with the threshold of undersaturated environmental conditions marked as a horizontal dash line. The varying evolution in the magnitude of the seasonal range between different regions is due to the complex interplay between changes in stratification, ocean circulation, and sea-ice extent, and distorted due to the non-linear nature of the saturation scale. The corresponding regions from which the annual ranges are calculated are shown shaded. Global ocean surface averages (bottom) are shown, from left to right: CO_2 partial pressure, $pH_{(SWS)}$ and calcite and aragonite saturation.

the structural integrity of coral reefs. Less well calcified reefs are becoming increasingly susceptible to physical and biological erosion as recently shown for the eastern equatorial Pacific (Manzello et al., 2008) (Fig. 1).

In addition, because calcite and aragonite saturation decreases with increasing pressure (Caldeira and Berner, 1999; Orr et al., 2005), organisms living at depth in areas with fast CO_2 uptake such as the North East Atlantic (Fig. 1) will on average be exposed to undersaturated waters before surface dwelling organisms, a process which is predicted to start to occur by 2080 (Guinotte et al., 2006).

The major groups of calcifying plankton are coccolithophorids, foraminifers and pteropods (Fig. 2). While all of them are important parts of the food web, pteropods are of special importance in the high latitude oceans (Hunt et al., 2008). In benthic ecosystems, key species such as sea- and heart urchins (Shirayama and Thornton, 2005; Miles et al., 2007), brittlestars (Dupont et al., 2008; Wood et al., 2008), and economically important species such as oysters and mussels (Gazeau et al., 2007) will first start to be

affected seasonally as pH and carbonate ions progressively shift lower. 'Ecosystem engineers' such as cold water and tropical corals are also sensitive to seawater with a decreasing saturation state with respect to aragonite. Cold-water corals such as *Lophelia pertusa,* forming reef-like structures in deep waters, are critical fish habitats and serve as important nursing grounds for a large number of organisms (Freiwald and Roberts, 2005; Guinotte et al., 2006). Tropical corals favour warm, sunlit, highly carbonate saturated waters (Kleypas et al., 2001) and support a high biodiversity and supply an important protein source for a large number of people through fisheries (Guinotte and Fabry, 2008), provide shore protection and reduce the impact of waves on low-lying countries (Kunkel et al., 2006).

Predicting the impacts of ocean acidification on marine calcifiers as a whole is difficult since the major groups carry out calcification via different routes and mechanisms. For example, in the coccolithophorid microalgae calcification occurs in an intracellular compartment (the coccolith vesicle) which is buffered against external perturbations (Brownlee and Taylor, 2004). In contrast,
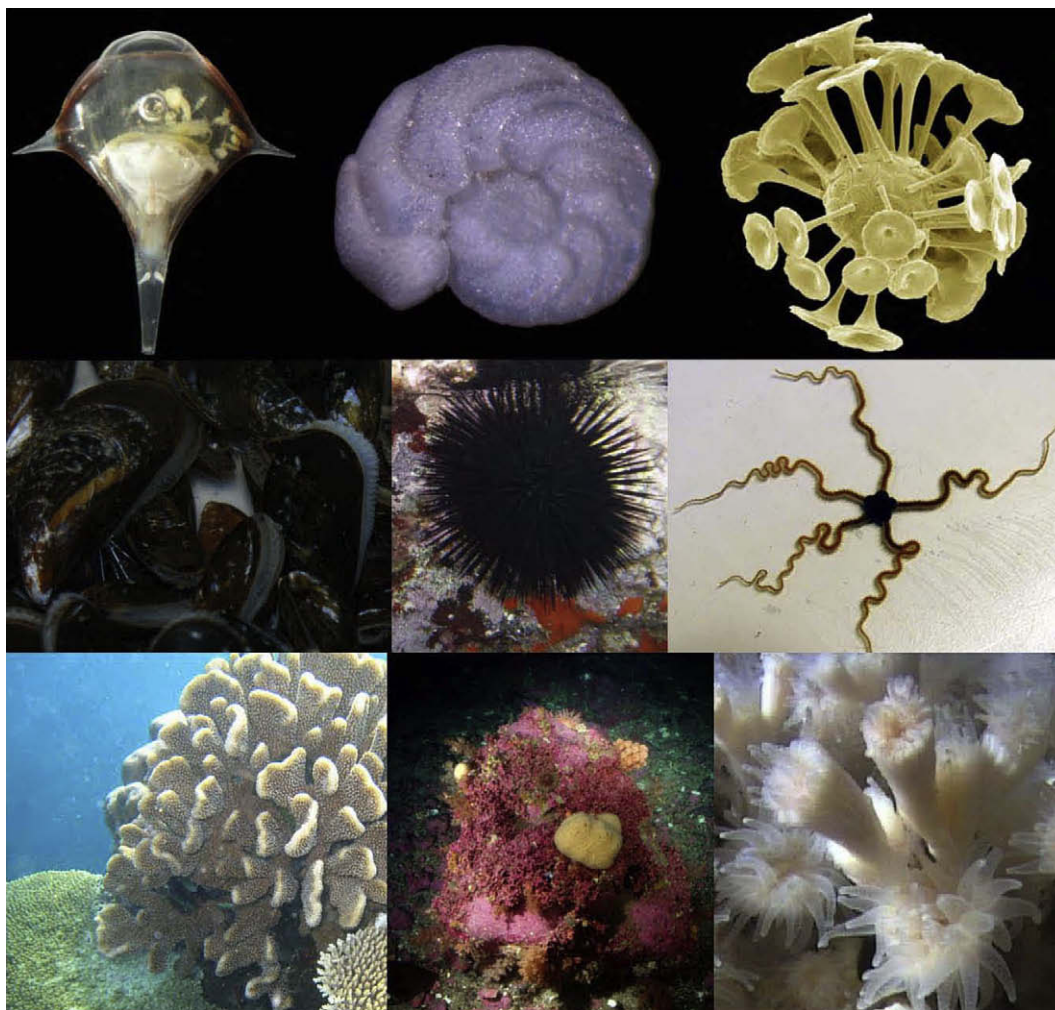
Fig. 2. Photos of representatives of calcifying groups thought to be vulnerable to ocean acidification from top left to bottom right: pteropod (Jeremy Young, NHM), benthic foraminifer (James Rae, UBristol), coccolithophore (Jeremy Young, NHM), blue mussel (Frédéric Gazeau, Villefranche), sea urchin (Helen Findlay, PML), brittlestar (Sam Dupont, UGothenburg), tropical coral (Malcolm Shick, UMaine), coralline algae (Armin Form, IFM-GEOMAR), cold water coral (Karen Hissmann, IFM-GEOMAR).

in foraminifera and corals the site of calcification occurs in an enclosed essentially extracellular space (Erez, 2003). In more complex multicellular organisms, such as crustaceans and pteropods, metabolic energy balance and whole animal acid–base regulation may be important in determining the responses of calcification to decreased seawater pH and reduced carbonate ion saturation state (Wheatly and Henry, 1992). Calcification is just one process in an organism, which may be impacted by acidification. Changes in other important physiological processes may also be impacted, such as metabolic processes (Wood et al., 2008), photosynthesis (Palacios and Zimmerman, 2007; Zondervan, 2007) or nitrogen fixation (Barcelos e Ramos et al., 2007; Hutchins et al., 2007; Levitan et al., 2007).

The great majority of research, either carried out with projected pH/CO_2 scenarios for the end of this century (Solomon et al., 2007) or with far higher CO_2 levels to test for the physiological reactions, has shown the effects of ocean acidification on these organisms to be deleterious. Most experiments indicate that coccolithophores, the most abundant calcareous phytoplankton (Fig. 2, top row), experience decreased rates of calcification in response to elevated CO_2 although experimental evidence suggests the potential for considerable variability in response between different coccolithophore species and strains (Riebesell et al., 2000; Zondervan et al., 2001; Langer et al., 2006; Iglesias-Rodriguez et al., 2008). Both main groups of calcareous zooplankton have been found to be highly sus-

ceptible to low carbonate saturation state of seawater. The aragonite shells of pteropods (Fig. 2, top row) show a decline in calcification by 28% when pH decreased by 0.34 (Comeau et al., 2009), ultimately leading to dissolution when seawater is undersaturated with respect to aragonite (Feely et al., 2004; Orr et al., 2005). Similarly, the shell weight decreases in planktic foraminifers in concert with carbonate ion concentration decrease (Bijma et al., 1999; Barker and Elderfield, 2002).

Processes other than calcification are also influenced by ocean acidification. For example, the nutritional quality of food may also change with increasing acidification. Enhanced carbon fixation at elevated CO_2 increases the C:N stoichiometry of phytoplankton, the primary food sources (Riebesell et al., 2007), at the same time as particle size decreases and phytoplankton community structure changes (Engel et al., 2008). Additionally, phytoplankton is the main producer of organic material that is subsequently exported into the deep ocean, thereby sequestering large amounts of carbon from the atmosphere (Broecker and Peng, 1982). Changes to phytoplankton composition and productivity (Engel et al., 2008) could therefore have significant impacts on food webs and climate.

Benthic organisms also show sensitivity to increased dissolved CO_2 and decreasing pH. In experiments at 560 ppm, less than 180 ppm higher than today, sea urchins exhibited reduced growth and survival rates over the 26 week duration of the experiment (Shirayama and Thornton, 2005). The two species of sea urchin

displayed species specific changes in growth and survival, high-lighting the dangers of oversimplification by interpolating from one species to the reaction of an entire group. Changes in pH did not just influence the growth of the adult, but moderate changes in pH (0.4) had a negative impact on the development of sperm, embryos and larvae (Havenhand et al., 2008). Brittlestars (Fig. 2, middle row) showed muscle wastage in their arms as a trade-off to increase their calcification (Wood et al., 2008) and they exhibited reduced larval development, growth and survival (Dupont et al., 2008) at pH predicted for the latter half of this century. At the same level, tropical crustose coralline algae showed a reduction in growth of 91% and of recruitment of 77% (Kuffner et al., 2008). Gastropods did not display significant increases in mortality but a significant reduction in height and weight compared to experiments at current pH was observed after 12 weeks at 560 ppm (Shirayama and Thornton, 2005). Similar changes in growth rate have been determined for other molluscs. The blue mussel and the Pacific oyster showed a reduction in calcification by 25% and 10%, respectively, at CO_2 values predicted for the end of the century (Gazeau et al., 2007). The smaller reduction in calcification of the invader into European shelf seas, the Pacific oyster, may give the species a competitive advantage over the endemic blue mussel. Ries et al. (2009) found that the shells of a third of the investigated calcifiers began to dissolve (on a net basis) under high CO_2 conditions and the gross morphology (and presumably function) of many of the shells was modified. Some species, however, increased their calcification or showed no change. It is important to consider trade-offs as energy gets diverted from other life sustaining physiological activities to calcification which may not be sustainable in the long term (Wood et al., 2008). Any changes in the physiology, making one organism fitter than it has been previously, could result in significant changes to complex marine food webs and ecosystems by, for example, over grazing or growth or out competing.

Laboratory experiments on cold-water corals showed a decrease in calcification of 30% at a pH reduction of 0.15 and of 56% when pH was reduced to 0.3 relative to ambient pH (Maier et al., 2009). In contrast to their tropical counterparts they can be affected by both decreasing carbonate saturation reaching down from the surface layer and shoaling of the aragonite saturation horizon (Hoegh-Guldberg et al., 2007). Future projections indicate that 70% of cold-water corals are likely to experience aragonite undersaturation this century (Guinotte et al., 2006), which will lead to dissolution of the skeletons in the absence of any protection mechanisms.

While there is ample experimental evidence for physiological impacts caused by ocean acidification, we do not know which organisms can take advantage of niches that become available as pH sensitive species decline in abundance and fitness (Fig. 3). Synergistic effects of ocean warming, deoxygenation and ocean acidification will further reduce organism fitness and survival potentially amplifying the effects each stressor poses on species (Pörtner and Farrell, 2008; Walther et al., 2009). For example, as oceans warm, the optimal temperature for certain species of calcifying organism may be driven to shift to higher latitudes but these have lower carbonate saturation levels, resulting in a niche squeezed between two stressors.

Scaling up from experimental results to ecological forecasts is problematic because much of the available evidence is based on short-term single species experiments. In cases where more than one species of a phylum have been exposed to high CO_2 conditions (Langdon and Atkinson, 2005; Shirayama and Thornton, 2005; Langer et al., 2006), significant differences in sensitivities have been detected. When extrapolating experimental responses to large scale processes such as primary productivity, nitrogen fixation, biodiversity loss and regime shifts, the complexity of the processes limits their predictability, and while changes in these processes are likely, we cannot predict their scale and impact with certainty with current knowledge.

Experiments to date have been largely designed to investigate the physiological reactions to ocean acidification but are too short-lived (days to weeks) to take the long-term impacts of adaptation into account. However, sobering lessons from the Earth's distant past, available to us from the palaeo-record, show that some previous acidification events resulted in extinction of benthic marine micro-calcifiers with a loss of their diversity persisting for hundreds of thousands of years (Thomas, 2007). The dramatic speed of future pH decline and its environmental pressure on marine calcifiers is likely unprecedented in the past 65 millions years (Ridgwell and Schmidt, 2010). The estimated rate of change of ocean pH during the onset of even the largest of these previous acidification events was an order of magnitude lower
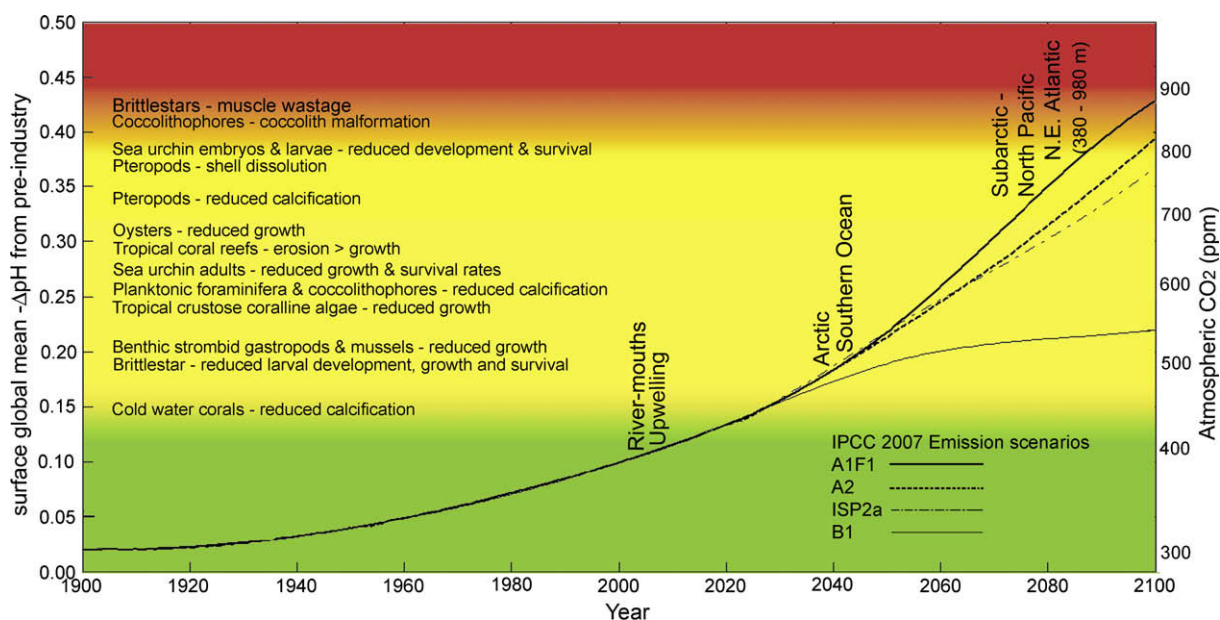

Fig. 3. Projections for atmospheric CO_2 and surface global mean $pH_{(SWS)}$ difference from pre-industrial to 2100 for IPCC 2007 Emission scenarios A1F1, A2, ISP92a and B1 (Nakicenovic et al., 2000). Simplified summary of the experimentally determined biological impacts on the left. On the right: marked above the pH–CO_2 curves are the years at which the first localized seasonal occurrence of aragonite undersaturation have been projected to occur for the regions given (for references see text).

(over several thousands years) than our predicted current rate of change (over 10s to 100s of years) (Panchuk et al., 2008). While surface dwelling marine plankton was apparently able to adapt to past rates of change (Gibbs et al., 2006), the paleo-record indicates that these events were associated with significant changes in species composition (Gibbs et al., 2006). Impacts of the much faster current rate of acidification are likely to be significantly more severe.

Oceans represent 70% of Earth's surface and support vast biodiversity and provide major food resources for humankind. Ocean acidification is happening now and the speed is rapid. The more CO_2 we emit to the atmosphere the more the oceans will acidify and the greater the impact on marine ecosystems (Fig. 3). How much is too much – what constitutes 'dangerous anthropogenic interference' with ocean chemistry? Attempts to define dangerous anthropogenic interference with climate suggest a warming of more than 1 °C relative to the year 2000 should be avoided which is equivalent to 450–475 ppm CO_2 in the atmosphere (Hansen et al., 2007, 2008). For ocean acidification, research to date indicates physiological and developmental impact at pH changes of 0.15–0.2 relative to today, i.e. long before carbonate undersaturation starts to occur anywhere at the surface, which is equivalent to values around 530 ppm CO_2 and projected for 2050 (Fig. 3). Annual undersaturation with respect to aragonite is predicted for parts of the Arctic Ocean by 2040–2050 (Steinacher et al., 2008) (490 ppm CO_2), seasonally for the Southern Ocean by 2040 (McNeil and Matear, 2008) and annually by 2050 (Orr et al., 2005) to 2060–2070 (580–590 ppm CO_2) (Hoegh-Guldberg et al., 2007; Cao and Caldeira, 2008; Steinacher et al., 2008; Fig. 1). Even by these times, there are likely to be earlier local impacts, for example in upwelling areas. Beyond this, the severity will increase substantially with vast swaths of the ocean becoming increasingly corrosive or energetically challenging to many calcifying organisms (Fig. 3).

It is important not to cross the threshold of dangerous ocean acidification as it may lead to profound changes to marine species, biodiversity and food webs – a decision point for humankind that will affect marine life and the economically and societally vital services that marine ecosystems provide. Increased ocean acidification with increasing CO_2 emissions is a certainty, but predicting the impact on marine biology and the value of ecosystem services that a future low pH ocean will sustain is currently rather less certain. A recommendation based on model projections of undersaturation with respect to aragonite (<550 ppm CO_2) reflects the chemistry of the ocean but is likely too high to avoid detrimental effects to many marine biota (Fig. 3). Based on current knowledge of marine impacts as discussed above, we recommend to the climate change policy makers that 500 ppm atmospheric CO_2 should be avoided. To ensure no large-scale risk to marine organisms and ecosystems, we strongly suggest taking the precautionary principle of a threshold of 450 ppm CO_2.

Author contributions

The work was initiated by C.T., the model data has been generated by M.E., A.J.R., the paper written by C.T., D.N.S., A.J.R., the figures generated by A.J.R., D.N.S., H.S.F., all authors discussed the results and contributed to the text.

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