

# Ocean acidification due to increasing atmospheric carbon dioxide

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# Ocean acidification due to increasing atmospheric carbon dioxide

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## Summary

The oceans cover over two-thirds of the Earth's surface. They play a vital role in global biogeochemical cycles, contribute enormously to the planet's biodiversity and provide a livelihood for millions of people.

The oceans are absorbing carbon dioxide (CO<sub>2</sub>) from the atmosphere and this is causing chemical changes by making them more acidic (that is, decreasing the pH of the oceans). In the past 200 years the oceans have absorbed approximately half of the CO<sub>2</sub> produced by fossil fuel burning and cement production. Calculations based on measurements of the surface oceans and our knowledge of ocean chemistry indicate that this uptake of CO<sub>2</sub> has led to a reduction of the pH of surface seawater of 0.1 units, equivalent to a 30% increase in the concentration of hydrogen ions.

If global emissions of CO<sub>2</sub> from human activities continue to rise on current trends then the average pH of the oceans could fall by 0.5 units (equivalent to a three fold increase in the concentration of hydrogen ions) by the year 2100. This pH is probably lower than has been experienced for hundreds of millennia and, critically, this rate of change is probably one hundred times greater than at any time over this period. The scale of the changes may vary regionally, which will affect the magnitude of the biological effects.

Ocean acidification is essentially irreversible during our lifetimes. It will take tens of thousands of years for ocean chemistry to return to a condition similar to that occurring at pre-industrial times (about 200 years ago). Our ability to reduce ocean acidification through artificial methods such as the addition of chemicals is unproven. These techniques will at best be effective only at a very local scale, and could also cause damage to the marine environment. **Reducing CO<sub>2</sub> emissions to the atmosphere appears to be the only practical way to minimise the risk of large-scale and long-term changes to the oceans.**

All the evidence collected and modelled to date indicates that acidification of the oceans, and the changes in ocean chemistry that accompany it, are being caused by emissions of CO<sub>2</sub> into the atmosphere from human activities. The magnitude of ocean acidification can be predicted with a high level of confidence. The impacts of ocean acidification on marine organisms and their ecosystems are much less certain but it is likely that, because of their particular physiological attributes, some organisms will be more affected than others.

Predicting the direction and magnitude of changes in a complex and poorly studied system such as the oceans is very difficult. However, there is convincing evidence to suggest that acidification will affect the process of calcification, by which animals such as corals and molluscs make shells and plates from calcium carbonate.

The tropical and subtropical corals are expected to be among the worst affected, with implications for the stability and longevity of the reefs that they build and the organisms that depend on them. Cold-water coral reefs are also likely to be adversely affected, before they have been fully explored.

Other calcifying organisms that may be affected are components of the phytoplankton and the zooplankton, and are a major food source for fish and other animals. Regional variations in pH will mean that by 2100 the process of calcification may have become extremely difficult for these groups of organisms particularly in the Southern Ocean. Some shallow water animals, which play a vital role in releasing nutrients from sediments, also calcify, and may be affected by changes in the chemistry of the oceans. Some studies suggest that growth and reproduction in some calcifying and non-calcifying marine species could be reduced due to the projected changes in ocean chemistry.

From the evidence available it is not certain whether marine species, communities and ecosystems will be able to acclimate or evolve in response to changes in ocean chemistry, or whether ultimately the services that the ocean's ecosystems provide will be affected. **Research into the impacts of high concentrations of CO<sub>2</sub> in the oceans is in its infancy and needs to be developed rapidly. We recommend that a major, internationally coordinated effort be launched to include global monitoring, experimental, mesocosm and field studies. Models that include the effects of pH at the scale of the organism and the ecosystem are also necessary. The impacts of ocean acidification are additional to, and may exacerbate, the effects of climate change. For this reason, the necessary funding should be additional and must not be diverted from research into climate change.**

Oceans play a very important role in the global carbon cycle and Earth's climate system. There are potentially important interactions and feedbacks between changes in the state of the oceans (including their pH) and changes in the global climate and atmospheric chemistry. Changes in the chemistry of the oceans will reduce their ability to absorb additional CO<sub>2</sub> from the atmosphere, which will in turn affect the rate and scale of global warming. The knowledge of these impacts and effects is currently poor and requires urgent consideration. **The understanding of ocean acidification and its impacts needs to be taken into account by the Intergovernmental Panel on Climate Change and kept under review by international scientific bodies such as the Intergovernmental Oceanographic Commission, the Scientific Committee on Oceanic Research and the International Geosphere-Biosphere Programme.**

The socio-economic effects of ocean acidification could be substantial. Damage to coral reef ecosystems and the fisheries and recreation industries that depend on them could amount to economic losses of many billions of dollars per year. In the longer term, changes to the stability of coastal reefs may reduce the protection they offer to coasts. There may also be direct and indirect effects on commercially important fish and shellfish species.

Marine ecosystems are likely to become less robust as a result of the changes to the ocean chemistry and these will be more vulnerable to other environmental impacts (such as climate change, water quality, coastal deforestation, fisheries and pollution). **The increased fragility and sensitivity of marine ecosystems needs to be taken into consideration during the development of any policies that relate to their conservation, sustainable use and exploitation, or the communities that depend on them.**

**If the risk of irreversible damage arising from ocean acidification is to be avoided, particularly to the Southern Ocean, the cumulative future human derived emissions of CO<sub>2</sub> to the atmosphere must be considerably less than 900 Gt C (gigatonnes of carbon) by 2100.**

**In setting targets for reductions in CO<sub>2</sub> emissions, world leaders should take account of the impact of CO<sub>2</sub> on ocean chemistry, as well as on climate change. These targets must be informed by sound science.**

**Ocean acidification is a powerful reason, in addition to that of climate change, for reducing global CO<sub>2</sub> emissions. Action needs to be taken now to reduce global emissions of CO<sub>2</sub> to the atmosphere to avoid the risk of irreversible damage to the oceans. We recommend that all possible approaches be considered to prevent CO<sub>2</sub> reaching the atmosphere. No option that can make a significant contribution should be dismissed.**





# 1 Introduction

## 1.1 Background to the report

Covering around 70% of the planet, the oceans play a central role in the Earth's major processes. They are host to thousands of species of organisms, which live in a variety of habitats and ecosystems. Carbon dioxide (CO<sub>2</sub>) emitted to the atmosphere by human activities is absorbed by the oceans, making them more acidic (lowering the pH—the measure of acidity). Initial evidence shows that the surface waters of the oceans, which are slightly alkaline, are already becoming more acidic: we refer to this process as ocean acidification. There is growing concern that as atmospheric concentrations of CO<sub>2</sub> continue to rise, the increasing acidity will have significant effects on the marine system.

In recent years global warming and the resulting climate changes, has received considerable global attention. There is now a clear scientific consensus that increasing atmospheric levels of CO<sub>2</sub> (one of the major greenhouse gases), resulting mainly from human activities, are causing global mean surface temperatures to rise (IPCC 2001).

Ocean acidification is an additional concern to that of climate change, but the threat it poses to the marine environment has only recently been recognised. Parts of the international scientific community are beginning to take this issue seriously, for example the 2004 UNESCO symposium on the Oceans in a High-CO<sub>2</sub> World. An understanding of the chemical processes involved when CO<sub>2</sub> is absorbed from the atmosphere and dissolves in seawater is fairly well established. However, much less is known about the oceans and the biological and chemical processes of the life within them. Therefore predicting the impacts of ocean acidification is a complex and significant challenge.

For this reason the Royal Society has undertaken this study to provide a concise overview of the present state of scientific knowledge of ocean acidification and its likely impacts on marine organisms. This report will be of interest to those taking decisions and making policies on climate change, energy policy and environmental protection; for scientists studying the oceans, atmosphere and climate; and for anyone who is interested in the impact of human activities on the natural processes of our planet.

## 1.2 The oceans and carbon dioxide: acidification

Carbon dioxide is being produced in substantial quantities mainly through the combustion of fossil fuels, cement production, agriculture and deforestation. The concentration of CO<sub>2</sub> in the atmosphere has been increasing from its recent pre-industrial level of about 280 parts per million (ppm) to about 380 ppm today. What is significant for biological systems is that the rate of this

increase is unprecedented since the peak of the last Ice Age—for at least 20 000 years (IPCC 2001). Atmospheric CO<sub>2</sub> levels are predicted to continue to increase for at least the next century and probably longer, and unless emissions are substantially reduced, may well reach levels exceeding 1 000 ppm by 2 100, higher than anything experienced on Earth for several million years.

Oceans play a fundamental role in the exchange of CO<sub>2</sub> with the atmosphere. Over the past 200 years, since pre-industrial times, the oceans have absorbed about a half of the CO<sub>2</sub> emissions produced from burning fossil fuels and cement manufacture. This demonstrates the integral role that oceans play within the natural processes of cycling carbon on a global scale—the so-called carbon cycle.

The oceans and the organisms they support contain about 38 000 Gt C (gigatonnes of carbon; 1 Gt C = 10<sup>15</sup> grams) (Figure 1). This accounts for about 95% of all the carbon that is in the oceans, atmosphere and terrestrial system, constituting a substantial reservoir of carbon. As we explain in Section 2, the chemical properties of the dissolved carbon in this system enable the oceans to buffer, or neutralise, changes in acidity due to the uptake of CO<sub>2</sub> emissions. However, as absorption of the CO<sub>2</sub> emissions from human activities increases (currently about 2 Gt C per year), this reduces the efficiency of the oceans to take up carbon. Carbon dioxide exchange is a two-way process, with the oceans and atmosphere absorbing and releasing CO<sub>2</sub>. A decrease in the amount of CO<sub>2</sub> absorbed by the oceans will mean that relatively more CO<sub>2</sub> will stay in the atmosphere. This will make global efforts to reduce atmospheric concentrations of CO<sub>2</sub> and the associated climate change more difficult.

The surface waters of the oceans are slightly alkaline, with an average pH of about 8.2, although this varies across the oceans by ±0.3 units because of local, regional and seasonal variations. Carbon dioxide plays an important natural role in defining the pH of seawater (a brief account of measures of acidity such as pH, and the acid–base chemistry of the CO<sub>2</sub>–carbonate system in the oceans, is given in Annex 1). When CO<sub>2</sub> dissolves in seawater it forms a weak acid, called carbonic acid. Part of this acidity is neutralised by the buffering effect of seawater, but the overall impact is to increase the acidity. This dissolution of CO<sub>2</sub> has lowered the average pH of the oceans by about 0.1 units from pre-industrial levels (Caldeira & Wickett 2003). Such a value may seem small but because of the way pH is measured, as we explain in Section 2, this change represents about a 30% increase in the concentration of hydrogen ions, which is a considerable acidification of the oceans. Increasing atmospheric concentration of CO<sub>2</sub> will lead to further acidification of the oceans.

In Section 2 we outline the main chemical reactions associated with ocean acidification. We look at the effects

on ocean chemistry that CO<sub>2</sub> emissions from human activities have already caused and consider how the chemistry, nutrients and trace metals of the oceans may change with future emissions. These changes will affect the many important natural processes that are affected by its acidity/alkalinity (pH).

### **1.3 Acidification and the surface oceans**

In this report we use the term 'surface oceans' to describe the near-surface waters where exchange of CO<sub>2</sub> occurs. Only the near-surface waters, or surface layers, of the oceans (down to about 100 m on average) are well mixed and so in close contact with the atmosphere. Carbon dioxide in the atmosphere dissolves in the surface waters of the oceans and establishes a concentration in equilibrium with that of the atmosphere. Molecules of CO<sub>2</sub> exchange readily with the atmosphere and on average only remain in the surface waters for about 6 years. However mixing and advection (vertical motions, sinking and upwelling) with the intermediate and deep waters of the oceans (down to about 1 000 m and 4 000 m respectively) is much slower, and takes place on timescales of several hundred years or more. Over time this mixing will spread the increased atmospheric uptake of CO<sub>2</sub> to the deeper oceans. Owing to this slow mixing process most of the carbon stored in the upper waters of the oceans will be retained there for a long time. This makes the impacts in the surface waters greater than if the CO<sub>2</sub> absorbed from the atmosphere was spread uniformly to all depths of the oceans.

### **1.4 Ocean life and acidification**

Most of the biological activity in the oceans (and all of the photosynthesis) takes place in the near-surface waters through which sunlight penetrates; the so-called photic zone.

Marine organisms are, by definition, adapted to their environment. However, changes in ocean chemistry, especially rapid modifications such as ocean acidification, could have substantial direct and indirect effects on these organisms and upon the habitats in which they live. Direct effects include the impact of increasing CO<sub>2</sub> concentration and acidity, which may affect all stages of the life cycle. Indirect effects include the impact on organisms arising from changes in availability or composition of nutrients as a result of increased acidity.

One of the most important implications of the changing acidity of the oceans relates to the fact that many marine photosynthetic organisms and animals, such as corals, make shells and plates out of calcium carbonate (CaCO<sub>3</sub>). This process of 'calcification', which for some marine organisms is important to their biology and survival, is impeded progressively as the water becomes acidified (less alkaline). This adverse effect on calcification is one of

the most obvious and possibly most serious of the likely environmental impacts of ocean acidification.

Any changes in the biological processes in the surface ocean waters will also affect the deeper water of the oceans. This is because organisms and habitats living at the lower levels of the oceans — far from the sunlight — rely mainly on the products created by life in the surface waters. On a longer timescale, these organisms may also be vulnerable to acidification and changes in ocean chemistry as higher levels of CO<sub>2</sub> mix throughout the oceans.

In Section 3 of the report we explore the biological systems of the oceans and highlight processes and groups of species that may be vulnerable to changes in ocean chemistry. We examine how effects on organisms may affect populations of species; how these will affect interactions between species; and finally we consider whether species will acclimatise or evolve in response to ocean acidification. Section 4 looks at how these changes will affect ecosystems most likely to be at risk, such as coral reefs. Coral structures provide a valuable habitat for many other species, but being composed of CaCO<sub>3</sub> could be most at risk from increasing surface ocean CO<sub>2</sub> concentrations.

### **1.5 Interaction with the Earth systems**

Ocean acidification will not occur in isolation from the rest of the Earth systems. Oceans play a significant role in the regulation of global temperature and so affect a range of climatic conditions and other natural processes. The Earth's climate is currently undergoing changes as a result of global warming, which is having an impact across many chemical and biological processes. Considerable interactions may exist between all these processes, which may have beneficial or adverse impacts, alongside those of ocean acidification. In Section 5 we identify the important interactions and consider the possible impacts of changes in ocean chemistry on other global processes.

### **1.6 Adaptation to and mitigation of ocean acidification**

Any changes in natural resources as a result of ocean acidification could impact upon the livelihoods of people who rely on them. In Section 6 we look at the areas where there could be large socio-economic effects and evaluate the potential costs of these impacts.

Apart from reducing emissions to the atmosphere, engineering approaches (such as adding limestone, a carbonate material) have been suggested for tackling ocean acidification. These approaches aim to reduce some of the chemical effects of increased CO<sub>2</sub> through the addition of an alkali to the oceans. In Section 6 we

briefly evaluate the potential of some of these methods to mitigate ocean acidification.

### **1.7 Artificial deep ocean storage of carbon dioxide**

Our report focuses on ocean acidification as a result of increasing CO<sub>2</sub> being absorbed from the atmosphere. We do not directly address the issue of the release and storage of CO<sub>2</sub> on the ocean floor and in the deep oceans as part of a carbon capture and storage (CCS) programme. As the report does address the possible effects of increased CO<sub>2</sub> on organisms and ocean chemistry, some of our findings will be relevant to those interested in CCS. The concept of CCS is to capture emissions of CO<sub>2</sub> from power generation for example, and to store them, for thousands of years, in places that

are isolated from the atmosphere, such as in liquid form on the seabed in the deep oceans and in underground geological structures. This subject is part of a forthcoming special report on carbon capture and storage by the Intergovernmental Panel on Climate Change (IPCC), due in late 2005.

### **1.8 Conduct of the study**

The Royal Society convened a working group of international experts across several scientific disciplines to write this report. The Council of the Royal Society has endorsed its findings. We are very grateful to those individuals and organisations (listed in Annex 2) who responded to our call for evidence to inform this study. These have been valuable contributions, and in many cases have been reflected in our report.



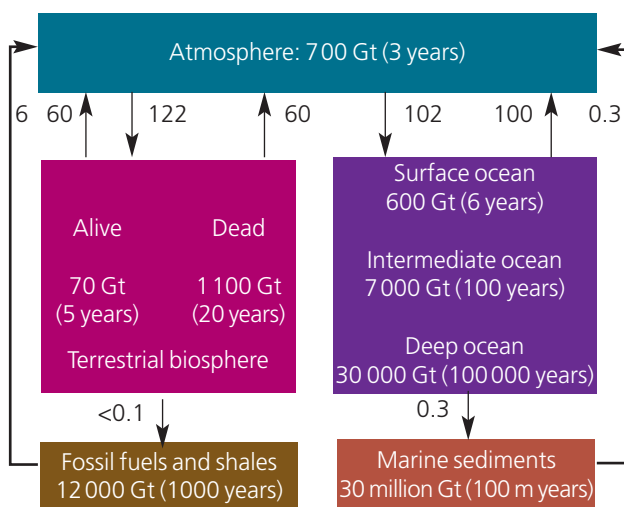
## 2 Effects of atmospheric CO<sub>2</sub> enhancement on ocean chemistry

### 2.1 Introduction

The oceans are a significant store of carbon within the Earth systems. They readily exchange carbon in the form of CO<sub>2</sub> with the atmosphere and provide an important sink for CO<sub>2</sub>. Human activities are releasing CO<sub>2</sub> that would otherwise be locked away from the atmosphere in geological reservoirs. Because of these changes, atmospheric concentrations of CO<sub>2</sub> are higher today than for at least 420 000 years (IPCC 2001).

Approximately one-half of the CO<sub>2</sub> produced by fossil fuel burning and cement production as a result of human activities in the past 200 years is being taken up by the oceans. This absorption process is chemically changing the oceans, in particular increasing its acidity. In this section we consider the evidence of increased uptake of CO<sub>2</sub> by the oceans over the past century and how this reflects changes in atmospheric CO<sub>2</sub> levels and ocean acidity. We provide an overview of the chemical processes involved as CO<sub>2</sub> dissolves in the oceans; how ocean chemistry responds to changes in CO<sub>2</sub> levels; and an introduction to how these changes may affect the biological systems, which are considered further in Sections 3 and 4.

*Figure 1. Diagram of the global carbon cycle showing sizes of carbon reservoirs (units are Gt (gigatonnes): 1 Gt = 10<sup>15</sup> grams) and exchange rates ('fluxes') between reservoirs (units are gigatonnes per year) in the terrestrial (green) and the oceanic (dark blue) parts of the Earth system. Also shown are 'residence times' (in years) of carbon in each reservoir: however, some mixing between the deep oceans and marine sediments does occur on shorter timescales. Carbon exchanges readily between the atmosphere, the surface oceans and terrestrial biosphere. However, the residence time of carbon in the atmosphere, oceans and biosphere combined, relative to exchange with the solid Earth, is about 100 000 years. (Reprinted and redrawn from Holmen (2000) with permission from Elsevier.)*



### 2.2 The impact of increasing CO<sub>2</sub> on the chemistry of ocean waters

#### 2.2.1 The oceans and the carbon cycle

Carbon exists throughout the planet in several 'reservoirs' and in a variety of forms (Figure 1). The exchange of carbon between the important reservoirs of the biosphere, atmosphere and oceans is known as the carbon cycle. One of the more commonly known exchanges of carbon in this cycle is its absorption, in the form of CO<sub>2</sub>, by trees and herbaceous plants on land during photosynthesis, also known as primary production (the production of organic from inorganic carbon), and subsequent release back into the atmosphere by respiration. Carbon dioxide also dissolves in the oceans and can be released back into the atmosphere, making the oceans a considerable point of exchange in the carbon cycle. Organisms within the surface ocean exchange CO<sub>2</sub> in much the same way as the biological processes on land. Although the biological uptake of CO<sub>2</sub> per unit area of the surface oceans is lower than that in most terrestrial systems, the overall biological absorption is almost as large as that in terrestrial environment. This is because the surface area of the oceans is so much larger (Field et al 1998).

The oceans are a substantial carbon reservoir. When measured on short timescales of hundreds of years, their greatest exchanges of carbon are with the atmosphere. The pre-industrial oceanic carbon reservoir has been estimated at about 38 000 Gt, compared with about 700 Gt in the atmosphere and somewhat less than 2 000 Gt in the terrestrial biosphere (approximately 700 Gt as biomass and 1 100 Gt as soil) (Brovkin et al 2002). These reservoirs exchange quantities of carbon each year that are large relative to the amount of carbon stored within them. Figure 1 illustrates that the oceans are acting as an important carbon sink, absorbing 2 Gt C per year more CO<sub>2</sub> than they are releasing into the atmosphere. This is small in comparison to the amount of carbon that is cycled between the different reservoirs but is a significant proportion of the 6 Gt C per year released into the atmosphere from human activity (Figure 1).

The carbon buried in some reservoirs, such as rocks and organic-rich shale, exchanges with the other reservoirs on geologically long timescales. As a result, carbon in these reservoirs will not affect the atmosphere or oceans on short timescales (up to about 10<sup>3</sup> years) unless exchange rates are artificially increased by human activity such as limestone mining, oil, gas and coal production. It is the carbon released by human activities that has produced increased atmospheric concentrations of CO<sub>2</sub> to levels unprecedented for at least 420 000 years and possibly for the past tens of millions of years (IPCC 2001).

## 2.2.2 The oceans and carbon dioxide

Carbon dioxide, like other gases, obeys Henry's law, which means that an increase in the atmospheric level of  $\text{CO}_2$  increases the concentration of  $\text{CO}_2$  in the surface oceans.

Carbon dioxide in the atmosphere is a chemically unreactive gas but, when dissolved in seawater, becomes more reactive and takes part in several chemical, physical, biological and geological reactions, many of which are complex (Annex 1).

One of the overall effects of  $\text{CO}_2$  dissolving in seawater is to increase the concentration of hydrogen ions, ( $[\text{H}^+]$ ), within it. This is the result of an initial reaction between water ( $\text{H}_2\text{O}$ ) and  $\text{CO}_2$  to form carbonic acid ( $\text{H}_2\text{CO}_3$ ). This weak acid readily releases the hydrogen ions to form the other types of dissolved inorganic carbon (Annex 1). As we explain in Annex 1, acidity is determined by the concentration of hydrogen ions. This is measured on the pH scale, with an acid having a pH of less than 7 and alkali having a pH of greater than 7 units. The more acidic a solution, the more hydrogen ions are present and the lower the pH. Therefore the amount of  $\text{CO}_2$  that dissolves in seawater has a strong influence on the resultant acidity/alkalinity and pH of the oceans.

In the oceans,  $\text{CO}_2$  dissolved in seawater exists in three main inorganic forms collectively known as dissolved inorganic carbon (DIC). These are: (i) aqueous  $\text{CO}_2$  (about 1% of the total); in this report this term also includes carbonic acid ( $\text{H}_2\text{CO}_3$ ), (as aqueous  $\text{CO}_2$  can be in either form), and two electrically charged forms, (ii) bicarbonate

( $\text{HCO}_3^-$ , about 91%) and (iii) carbonate ions ( $\text{CO}_3^{2-}$  about 8%). Thus under current ocean conditions, bicarbonate is the most abundant form of  $\text{CO}_2$  dissolved in seawater followed by carbonate and then aqueous  $\text{CO}_2$  (Figure 2). There is approximately an order of magnitude difference in abundance between each of the three forms; however, amounts vary somewhat with seawater temperature, salinity and pressure.

All three forms of dissolved  $\text{CO}_2$  are important for the biological processes of marine organisms. These processes include photosynthesis by marine algae (mostly phytoplankton), the production of complex organic carbon molecules from sunlight, and calcification, providing structures such as  $\text{CaCO}_3$  shells. When these organisms die or are consumed, most of the carbon either stays in the surface waters or is released back into the atmosphere. However, some of this  $\text{CaCO}_3$  and organic material falls as particle sediments to the deep oceans (Figure 3). The process whereby carbon is transferred from the atmosphere to the deep ocean waters and sediments is referred to as the 'biological pump'. By removing carbon from the surface waters and taking it to greater depths, the pump increases the capacity for the oceans to act as a sink for atmospheric  $\text{CO}_2$ . Any changes in the strength of this pump would have significant consequences on the amount of carbon being sequestered to the deep ocean environments and therefore removed from the atmosphere.

## 2.2.3 The oceans as a carbonate buffer

The relative proportion of the three forms of DIC ( $\text{CO}_2$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ ) reflects the pH of seawater and maintains it within relatively narrow limits. This DIC operates as a natural buffer to the addition of hydrogen ions—this is called the 'carbonate buffer'. If an acid (such as  $\text{CO}_2$ ) is added to seawater, the additional hydrogen ions react with carbonate ( $\text{CO}_3^{2-}$ ) ions and convert them to bicarbonate ( $\text{HCO}_3^-$ ). This reduces the concentration of hydrogen ions (the acidity) such that the change in pH is much less than would otherwise be expected (Annex 1). When atmospheric  $\text{CO}_2$  dissolves in seawater, the oceans increase in acidity but, because of the carbonate buffer, the resultant solution is still slightly alkaline.

The capacity of the buffer to restrict pH changes diminishes as increased amounts of  $\text{CO}_2$  are absorbed by the oceans. This is because when  $\text{CO}_2$  dissolves, the chemical processes that take place reduces some carbonate ions, which are required for the ocean pH buffer (Annex 1).

## 2.3 Natural variation in pH of the oceans

Surface oceans have an average pH globally of about 8.2 units. However, pH can vary by  $\pm 0.3$  units due to local, regional and seasonal factors. The two primary factors

Figure 2. Relative proportions of the three inorganic forms of  $\text{CO}_2$  dissolved in seawater. The green arrows at the top indicate the narrow range of pH (7.5–8.5) that is likely to be found in the oceans now and in the future. Note the ordinate scale (vertical axis) is plotted logarithmically (see Table 1 for numeric details and Annex 1 for further explanation).

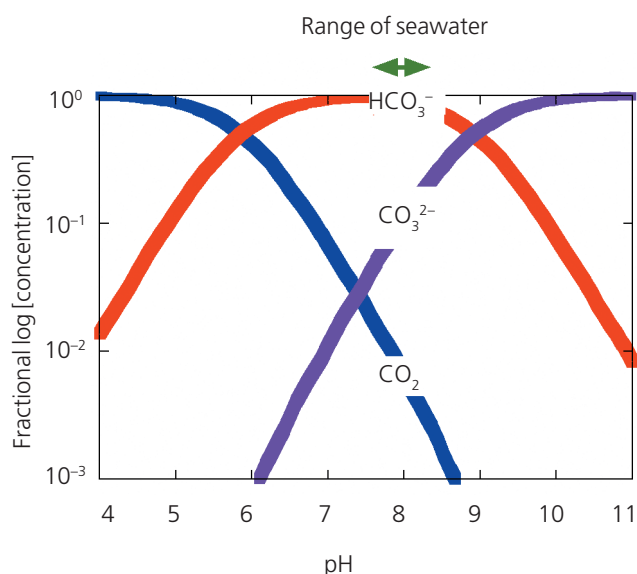
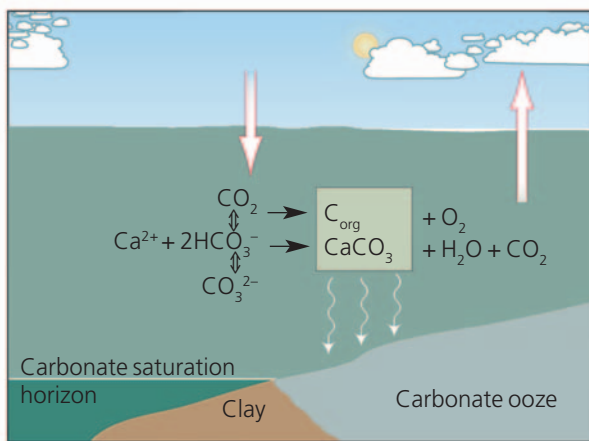


Figure 3. Diagram of the carbonate buffer and biological pump in the surface oceans. After absorption of  $\text{CO}_2$  into the oceans it is converted by the carbonate buffer. Calcification in the oceans also releases  $\text{CO}_2$ , some of which is returned to the atmosphere. The biological pump (represented as descending wiggly arrows) converts  $\text{CO}_2$  from the atmosphere into organic carbon ( $\text{C}_{\text{org}}$ ) and  $\text{CaCO}_3$  and transfers it to the deep ocean waters and sediments. The vertical scale is compressed: the process depicted by the equations and the 'box' occur within the surface oceans (top few hundred metres). This is far above the carbonate saturation horizon (Section 2.7.1), which for the calcite form, occurs at depths in the range of about 1.5 to 5 km and for the aragonite form, at depths in the range of about 0.5 to 2.5 km. (Reprinted with permission from Elderfield (2000); copyright ASSA).



governing the spatial distribution (Figure 4) of ocean pH are (i) temperature of the surface oceans and (ii) upwelling of  $\text{CO}_2$ -rich deep water into the surface waters. Lower surface water temperatures tend to increase  $\text{CO}_2$  uptake, whilst surface warming drives its release. When  $\text{CO}_2$  is released from the oceans, at constant temperatures, pH increases. In the deep oceans, the  $\text{CO}_2$  concentration increases as sinking organic matter from biological production (which varies seasonally) is decomposed. These additions of  $\text{CO}_2$  to the deep oceans cause its pH to decrease as the deep waters transit from the North Atlantic to the Pacific Ocean. When this  $\text{CO}_2$ -rich deep water upwells to the surface, it creates regions with lower-pH in the surface waters.

Seasonal changes such as those in temperature and in bio-productivity, including variations in photosynthesis and respiration, contribute to fluctuations in ocean pH (Gonzalez-Davila et al 2003). Coastal waters are more likely to be affected by the terrestrial system, such as run off from rivers, leading to wider variations in ocean pH in these areas (Hinga 2002).

Geographic pH variation for the global surface oceans (50 m) for the year 1994 is shown in Figure 4. The pH values are calculated using data from the Global Data Analysis

Project (GLODAP). Surface values range from 7.9 to 8.25 with a mean value of 8.08 (Sabine personal communication). The lowest values are observed in upwelling regions (eg Equatorial Pacific, Arabian Sea) where subsurface waters with lower pH values are brought to the surface. The highest values are observed in regions of high biological production and export. In these regions DIC is converted into organic carbon by phytoplankton and exported by the biological pump into the deeper oceans resulting in higher pH values in the surface waters.

In Sections 2.5 and 2.6 we evaluate the affect of increased atmospheric  $\text{CO}_2$  from human activities on surface ocean chemistry and pH, and compare these changes to natural and historical variations.

## 2.4 Factors affecting $\text{CO}_2$ uptake by the oceans

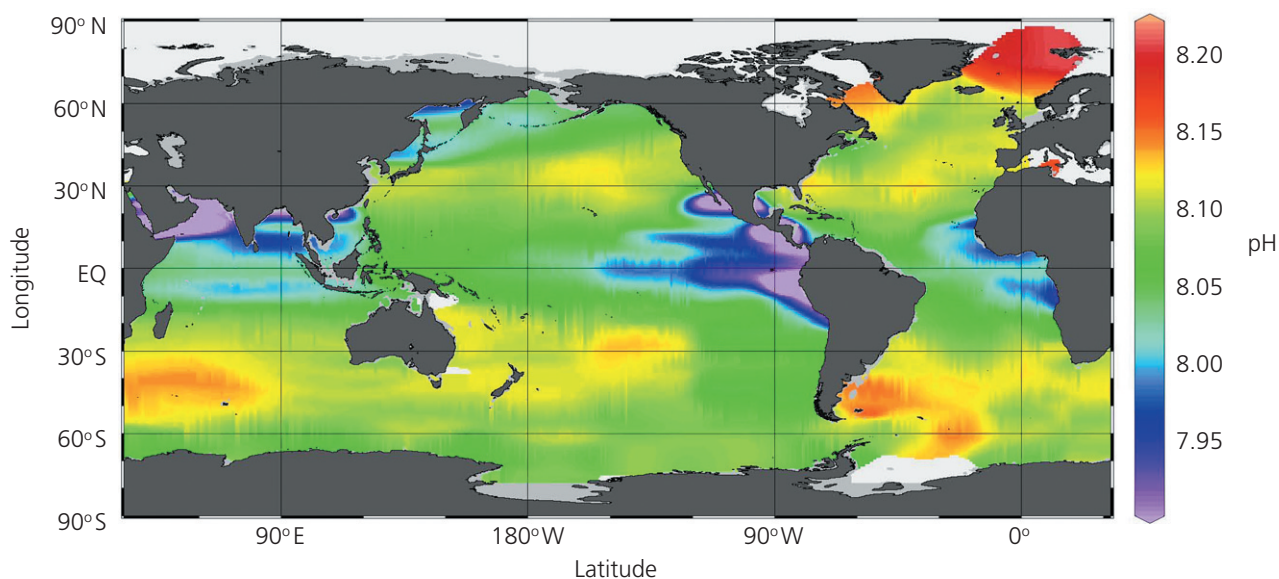
Several chemical, physical and biological factors have the potential to affect the uptake of  $\text{CO}_2$  by the oceans (Houghton et al 2001). Chemical processes that may affect  $\text{CO}_2$  uptake include changes to the  $\text{CO}_2$  buffering capacity (Sarmiento et al 1995) and the effects of temperature on  $\text{CO}_2$  solubility. Physical factors that affect uptake include increased ocean stratification due to increasing global temperatures. Warming of the oceans leads to increased vertical stratification (decreased mixing between the different levels in the oceans), which would reduce  $\text{CO}_2$  uptake, in effect, reducing the oceanic volume available to  $\text{CO}_2$  absorption from the atmosphere. Stratification will reduce the return flow of both carbon and nutrients from the deep oceans to the surface. Biologically linked processes, discussed in greater detail below and in Section 3, are perhaps the most difficult to evaluate; however, the removal of nutrients from the upper oceans with a slower return flow from the deep oceans could have negative impact on life in the surface oceans.

In addition to its effects upon  $\text{CO}_2$  uptake and ocean chemistry, any acidification of marine surface waters may influence parts of the Earth systems through the emission of gases to the atmosphere. These broader factors are considered in more detail in Section 5.

## 2.5 How oceans have responded to changes in atmospheric $\text{CO}_2$ in the past

We are only certain of the atmospheric  $\text{CO}_2$  concentrations over the past 420 000 years, the time for which we have an archive of ancient air trapped in bubbles of Antarctic ice (IPCC 2001). During this period the atmospheric concentrations have always been lower than today. With less certainty, we can reconstruct  $\text{CO}_2$  concentrations much further back in time. To do this we can use inferred reconstructions from 'proxy' data as diverse as boron isotopes in carbonates (Pearson and Palmer 2000), rocks derived from ancient soils (Cerling 1991), the stomata on fossil leaves, and models of the processes we believe

Figure 4. Map of mixed surface layer (upper 50 m) pH values in the global oceans for the nominal year 1994. The lowest values are observed in upwelling regions (eg Equatorial Pacific, Arabian Sea) where subsurface waters with lower pH values are brought to the surface. The highest values are observed in regions of high biological production and export. In these regions DIC is fixed by phytoplankton and exported by the biological pump into the deeper layers resulting in higher pH values in the surface waters. Values are calculated from the GLODAP DIC and total alkalinity dataset (Key et al 2004) using the Dickson & Millero refit of the Merbach carbonate dissociation constants (Dickson and Millero 1987). Physical oceanographic modelling is based on Bryan (1969) and Cox (1984).



control atmospheric  $\text{CO}_2$  (Berner 1994; Bergman et al 2004). Such studies agree that atmospheric  $\text{CO}_2$  has probably been relatively low for the past few million years, but that in the more distant past it was much higher than it is today. In the warm world of the Cretaceous for example (100 million years ago), concentrations were between three and ten times higher than present. Four hundred million years ago, before the land was colonised by forests, they were probably 20 times higher.

As we outlined in Section 2.2.2, as atmospheric  $\text{CO}_2$  levels increase so does the concentration of  $\text{CO}_2$  in the surface oceans. However it is unlikely that the past atmospheric concentrations would have led to a significantly lower pH in the oceans, as the rate at which atmospheric  $\text{CO}_2$  changed in the past was much slower compared with the modern day. The fastest natural changes that we are sure about are those occurring at the ends of the recent ice ages, when  $\text{CO}_2$  rose about 80 ppm in the space of 6000 years (IPCC 2001). This rate is about one-hundredth that of the changes currently occurring. During slow natural changes, the carbon system in the oceans has time to interact with sediments and stays therefore approximately in steady state with them. For example if the deep oceans starts to become more acidic, some carbonate will be dissolved from sediments. This process tends to buffer the chemistry of the seawater so that pH changes are lessened (see section 2.2.3 and Annex 1 for a more detailed review).

Data from the air trapped in Antarctic ice (IPCC 2001) show a variation of atmospheric concentration of  $\text{CO}_2$  from about 190 ppm to 300 ppm over the past 420 000

years. At constant temperature and alkalinity, this would represent a pH variation in the oceans of about 0.16 units, with the highest pH values when the atmospheric  $\text{CO}_2$  values are lowest at glacial maxima (the value was derived using the procedures employed in constructing Table 1). At constant concentration of  $\text{CO}_2$ , temperature influence on pH is minor. However, this figure is likely to be upper bound because interactions with carbonate sediments would diminish this pH variation. This carbonate-sediment buffering occurs on a time scale of less than 10 000 years, whereas the full range of glacial-interglacial change occurs on this time scale or longer. Estimates of glacial-interglacial deep-ocean pH changes of 0.12 (Ridgwell 2001) are consistent with these model calculations.

Proxy estimates from a study based on boron isotopes suggest that 50 million years ago, ocean pH was as much as 0.6 pH units lower than today (Pearson and Palmer 2000), though the interpretation of these data in terms of pH change is open to question (Pagani et al 2005). Models suggest that dissolution of  $\text{CaCO}_3$  sediments would have had sufficient time to buffer the change in pH in the past, even when the  $\text{CO}_2$  concentration of the atmosphere was high.

Other proxy estimates have been made for pH at the peak of the more recent Ice Age, about 20 000 years ago, when atmospheric  $\text{CO}_2$  concentrations were 190 ppm compared with today's value of about 380 ppm. One estimate, also based on boron isotopes (Sanyal et al 1995), suggests that the pH of the oceans was 0.3 units



higher than today (that is, more alkaline). This implies that doubling of CO<sub>2</sub> decreases pH by 0.3 units. However, another estimate, based on the preservation of marine calcifying organisms (Anderson & Archer 2002), suggests that there was no such whole-ocean pH change.

We caution, therefore, that there is substantial uncertainty in both proxy and model reconstructions, and that these uncertainties increase as one goes back from centuries to millennia and to millions of years in time.

## **2.6 Change in ocean chemistry due to increases in atmospheric CO<sub>2</sub> from human activities**

Based upon current measurements of ocean pH, analysis of CO<sub>2</sub> concentration in ice cores, our understanding of the rate of CO<sub>2</sub> absorption and retention in the surface oceans, and knowledge of the CaCO<sub>3</sub> buffer (Section 2.2.2), it is possible to calculate that the pH of the surface oceans was 0.1 units higher in pre-industrial times (Caldeira & Wickett 2003; Key et al 2004). This 0.1 pH change over about the past 200 years corresponds to about a 30% increase in the concentration of hydrogen ions.

It is also possible to make projections of likely further pH reductions in seawater over the next centuries as a result of additional atmospheric CO<sub>2</sub> emissions. These projections of future pH change (Table 1; Caldeira & Wickett in press) show that if CO<sub>2</sub> from human activities is allowed to continue on present trends this will lead to a decrease in pH of up to 0.5 units by the year 2100 in the surface oceans. This corresponds to a three fold increase in the concentration of hydrogen ions from pre-industrial times, which is an increase in ocean pH outside the range of natural variation and probably to a level not experienced for at least hundreds of thousands of years and possibly much longer (Sections 2.3 and 2.5). Critically, the rate of change is also probably at least 100 times higher than the maximum rate during this time period.

### **2.6.1 Change to the oceans due to CO<sub>2</sub> enhancement in recent centuries**

It is possible to measure the amount of carbon added to seawater over the past two centuries as a result of human activities. This information has been developed using a substantial database taken through the global oceans observing programmes of the World Ocean Circulation Experiment and the Joint Global Ocean Flux Study in the 1990s. In these programmes data were collected from around 10 000 monitoring stations. This data set provides the most accurate and comprehensive overview of the past and current distribution of DIC in the oceans.

Ocean observations indicate increases in DIC as a result of additional CO<sub>2</sub> being absorbed from the atmosphere. Using a sophisticated tracer technique (Gruber et al 1996), this DIC can be separated into naturally occurring dissolved carbon in seawater and that added to the oceans by

human activity. This is estimated using the relationship between the variables in seawater (nutrients, DIC, alkalinity etc) that are assumed to be free of excess CO<sub>2</sub>, and by then subtracting this inferred natural DIC concentration from the observed increased seawater concentration.

Using this approach, it can be estimated that between 1800 and 1994 the oceans have absorbed about 48% of the total CO<sub>2</sub> emitted by human activities, mainly by fossil fuel burning and cement manufacturing. This has been deduced from the measurement of total DIC (106 ± 17 Gt C) and extrapolating for the regions of oceans not surveyed, leading to a sum of 118 ± 19 Gt C over this period. A continuation of trends inferred for the 1980s and 1990s from ocean models and atmospheric observations would indicate that over 140 Gt C (over 500 Gt CO<sub>2</sub>) resulting from human activities reside in the oceans today. Even though uncertainties exist due to the estimates in the amount of CO<sub>2</sub> from human activities and errors in mapping, this number is probably accurate better than 20%. Analysis of this data shows that the uptake and redistribution of CO<sub>2</sub> varies geographically due to temperature and ocean circulation currents (Section 2.3) (Sabine et al 2004).

Given that CO<sub>2</sub> enters the oceans by exchange across the air–sea interface, it follows that analysis of the distribution of CO<sub>2</sub> uptake show highest values (and therefore the greatest pH change), in near-surface waters. As it takes many centuries for the downward mixing of CO<sub>2</sub>, little of the CO<sub>2</sub> derived from human activities has yet reached the deep oceans. When averaged for the oceans globally, about 30% of the anthropogenic CO<sub>2</sub> is found at depths shallower than 200 m, with 50% at depths less than 400 m, leading to the conclusion that most of the CO<sub>2</sub> that has entered the oceans as a result of human activity still resides in relatively shallow waters.

### **2.6.2 How oceanic pH will change in the future**

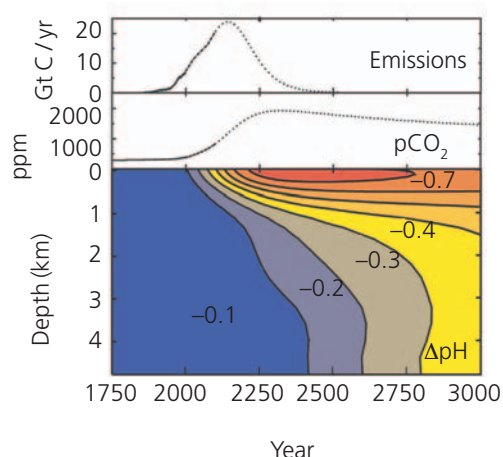
As we have shown in the previous section, it is possible to make projections of the extent to which oceanic pH will fall as a consequence of increases in CO<sub>2</sub> from human activities. The simplest estimate, takes a situation where human CO<sub>2</sub> emissions continue to be released on current trends; considers the surface oceans as a single ‘box’ at a constant temperature (25 °C) and salinity with an initial (pre-industrial) pH of 8.2 units, and assumes no mixing with the deeper oceans. Under these circumstances it is predicted that pH will fall to below 7.9 by 2100 (Zeebe and Wolf-Gladrow 2001).

A more detailed analysis of projected pH changes has been done using an ocean general-circulation model with observed atmospheric CO<sub>2</sub> from 1975 to 2000 and a projected mid-range CO<sub>2</sub> emission scenario (IPCC IS92a scenario (Houghton et al 2001)) for 2000–2100 (Caldeira & Wickett 2003). The results are shown in Figure 5 where, assuming that after 2100 emissions follow a logistic

function for the burning of the remaining fossil-fuel resources, emissions of CO<sub>2</sub> from human activities have peaked around 2 150. However, the CO<sub>2</sub> remains in the atmosphere at a high concentration for several thousand years, before it is absorbed by the oceans or the terrestrial biosphere. The initial changes in the surface ocean pH are rapid, but as CO<sub>2</sub> continues to be absorbed from the atmosphere it is slowly transferred to the deep oceans (including ocean sediments) by mixing and through the biological pump, with subsequent changes in pH.

The study predicts a possible decrease in pH of 0.5 units by the year 2 100 in the surface oceans, which, as stated earlier, corresponds to a three fold increase in the

*Figure 5. Projected change in pH of the oceans due to release of CO<sub>2</sub> from human activities. The top layer of the diagram shows past and projected emissions of CO<sub>2</sub> to the atmosphere in Gt C per year. Carbon dioxide emission trends are based on mid-range CO<sub>2</sub> emission scenario (IPCC IS92a scenario (Houghton et al 2001)). The decrease in emissions after 2150 assumes that human activities will continue at levels until the eventual burning of the remaining fossil fuel resources. The second layer shows historical atmospheric CO<sub>2</sub> levels to 1975, observed atmospheric CO<sub>2</sub> concentrations from 1975 to 2000 and predicted concentrations to year 3000. The decrease in atmospheric CO<sub>2</sub> levels after 2400 reflects the excess of uptake of CO<sub>2</sub> by the oceans and sequestered down to the oceans' sediments. The coloured sections at the bottom of the figure show the projected average change in ocean pH with depth. The Figure assumes the chemistry and pH is uniform on the horizontal plane throughout the oceans. The maximum reduction in the surface oceans shown is 0.77 units. The vertical variations relate to mixing over time of the surface waters with deeper parts of the oceans and chemical reactions in the deep oceans. These CO<sub>2</sub> effects were estimated using the Lawrence Livermore National Laboratory (LLNL) ocean general-circulation model. Physical oceanographic modelling is based on Bryan (1969) and Cox (1984). (Reprinted with permission from Nature in Caldeira & Wickett Anthropogenic carbon and ocean pH. Copyright 2003, Macmillan Publishers Ltd. <http://www.nature.com>).*



concentration of hydrogen ions from pre-industrial times. The simulated atmospheric CO<sub>2</sub> exceeds 1 900 ppm at around 2300, and the maximum reduction in pH in the oceans' surface would be 0.77 units (Figure 6). The lowering of pH would be moderated slightly by factors such as changes in temperature, but by less than 10%. Taking this example, even at high CO<sub>2</sub> concentrations, with a significant lowering of ocean pH, the carbonate buffer means that the oceans are still slightly alkaline (ie a pH of less than 7). These changes in ocean pH are outside the range of natural variability and, as we evaluate in Sections 3 and 4, could have a substantial affect on and biological processes in the surface oceans.

Even the current level of ocean acidification is essentially irreversible during our lifetimes. It will take tens of thousands of years for ocean chemistry to return to a condition similar to that occurring at pre-industrial times, about 200 years ago.

The delay arises because it takes tens of thousands of years for mixing to take place throughout the oceans. This mixing is required to bring up compounds from the oceans' sediments to buffer the changes as a result of increased CO<sub>2</sub> on ocean surface chemistry. As we have highlighted above, the oceans have in the past been able to adapt to increased atmospheric CO<sub>2</sub> levels because the rate of change took place over time periods that enabled sufficient mixing with deeper waters.

Warming of the oceans, as a result of global warming, may also reduce the rate of mixing with deeper waters and this would further delay recovery.

## 2.7 The role of carbon chemistry in ocean systems

Below we provide an introduction to the important chemical changes that are predicted to affect marine biological processes.

### 2.7.1 Effects on calcium carbonate and saturation horizons

Marine organisms that construct CaCO<sub>3</sub> structures, such as shells, are dependent on the presence of bicarbonate and carbonate forms of dissolved inorganic carbon in seawater. Once formed, CaCO<sub>3</sub> will dissolve back into the water unless the surrounding seawater contains sufficiently high concentrations of carbonate ions (CO<sub>3</sub><sup>2-</sup>) (ie it is saturated) (Annex 1). Calcium carbonate also becomes more soluble with decreasing temperature and increasing pressure, and hence with ocean depth. It is also affected by the flow of CO<sub>2</sub>-rich deep waters between ocean basins (Section 2.3). A natural boundary develops in seawater as a result of these different variables. This is known as the 'saturation horizon' and it identifies a clear depth of seawater above which CaCO<sub>3</sub> can form, but below it dissolves.

The marine organisms that produce  $\text{CaCO}_3$  shells live above the saturation horizon, where  $\text{CaCO}_3$  does not readily dissolve. Increasing  $\text{CO}_2$  levels and the resultant lower pH of seawater decreases the saturation state of  $\text{CaCO}_3$  and raises the saturation horizon closer to the surface. Therefore increases in surface ocean  $\text{CO}_2$  levels could have severe consequences for organisms that make external  $\text{CaCO}_3$  shells and plates.

Calcium carbonate exists in two commonly occurring forms: aragonite and calcite (Box 1). Because the aragonite form of  $\text{CaCO}_3$  is more soluble than calcite, the aragonite saturation horizon is always nearer the surface of the oceans than the calcite saturation horizon. Therefore calcifying organisms that produce the calcite form of  $\text{CaCO}_3$  (coccolithophores and foraminifera) are possibly less vulnerable to changes in ocean acidity than those that construct aragonite structures (corals and pteropods) (see Figure 7 and Table 2 for a description of the key groups of relevant marine life within the oceans). Projected changes in pH and the calcite and aragonite saturation state in the surface oceans in 2100 under a range of possibilities for future  $\text{CO}_2$  emissions are shown in Figure 6 (based on IPCC 2000). When modelled under one of the more modest emission scenarios (B1), which projects cumulative  $\text{CO}_2$  emissions to be about 900 Gt C by 2100, the Southern Ocean is already undersaturated with respect to aragonite. This would mean that any aragonite  $\text{CaCO}_3$  structure produced by organisms in this environment would dissolve. The cold Southern Ocean is particularly vulnerable to changes in saturation levels because it currently has very low saturation levels. The impacts of changing carbonate saturation on ecosystems, particularly for coral reefs, and the Southern Ocean are examined in greater detail in Sections 4.2.1 and 4.2.2.

### **Box 1 Forms of calcium carbonate**

Calcium carbonate ( $\text{CaCO}_3$ ) exists in two main structures. These are (i) aragonite, which has orthorhombic symmetry in its structure, and (ii) calcite, which is trigonal. Both aragonite and calcite are abundant in organisms. However, because of its structure, calcite is less soluble.

As we describe in Sections 3 and 4, these  $\text{CaCO}_3$  structures are widespread and integral to the biology of key species in the marine ecosystem, including primary producers and herbivores.

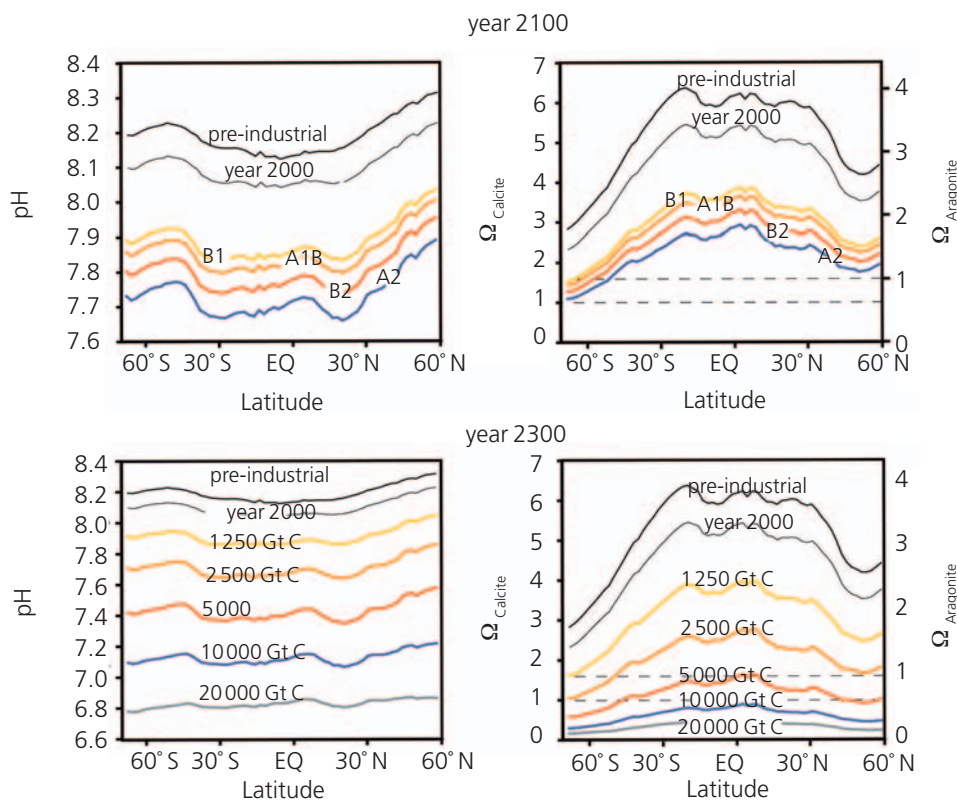
Throughout the report the phrase undersaturated with respect to  $\text{CaCO}_3$  (aragonite, calcite or both), refers to the situation where there is insufficient  $\text{CaCO}_3^{2-}$  available to prevent  $\text{CaCO}_3$  dissolving in sea water. In practice this also means there is insufficient  $\text{CO}_3^{2-}$  available for organisms to make  $\text{CaCO}_3$  structures. This results from factors, such as ocean acidification, changing ocean chemistry.

The saturation level of the calcite and aragonite horizons can be mapped, and the changes can be shown between the present and pre-industrial locations of the horizons resulting from penetration of  $\text{CO}_2$  into seawater from human activities (Feely et al 2004). Lower seawater temperature towards the poles means that the saturation levels are lower at higher latitudes (Figure 5). Across most of the oceans the saturation horizon, for the calcite form, occurs at depths between 1.5 to 5 km and, for the aragonite form, at depths between 0.5 to 2.5 km below the surface of the oceans.

The production of  $\text{CaCO}_3$  by free-floating organisms plays a key role in the biological pump (Figure 3). Once the organism dies, the  $\text{CaCO}_3$  causes it to sink, thereby taking its carbon content to the deeper waters. If the saturation horizon moves closer to the surface, this would lead to both a reduced production of  $\text{CaCO}_3$  by organisms and an increased dissolution of calcified structures. These effects may have serious consequences for the amount of carbon that is produced in the near-surface waters and sequestered into the deeper oceans. However effects of this kind may be offset by an increase in the production of other organic carbon compounds by surface marine organisms. The biological role of  $\text{CaCO}_3$  and organic carbon is discussed in more detail in Section 3.5.

The formation of  $\text{CaCO}_3$  leads to an increased  $\text{CO}_2$  concentration in the water. This apparently counterintuitive behaviour arises because two ions of bicarbonate ( $\text{HCO}_3^-$ ) react with one ion of doubly charged calcium ( $\text{Ca}^{2+}$ ) to form one molecule of  $\text{CaCO}_3$ , which leads to the release of one molecule of  $\text{CO}_2$ . Some of this released  $\text{CO}_2$  is converted to bicarbonate by the buffering process, outlined above and in Annex 1. Under current conditions, for each molecule of  $\text{CO}_2$  produced during calcification about 0.6 molecules are released, potentially to the atmosphere, while the rest is taken up by the bicarbonate-carbonate buffer (Ware et al 1992). As the capacity of the oceans to buffer  $\text{CO}_2$  decreases with increasing acidity, this ratio is expected to increase. Specifically, if  $\text{CO}_2$  emissions continue at their present rate, atmospheric concentration is estimated to reach about 700 ppm by 2100 (IPCC 2001). It is then estimated that, by 2150, for each  $\text{CO}_2$  molecule produced from calcification 0.79 molecules would be potentially released to the atmosphere (Zondervan et al 2001). This would increase the total emission of  $\text{CO}_2$  from the oceans as a result of the calcification process by about 0.22 Gt C per year, and this would lead to a change in  $\text{CO}_2$  emissions from about 0.63 Gt C per year in 1850 to about 0.85 Gt C per year in 2150 (Zondervan et al 2001). However, it is important to stress that this calculation assumes that the rate of calcification would remain constant, at about 1 Gt C per year, and not be affected by changes in the acidity. A decrease in calcification resulting from increased acidity would counteract this increase and according to some estimates, would decrease the total emission from the oceans, providing a

Figure 6. Modelled variations in pH and calcite ( $\Omega_{\text{Calcite}}$ ) and aragonite ( $\Omega_{\text{Aragonite}}$ ) saturation state in the surface oceans modelled for a range possibilities for future  $\text{CO}_2$  emissions in 2100 (top panels). The bottom panels show the total amount of carbon projected to be emitted by 2300 (based on IPCC 2000). B1 represents the most benign scenario with lowest  $\text{CO}_2$  emissions, whereas A2 and B2 could be regarded as the changes predicted to occur if  $\text{CO}_2$  emissions continue at current levels. Pre-industrial and year 2000 values shown at the top are calculated from Key et al (2004). Dashed lines show calcite and aragonite saturation horizons where a saturation state of less than 1 is undersaturated. The Southern Ocean is regarded as the area below latitude  $50^\circ\text{S}$ . As the graphs on the right indicate the Southern Ocean will be undersaturated for aragonite by 2100 under the A2 scenario. By 2300 even ambitious targets for emissions will lead to undersaturation across large parts of the oceans. Chemistry changes are computed from zonal mean average concentrations in the three-dimensional ocean model. (Caldeira & Wickett in press). Copyright 2005, American Geophysical Union. (Physical oceanographic modelling is based on Bryan (1969) and Cox (1984)).



negative feedback on increasing atmospheric  $\text{CO}_2$  concentrations (Zondervan et al 2001). Essentially this is an area of great uncertainty. This example is provided, in part to highlight the complexity of the interactions between the chemical and biological processes in the oceans.

### 2.7.2 Impacts of acidification on the chemistry of nutrients and toxins

Substances in seawater other than the components of the  $\text{CO}_2$ -bicarbonate-carbonate system are significant for life in the oceans as nutrients or as toxins. Nutrients are essential for life, whereas toxins are damaging. In some cases essential nutrients act as toxins when present at high concentrations; examples are the trace elements copper and zinc. In addition to changes in the carbonate system, ocean acidification is expected to produce changes in ocean chemistry that may affect

the availability of nutrients and toxins to marine organisms.

The chemical form of an element in seawater (its speciation) is affected by the presence of other chemical 'species' with which it may interact. Among these is the hydrogen ion concentration. Metals exist in two forms in seawater; complex and free dissolved. The main concern about changes in metal speciation is that it is generally the free dissolved form that is most toxic. A decrease in pH generally increases the proportion of free dissolved forms of toxic metals.

However, the impact (deleterious or advantageous) of pH-induced changes in seawater speciation is difficult to determine. The role of trace elements in the biochemistry, and of trace element availability on the growth of marine micro-organisms are topics of active research.

Phytoplankton growth rates are known to be limited by iron

Table 1. Changes to ocean chemistry and pH estimated using the OCMIP3 models calculated from surface ocean measurements and our understanding of ocean chemistry. Note that the concentration of bicarbonate ion ( $\text{HCO}_3^-$ ) and carbonic acid ( $\text{H}_2\text{CO}_3$ ) increase with rising atmospheric concentration of  $\text{CO}_2$  while carbonate ion ( $\text{CO}_3^{2-}$ ) decreases. The average pH of the surface ocean waters decreases with increasing atmospheric  $\text{CO}_2$  concentration. (Assumptions used in model: Total alkalinity = 2324 mol/kg, temperature = 18° C. All other assumptions as per OCMIP3 (Institut Pierre Simon Laplace 2005). Aragonite and calcite saturation calculated as per Mucci & Morse (1990). Physical oceanographic modelling is based on Bryan (1969) and Cox (1984).

	Pre-industrial	Today	2 × pre-industrial	3 × pre-industrial	4 × pre-industrial	5 × pre-industrial	6 × pre-industrial
Atmospheric concentration of $\text{CO}_2$	280 ppm	380 ppm	560 ppm	840 ppm	1120 ppm	1400 ppm	1680 ppm
$\text{H}_2\text{CO}_3$ (mol/kg)	9	13	19	28	38	47	56
$\text{HCO}_3^-$ (mol/kg)	1768	1867	1976	2070	2123	2160	2183
$\text{CO}_3^{2-}$ (mol/kg)	225	185	141	103	81	67	57
Total dissolved inorganic carbon (mol/kg)	2003	2065	2136	2201	2242	2272	2296
Average pH of surface oceans	8.18	8.07	7.92	7.77	7.65	7.56	7.49
Calcite saturation	5.3	4.4	3.3	2.4	1.9	1.6	1.3
Aragonite saturation	3.4	2.8	2.1	1.6	1.2	1.0	0.9

availability over at least 10% of the oceans' surface (Boyd et al 2000). Therefore any effect of pH on iron speciation may be important in these areas and reduce the iron limitation, as one effect of reduced pH would be to increase the proportion of soluble to insoluble iron (Morel et al 2003).

A decrease in pH will also probably change the nature and form of particle surfaces in seawater and hence have an additional indirect effect on the speciation of trace metals (Mouvet & Bourg 1983). Indeed, the main impact of change in pH on speciation of trace metals may be to release previously bound metals from the sediment to the water column. This could be of particular importance in shallow seas.

There appear to have been no studies of the impact of change in pH on nutrient speciation. It therefore remains unclear whether such changes would significantly affect biological systems. However, theoretical speciation diagrams allow a qualitative prediction of the effect of pH on nutrient speciation (Zeebe & Wolf-Gladrow 2001). These show significant changes in speciation of phosphate, silicate, iron and ammonia within the range of decrease in pH considered in this report. Reduced pH would, for example, lower the concentrations of ammonia ( $\text{NH}_3$ ) in seawater in preference to ammonium ( $\text{NH}_4^+$ ). In mesotrophic coastal waters with frequently high nutrient concentrations, a change of pH from 8.1 to 7.8 halves the fraction of  $\text{NH}_3$  in the ratio of  $\text{NH}_4^+:\text{NH}_3$  (Raven 1986). Further quantitative research is required on the impacts of pH on nutrient speciation, concentration and availability and their non-equilibrium behaviour that is typical of natural systems.

The biological implications of these changes in chemical speciation are considered in Section 3.

## 2.8 Conclusions

The chemical changes in the oceans caused by increases in the concentration of  $\text{CO}_2$  in the atmosphere will include a lowering of the pH, an increase in dissolved  $\text{CO}_2$ , a reduction in the concentration of carbonate ions and an increase in bicarbonate ions.

The oceans are currently taking up about one tonne of  $\text{CO}_2$  associated with human activities per year for each person on the planet (IPCC 2001). Almost half of the  $\text{CO}_2$  produced in the past 200 years by burning fossil fuels and cement manufacture has been absorbed by the oceans. This has already resulted in a change to ocean chemistry, reducing surface seawater pH by about 0.1 units, which corresponds to an increase of about 30% in the concentration of hydrogen ions.

The affects of possible impacts of future cumulative  $\text{CO}_2$  emissions by 2100 have been modelled for the oceans. These models, including analyses from the GLODAP, International Carbon-cycle Model Intercomparison Project Phase 3 (OCMIP3) and the LLNL presented in this Section, rely on the same basic modelling approaches (Bryan 1969; Cox 1984). These studies show that even at a modest future projection of  $\text{CO}_2$  emissions, of about 900 Gt C, direct impact of ocean acidification is very likely to cause the Southern Ocean to become undersaturated with respect to aragonite. This would lead to severe consequences for organisms that make the aragonite form of  $\text{CaCO}_3$  shells and plates.

As more CO<sub>2</sub> enters the atmosphere from human activity, more will be taken up by the oceans (Table 1). If CO<sub>2</sub> emissions continue on current trends, this could result in the average pH of the surface oceans decreasing by 0.5 units below the level in pre-industrial times, by 2100. This is beyond the range of natural variability and represents a level probably not experienced for at least hundreds of thousands of years and possibly much longer (Caldeira & Wickett 2003). Critically, the rate of change is also at least 100 times higher than the maximum rate observed during this time

period. These changes are so rapid that they will significantly reduce the buffering capacity of the natural processes that have moderated changes in ocean chemistry over most of geological time.

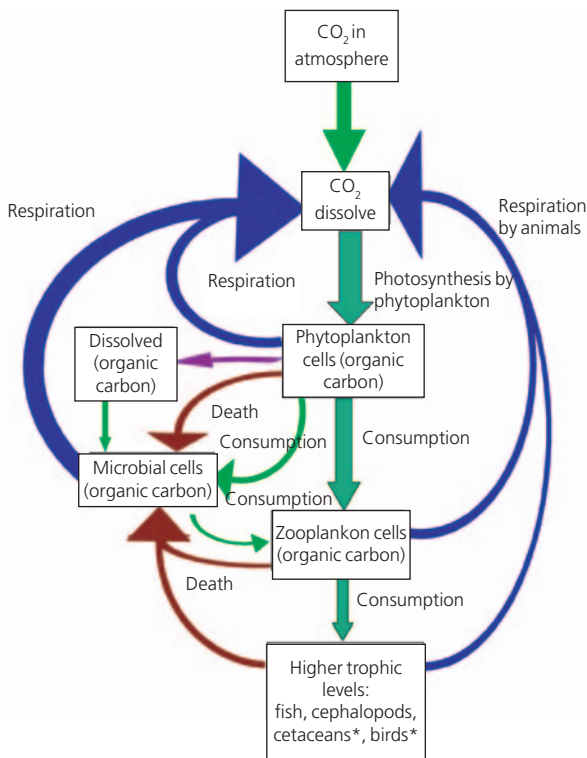
In Sections 3 and 4 we consider the biology of the marine system and examine the implications of the projected changes in ocean chemistry. We then examine the species, populations and ecosystems that may be vulnerable to changes in ocean chemistry.

# 3 Biological impacts: effects of changing ocean chemistry on organisms and populations

## 3.1 Introduction

The increase in surface ocean CO<sub>2</sub> and the corresponding decrease in pH predicted for 2100 represent an extent of change in sea surface chemistry that has not been experienced for at least the past 420 000 years and possibly much longer (Section 2.5). As significant is the rate of this change, which is at least 100 times the maximum rate observed during this time period (Section 2.5). Such extents, and rates, of change will inevitably have effects on organisms in the oceans. Here we discuss the effects these changes in ocean chemistry have on present-day marine organisms (Figure 7; Table 2). We also consider the possibilities of acclimation or adaptation of organisms to the changing environment within the constraints of their current genetic

Figure 7. Importance of micro-organisms (phytoplankton and non-photosynthetic zooplankton and microbial cells) and of larger animals in the marine carbon cycle. The thickness of the lines indicates relative carbon flow through the pathway. \*Cetaceans (whales and dolphins) and birds release CO<sub>2</sub> to the atmosphere, not to water, but this is a minor pathway. The cycle assumes no net input of carbon or loss from the oceans. A similar diagram showing CO<sub>2</sub> flow patterns could also be produced for benthic primary producers, bringing in, for example echinoderms (such as starfish and sea urchins) among the larger animals, but with a similar major role for micro-organisms.



composition, as well as the potential for evolution (genetic changes selected in relation to the changed ocean chemistry).

Photosynthetic marine organisms play a major ecological role, providing more than 99% of the organic matter used by marine food webs. Converting dissolved CO<sub>2</sub> to organic carbon, they account for just under half of the total primary productivity on Earth (Field et al 1998). The vast majority occur as free-floating microscopic phytoplankton, over the whole of the surface oceans. They fix about 50 Gt of carbon per year into their bodies (Field et al 1998), with significant additional extracellular dissolved organic carbon (Engel et al 2004). Most of the organic matter produced by these photosynthetic organisms is immediately or ultimately consumed by other micro-organisms (Figure 7).

The other major primary producers in the oceans are the benthic (bottom-dwelling) photosynthetic organisms, such as seaweed, sea grasses and corals. Limited to shallower waters, they have a net primary productivity of about 1 Gt of carbon per year (Field et al 1998). Despite their limited role in global primary productivity, these benthic primary producers are crucial components of coastal ecosystems, providing, for example, habitats and breeding grounds for other species, as well as recycling nutrients and reducing coastal erosion by reducing the power of waves.

Higher up the marine food webs are the multicellular animals. Although these are dependent on the availability of the micro-organisms for food, and are therefore affected indirectly by changes in ocean carbon chemistry, the physiology of these complex organisms may also be affected directly by changes in ocean chemistry. For animals, such as fish, these direct effects of ocean acidification on their physiology, with other pressures such as fishing, are additional to any changes in the availability of their food species caused by changes in ocean chemistry.

Of all the organisms in the surface oceans the impacts are very likely to be most severe for the calcifying species (Table 2), such as molluscs, crustaceans, echinoderms, corals, large calcareous algae, foraminifera and some phytoplankton. This will occur principally because of a reduction in the availability of the chemical constituents needed for calcified shells and plates, although their physiology may also be affected.

In this section we outline what is known about these organisms and, starting at the base of the food chain, consider how they are likely to be affected by acidification. We consider the direct effect of CO<sub>2</sub> and pH changes on the organisms and the indirect effects

Table 2. Groups of calcified marine organisms with indications of their ability to photosynthesise, the form of CaCO<sub>3</sub> deposited and their habitat. Aragonite dissolves more rapidly at low carbonate concentrations than calcite. Photosynthesis in foraminifera and warm-water corals depends on symbiosis with algae (Lowenstam (1981), Berner & Berner (1996) and references in Section 3.5).

Organisms	Photosynthetic or non-photosynthetic	Form of calcium carbonate	Habitat
Foraminifera	Some photosynthetic	Calcite	Benthic
	Non-photosynthetic	Calcite	Planktonic
Coccolithophores	Photosynthetic	Calcite	Planktonic
Macroalgae*	Photosynthetic	Aragonite or calcite	Benthic
Corals: warm water	Photosynthetic	Aragonite	Benthic
	Non-photosynthetic	Aragonite	Benthic
Pteropod molluscs	Non-photosynthetic	Aragonite	Benthic
Non-pteropod molluscs*	Non-photosynthetic	Aragonite + calcite	Benthic or Planktonic
Crustaceans*	Non-photosynthetic	Calcite	Benthic or Planktonic
Echinoderms	Non-photosynthetic	Calcite	Benthic

\*Not all members of the group are calcified.

through changes in other resources on which they depend. In many cases there are few data, so for example we are generally unable to say whether organisms will be able to adapt to the changing environment in the short term, or evolve in the long term.

### 3.2 Effects of ocean acidification on photosynthetic and non-photosynthetic micro-organisms

This section looks at some of the possible major effects of increased CO<sub>2</sub> and the associated change in ocean pH on micro-organisms. As we discussed in Section 2.7, calcifying organisms could be particularly affected by changes in ocean pH. We therefore look at calcification in detail in Section 3.5. The discussion below considers the other possible effects, aside from calcification, from changes to ocean chemistry on marine organisms.

On land, plants take up CO<sub>2</sub> primarily by diffusion, although some have mechanisms that actively take up CO<sub>2</sub>. As a result, increasing atmospheric CO<sub>2</sub> generally has a positive effect on photosynthesis, productivity and growth (Ainsworth & Long 2005). In contrast, most marine phytoplankton have concentrating mechanisms that actively take up inorganic carbon; either as CO<sub>2</sub> or bicarbonate ions (HCO<sub>3</sub><sup>-</sup>) or both. Because they actively concentrate CO<sub>2</sub>, changes in the pH and CO<sub>2</sub> content of the water have less effect on their photosynthesis (Giordano et al 2005). Carbon-concentrating mechanisms are thought to be less widespread in benthic photosynthetic organisms (Giordano et al 2005).

Variation in the availability of nutrients caused by increasing CO<sub>2</sub> concentration and pH change may also have an indirect effect on the growth of photosynthetic organisms. In particular, changes in pH, as discussed in Section 2.7.2, will affect the availability of nutrients. This

may alter rates of growth and photosynthesis. Changes may also occur in the cell composition, which could affect the nutritional value of the micro-organisms to the animals that feed on them.

#### 3.2.1 Effects on phytoplankton: photosynthetic organisms

##### Photosynthesis

As we underline throughout the report, a reduction in ocean pH (acidification), is one of a number of changes to the oceans that results from increased atmospheric CO<sub>2</sub> levels. It is impossible to differentiate unequivocally between the effects of increased CO<sub>2</sub> and those of decreased pH in experiments on marine organisms, since there is significant co-variance of these environmental factors (see Annex 1). In almost all of the phytoplankton species examined to date, it has been found that doubling the present atmospheric CO<sub>2</sub> concentration has only a small direct effect, 10% or less, on the rate of photosynthesis (Beardall & Raven 2004; Schippers et al 2004; Giordano et al 2005; Figure 8). This conclusion comes from experiments performed on several species to examine their photosynthetic response to altered atmospheric CO<sub>2</sub> concentrations. In some experiments, algae were grown at present-day concentrations, and then exposed to varying CO<sub>2</sub> levels for measurement of their photosynthetic rate. In other experiments, species have also been grown for several generations at altered CO<sub>2</sub> concentrations before having their photosynthetic rates measured (Burkhardt et al 2001; Rost et al 2003; Beardall & Raven 2004). Generally, both types of experiment gave similar results, namely relatively small increases in photosynthesis. This lack of response is primarily due to the presence of carbon-concentrating mechanisms, which mean that even at today's CO<sub>2</sub> concentration photosynthesis is saturated with inorganic carbon.



An important exception to this has been found in the case of the globally very abundant calcifying phytoplankton *Emiliana huxleyi* (Figure 8). This organism exhibits a greater increase in photosynthetic rate in response to elevated  $\text{CO}_2$ . It might be expected to benefit from elevated  $\text{CO}_2$  as a result of this photosynthetic response. However, it is also observed to decrease calcification at elevated  $\text{CO}_2$ , which might offset any beneficial effect due to increased photosynthesis in terms of the growth and competitiveness of the organism (Section 3.5). A complete inhibition of photosynthesis (and growth) was found in two species of marine planktonic dinoflagellate 24 hours after exposure to high  $\text{CO}_2$  (Dason & Colman 2004), although the  $\text{CO}_2$  increase and corresponding pH decrease in those experiments was much greater than those considered likely by this report.

The evidence for the general lack of effect on photosynthesis due to changes in inorganic carbon concentrations resulting from increased atmospheric  $\text{CO}_2$  has been derived mainly from laboratory studies. Many laboratory experiments have involved artificially altering the total inorganic carbon concentrations, the pH value, or both. As a result, the ratios of  $\text{CO}_2$  and  $\text{HCO}_3^-$  do not mimic the change that would be found if atmospheric  $\text{CO}_2$  was increased (Giordano et al 2005). Some experiments that change the gas phase of  $\text{CO}_2$ , to mimic the situation in the real world, have been carried out in the laboratory and in mesocosms. The results are similar to those from the other types of manipulation of the inorganic carbon system (Burkhardt et al 2001; Rost et al 2003).

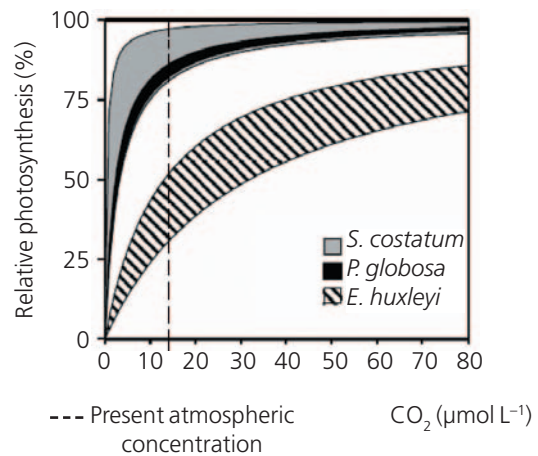
Most of the experiments conducted on marine phytoplankton have been short term and did not provide sufficient time for any genetic modifications that might allow them to adapt to the change in conditions. Further long-term experiments are required to determine if the organisms will evolve to take advantage of the increased  $\text{CO}_2$ . This is discussed further in Section 3.6.

### Growth and composition

Experiments carried out so far show that increased (even double) atmospheric  $\text{CO}_2$  concentrations have relatively little direct effect on the growth rate and the elemental composition of marine phytoplankton (Burkhardt et al 1999; Gervais & Riebesell 2001). There is also the possibility of indirect effects through changes in nutrient availability and in the toxic substances, resulting from the decreased pH (Section 2.7.2).

In recent mesocosm studies (Riebesell personal communication) there was an increase in inorganic carbon assimilation, and also in the ratios of carbon to nitrogen and carbon to phosphorus in phytoplankton, at 750 ppm  $\text{CO}_2$  compared with the present day (380 ppm)  $\text{CO}_2$  levels. Other studies showed little effect of such

Figure 8. Photosynthesis of phytoplankton species differ in sensitivity to  $\text{CO}_2$  concentrations. Although most species (here *Skeletonema costatum* and *Phaeocystis globosa*) reach their maximum photosynthetic rate under present-day ambient  $\text{CO}_2$  levels (14.7  $\mu\text{mol}$  per litre), some species, such as the coccolithophore *Emiliana huxleyi* show increased rates of photosynthesis when  $\text{CO}_2$  is increased above present levels. This raises the possibility that coccolithophores may benefit directly from the current increase in atmospheric  $\text{CO}_2$ . The range in photosynthetic rates for each organism reflects the extent of which the physiology of the organism changes as a function of the concentration of  $\text{CO}_2$  at which they are grown. (Reprinted from Rost & Riebesell (2004) with permission of Springer Science and Business Media).



changes in  $\text{CO}_2$  on the productivity of a natural assemblage of phytoplankton species (Hein & Sand-Jensen 1997; Tortell et al 2002).

The effect that increasing  $\text{CO}_2$  has on growth rate and cell composition needs to be superimposed on the availability of other resources. Some of these resources can be limiting: for example, nitrogen for much of the world's oceans; and for parts of the oceans or at particular times, iron and phosphorus. Climate change may alter this availability, with rising temperatures tending to increase stratification and reduce mixing with nutrient-enriched deeper waters. In areas when there is deep mixing (tens of metres or more) of the surface oceans, light can become a limiting factor for phytoplankton growth. It is known that, measured over short periods, the dependence of photosynthesis on the  $\text{CO}_2$  concentration during growth is affected by the availability of these resources (Giordano et al 2005).

Many of the data on growth and composition have come from laboratory experiments. However, these experiments have not always been performed under the nutrient-limiting conditions that may occur in the oceans. Further experiments are needed to show the effects of total nutrient concentrations and ratios of nutrient species, such as nitrogen, phosphate, iron and (for diatoms) silicic acid.

There are insufficient data to draw any conclusions about the impacts that increasing CO<sub>2</sub> might have on the growth and composition of marine phytoplankton. In addition, experiments so far have not been long enough to indicate if existing species will be able to evolve to changing conditions. However, any reduction in the total biomass production by phytoplankton, either through reduced photosynthesis or from greater energy demand to obtain nutrients, could have significant implications for marine food webs. In addition, these effects of increasing CO<sub>2</sub> concentrations need to be considered in relation to other environmental changes. Further experiments are needed on the effect of changes in pH on phytoplankton nutrition for nutrients supplied as solutes whose extent of ionisation varies with pH in the relevant range of pH values; such experiments should use both growth-limiting and growth-saturating concentrations of the nutrients.

### ***Extracellular polysaccharides***

For phytoplankton, a significant component of the organic carbon produced by photosynthesis is dissolved extracellular organic carbon, of which much is polysaccharide. Production of extracellular dissolved organic carbon is a rather variable fraction of photosynthesis, with 3–40% found for different natural marine planktonic systems. This provides an important food source for non-photosynthetic micro-organisms in the surface oceans. The proportion of the total organic carbon produced by cells that appears as extracellular polysaccharides is increased by higher CO<sub>2</sub> concentrations, but additional photosynthesis (for example in *E. huxleyi*; Figure 8) with increased CO<sub>2</sub> could increase the rate of extracellular organic carbon production (Engel 2002; Engel et al 2004, 2005).

These polysaccharides are also important in the aggregation and then sedimentation of phytoplankton cells and other particles (Engel et al 2004). This means that increased CO<sub>2</sub> could potentially increase particle sedimentation in the 'biological pump' (Section 2.2.2). However, this needs to be balanced against reductions in calcification by coccolithophores caused by increased CO<sub>2</sub> levels (Riebesell et al 2000; Section 2.7.1), reducing the input of mineral ballast and hence decreasing the rate of sinking of the aggregates (Section 5.2).

Further work is needed to understand how increases in CO<sub>2</sub> affect organic carbon sedimentation, and the consequences for feedback effects on surface CO<sub>2</sub> concentrations and on the absorption of CO<sub>2</sub> from the atmosphere, and hence to the global carbon cycle.

### **3.2.2 Effects on non-photosynthetic micro-organisms**

Non-photosynthetic micro-organisms in the oceans include archaea, bacteria, fungi and a range of protists including flagellates and ciliates. They feed on organic

particles, dissolved organic matter and inorganic nutrients, producing CO<sub>2</sub> and other gases such as halo-carbons (Section 5). These organisms play major roles in the marine carbon cycle, because they are the main means by which primary productivity in the oceans is recycled to CO<sub>2</sub> (del Giorgio & Williams 2005; Figure 7). They are abundant in the open oceans as well as in muddy and sandy benthic habitats (Section 3.3). Although their physiology suggests that they will respond to increased CO<sub>2</sub> in the surface oceans and to decreased pH, there are few data available to demonstrate any responses and therefore impact that this might have on the functioning of the organisms in their natural environment.

Like photosynthetic micro-organisms, non-photosynthetic micro-organisms are affected by changes in the concentration and speciation of nutrients as a result of changes in pH (Section 2.7.2). Seawater pH also affects the mechanisms that transport these solutes into the cells. Apart from depending on photosynthetic micro-organisms for food, the non-photosynthetic micro-organisms that grow in the illuminated surface oceans are in direct competition with them for inorganic nutrients, but not for CO<sub>2</sub>. Any changes in this nutrient supply may alter the productivity of either group.

Compared with marine photosynthetic phytoplankton, non-photosynthetic micro-organisms have a greater metabolic diversity. One example of a metabolic process is nitrification (conversion of ammonia (NH<sub>3</sub>) and ammonium (NH<sub>4</sub><sup>+</sup>) to nitrate), which occurs mainly in the non-illuminated part of the oceans. The organisms responsible for this part of nitrification can only use ammonia as their substrate. In experiments simulating the pH decrease likely to occur in very high CO<sub>2</sub> concentrations, Heusemann et al (2002) found a drastic reduction in the rate of nitrification. If this concentration was reached in surface waters it could lead to accumulation of ammonium instead of nitrate. However, these experiments were done at significantly greater concentrations of CO<sub>2</sub> than is likely to occur as a result of human-produced emissions of CO<sub>2</sub> to the atmosphere.

Micro-organisms and dead organic particles provide a valuable food supply for benthic invertebrate detrital and suspension feeders, again producing CO<sub>2</sub> and inorganic nutrients. The micro-organisms living deeper in muddy and sandy sediments are less exposed to the direct influence of increases in surface ocean CO<sub>2</sub> than are those living nearer the sediment surface or in the plankton (Section 4.2.3).

### **3.3 Effects of ocean acidification on photosynthesis in benthic organisms**

The dominant primary producers growing on the sea bed, in areas where the oceans are shallow enough to allow photosynthesis to occur, are large algae (seaweeds), marine flowering plants (seagrasses) and, in some

warmer waters, photosynthetic coral reefs. The seagrasses mainly grow rooted in mud or sand, whereas most seaweed and all corals are attached to solid, rocky substrata.

Compared with the work on phytoplankton, fewer data are available on the effects of increased concentration of CO<sub>2</sub> on photosynthetic rate and especially on growth rate and composition of seaweeds, seagrasses and the alga–invertebrate and alga–protist symbioses, such as corals and benthic foraminifera (Beer et al 2002; Giordano et al 2005). However, compared with marine phytoplankton, there seems to be a larger fraction of the species of benthic macro-organisms studied that show increased rates of photosynthesis as CO<sub>2</sub> is increased above the present atmospheric level (Giordano et al 2005). Experiments conducted on a species of red seaweed, that are believed to rely on CO<sub>2</sub> entry by diffusion, found that CO<sub>2</sub> at twice the present atmospheric level increased the growth rate very significantly (Kübler et al 1999). It is difficult to draw conclusions about whether benthic plants rely more on CO<sub>2</sub> diffusion than phytoplankton as there is insufficient information about the use of carbon-concentrating mechanisms.

It would be unwise to generalise from these very limited data. More work is needed to establish how the production of organic material by these benthic organisms responds to increased CO<sub>2</sub> in the surface oceans. However, this community of primary producers plays an important ecological and economical role; any change in their productivity could have significant implications.

### **3.4 Effects of ocean acidification on multicellular animals**

#### **3.4.1 Changes to physiology of larger animals**

The larger marine animals that live in the oceans and do not breathe air, such as fish and the larger invertebrates including some zooplankton, take up oxygen and lose respired CO<sub>2</sub> through their gills. Increased CO<sub>2</sub> and decreased pH could have a major effect on this respiratory gas exchange system. This is because oxygen is much harder to obtain from surface seawater than it is from air, mainly due to the lower oxygen concentration in water. The processes involved in supplying oxygen to the gills means that more CO<sub>2</sub> is removed from these aquatic animals than is removed from air breathing animals of a similar size. This more ready removal of CO<sub>2</sub> from body fluids means that the level and range of CO<sub>2</sub> concentration in the bodies of water-breathing animals are much lower than is the case for air-breathing animals. As a result, large water breathing marine animals are more sensitive to changes in the CO<sub>2</sub> concentration in the surrounding seawater than are large air-breathing animals. This has important implications as increased CO<sub>2</sub>

will acidify the body tissues and fluids and affects the ability of blood to carry oxygen.

Known as hypercapnia, acidification of body fluids of marine animals as a result of increasing external CO<sub>2</sub> occurs rapidly, in a matter of hours. In addition to reducing the pH, increased CO<sub>2</sub> concentration also changes the levels of bicarbonate and other ions. Small changes can be buffered within the cell, but larger changes require the active secretion of ions out of the body through specialised cells. In fish, the structure and activity of some of these secretion cells changes after 24 hours of hypercapnia. Some fish can change the density of these cells in a matter of hours or days, giving them greater tolerance to acidification (Ishimatsu et al 2004).

There is strong experimental evidence that acidosis of tissues will decrease cellular energy use and lower respiratory activity (Pörtner et al 2000, 2004). Evidence is also increasing of lower rates of protein synthesis, under these conditions, with impacts on almost all aspects of the functioning of larger animals including growth and reproduction (Langenbuch & Pörtner 2002, 2003). Experiments have shown that rising external atmospheric CO<sub>2</sub> will increase mortality, in some cases quite significantly (Kikkawa et al 2004). However, these experiments correspond to higher seawater CO<sub>2</sub> concentrations than are expected up to 2100, and more research is needed to understand if large mortality events, such as fish kills, will result from even the extreme projections of future atmospheric CO<sub>2</sub> concentrations.

Some animals, particularly deep sea fish and Cephalopods such as squid, are very sensitive to increases in external CO<sub>2</sub> (Ishimatsu et al 2004). Squid are particularly sensitive because of their highly muscular and energy-demanding way of movement (jet propulsion), which is fundamentally different from the lower-energy demands of undulatory swimming seen in fish (Pörtner and Zielinski 1998). This high-energy use requires a good supply of oxygen from the blood. However, this can be severely compromised by increasing CO<sub>2</sub> concentration, as it lowers the pH of the blood thereby reducing its ability to carry oxygen. However, the experiments (Pörtner and Reipschläger 1996) showing large effects involve CO<sub>2</sub> concentrations higher than those considered reasonable given projected future CO<sub>2</sub> concentrations, and further work is needed to explore the effects of smaller increases in seawater CO<sub>2</sub> concentrations.

#### **3.4.2 Changes to reproduction in larger animals**

The effects of increasing CO<sub>2</sub> on multicellular animals appear to vary throughout the lifecycle. In freshwater fish, pH is known to affect the physiology and activation of sperm. In steelhead trout (*Oncorhynchus mykiss*), for example, decreasing pH from 8.5 to 7.5 units by increasing the partial pressure of CO<sub>2</sub> resulted in a 40% reduction in respiration rate (Ingermann et al 2003). It is not known whether marine fin-fish are equally sensitive,

but significant loss (40%) of sperm motility of Pacific oysters (*Crassostrea gigas*) has been shown in much larger changes in pH from 8 to 6 units (Dong et al 2002); however, this is beyond any expected changes in the oceans due to increases in atmospheric CO<sub>2</sub> concentration up to the year 2300. Experiments have also demonstrated significant decreases in egg production by copepods, but no effect on survival of adults, over the 8 days tested using CO<sub>2</sub> values well in excess of what is expected in future oceans (Kurihara et al 2004a, 2004b). In another experiment, lower pH decreased hatching of the egg sacs of a gastropod mollusc (*Babylonia areolata*) farmed in the Far East (Luo et al 2004). Other studies using very high concentrations of CO<sub>2</sub>, beyond what is expected in the future oceans, have also shown effects on the embryos and larvae of silver sea bream (*Pagrus major*) (Ishimatsu et al 2004) and on the reproductive success of sea urchins (Kurihara et al 2004a). These experiments suggest that the early stages of the life cycle may show the greatest sensitivities to increased CO<sub>2</sub> concentrations, with potentially widespread implications for population size, community structure and biodiversity. However, as with effects on other life-cycle stages, the CO<sub>2</sub> concentrations used in these were greater than those considered likely in the future oceans. There is an urgent requirement for experiments addressing the effects of smaller increases in CO<sub>2</sub> on the reproduction of marine animals.

### 3.5 Effects of ocean acidification on calcifying organisms

#### 3.5.1 Introduction

The formation of shells or plates of CaCO<sub>3</sub>, by calcification, is a widespread phenomenon among marine organisms, such as most molluscs, corals, echinoderms, foraminifera and calcareous algae. Although it is not always clear what function this calcification has, it seems integral to their biology; so any decrease in calcification, as a result of increased CO<sub>2</sub>, is therefore likely to have significant consequences such as the weakening of coral skeletons and reef structures generally.

Calcification is a tightly controlled process and generally requires biological initiation even in the present day surface seawater which is super-saturated with respect to CaCO<sub>3</sub>. However, the mechanism of calcification is currently poorly understood. It can be intracellular, in specific calcifying compartments, or on external surfaces, which suggests that large differences exist in the mechanisms and transport routes leading up to the precipitation reaction. The various groups of calcifying organisms also differ in the crystal structure and chemical composition of their carbonate skeletons (Section 2.7.1; Table 2). Whereas corals and a group of molluscs called pteropods precipitate aragonite, coccolithophores (calcifying phytoplankton) and foraminifera (protist plankton) produce the less soluble calcite, generally in

internal compartments. Mollusc shells consist of layers of either all aragonite or inter-layered aragonite and calcite. Echinoderms, which include sea urchins, sea stars and brittle stars, form calcite structures that are high in magnesium and have a very high porosity often exceeding 50%. Calcareous benthic algae precipitate either high-magnesium calcite or aragonite and perform the important function of 'gluing' the skeletons of corals together to create reefs. Despite this variation the principal steps of calcification are likely to be similar in each case.

To make these calcareous structures, seawater has to be supersaturated with calcium (Ca<sup>2+</sup>) and carbonate (CO<sub>3</sub><sup>2-</sup>) ions to ensure that once formed the CaCO<sub>3</sub> does not dissolve. Lower pH reduces the carbonate saturation of the seawater, making calcification harder and also weakening any structures that have been formed. Although calcite is less soluble than aragonite, making it less susceptible to pH changes, the incorporation of magnesium into either form increases their solubility.

#### 3.5.2 Calcified protists and algae

Foraminifera are important in global ocean calcification in both the plankton and in bottom-dwelling environments. They are thought to form high-magnesium calcite during the initial stages of calcification, but without going through a step involving an amorphous precursor of high solubility (Erez 2003). This is in contrast with the echinoderms considered below (Section 3.5.3). The encapsulation of seawater has been proposed as the starting point for calcification for some calcifying organisms such as foraminifera (Erez 2003). During the calcification process the alkalinity of the captured water is lowered (the pH decreases). To compensate for this the organism is thought to actively raise the pH, which immediately increases the carbonate ion (CO<sub>3</sub><sup>2-</sup>) concentration. If the pH of the ambient water is already decreased, this process will therefore require more energy, which may explain the decrease in calcification with decreasing pH. Allocating more energy to calcification to counteract the effect of decreasing pH could mean that less is available for other vital metabolic processes, which may reduce the growth and fitness of the organism.

In laboratory experiments on the symbiont-bearing foraminiferans, the shell weights of *Orbulina universa* and *Globigerinoides sacculifer* varied with the carbonate ion concentration of the seawater (Bijma et al 1999, 2002). Similar results were obtained for the foraminifera *Amphistegina lobifera* and *A. hemprichii* (Erez 2003). A strong reduction in the calcification rate occurred as pH decreased from 9 to 7. The trend reverses above pH 9, with calcification rate decreasing as pH increases. A positive correlation between foraminiferal shell weight and the carbonate ion concentration (and the carbonate saturation state) is also observed in the palaeoceanographic record as a response to known glacial–interglacial changes in atmospheric CO<sub>2</sub> of the past 50 000 years (Barker & Elderfield 2002). Plotting

calcification rate versus the carbonate ion concentration reveals a similar slope, with a two- to threefold increase in calcification rate with  $\text{CO}_3^{2-}$  increasing from 100 to 400  $\mu\text{M}$  (Erez 2003).

Coccolithophores are planktonic algae whose photosynthesis, in the species investigated, is not saturated at present levels of  $\text{CO}_2$  (Section 3.2.1). The coccolithophores are considered to be the most productive calcifying organisms on Earth. They are covered with one to several layers of minute calcite platelets, the coccoliths. The coccoliths are produced inside the coccolithophore cells, and do not involve the internalisation of seawater (Berry et al 2002). Benthic macroalgae deposit either calcite or aragonite externally.

### 3.5.3 *Calcified larger animals*

Corals, crustaceans, echinoderms and molluscs are important calcified benthic animals, and calcified crustaceans and molluscs are significant members of many pelagic marine communities. As we show in Sections 3.5.4 and 4.2.1, the mechanical function of calcification is obvious in these calcified animals.

Echinoderms are among several groups that may be especially sensitive to ocean acidification. The larvae of sea urchins and also of molluscs have been shown to form skeletal parts consisting of magnesium-bearing calcite that form through an amorphous precursor phase, which is 30 times more soluble than calcite without magnesium (Politi et al 2004). The same type of skeletal material is used by most adult echinoderms. Lower pH in the oceans may inhibit the formation of these highly soluble amorphous calcite precursors, which echinoderms need in the construction of their shells. Further work is needed on the mechanism of calcification in echinoderms, in view of their importance in many coastal ecosystems: in some cases they are keystone predators (sea stars) or very important grazers (urchins). This is also true of coastal molluscs and arthropods, which in addition are also of great economic importance. Crustacea may be a particularly vulnerable group because of their dependence on the availability of calcium and bicarbonate ions for the mineralization of their exoskeleton after moulting. In freshwater species this mineralization the animals' ability to control blood pH is affected by changes in water composition in intensive culture, particularly in recirculation systems (Brown et al 1991). Similar effects may occur in marine species, although further work is needed to establish the significance of effects within the range of seawater  $\text{CO}_2$  concentrations considered in this report.

### 3.5.4 *Functions of calcification and effects of decreased calcification*

Decreased calcification may equally influence the organism's competitive fitness, but this ultimately

depends on the functional role of the calcareous structures or the metabolic function of the calcification process. The function of calcareous structures is obvious in some groups of organisms, such as for the structural frameworks of corals or the exoskeletons serving as mechanical protection in pteropods and foraminifera. Reduced calcification in corals can translate into declining coral cover and reduced, possibly disappearing, reef frameworks (Gattuso et al 1999; Kleypas et al 2001). A decrease in carbonate supersaturation may also weaken carbonate skeletal structures, making them more susceptible to erosion (both physical and biological) and dissolution. This effect, which will be most pronounced in aragonitic groups such as the pteropods, would presumably compromise the fitness of these organisms and could shift the ecological and evolutionary competitive advantage to non-calcifying organisms.

The function of calcification is less clear in other groups such as the coralline algae and coccolithophores. A variety of protective, metabolic and adaptive functions have been proposed for calcification in coccolithophores (Brownlee & Taylor 2004), but the evidence remains for the most part inconclusive.

In addition to structural roles for calcification, calcium carbonate deposits can also influence the acid-base balance in anoxia (absence of oxygen) (Booth et al 1984; Lindinger et al 1984). Anoxia occurs, counter-intuitively, when intertidal organisms are exposed to air at low tide and seal themselves off from exposure to the air in limiting water loss at the expense of preventing entry of oxygen.

As calcium carbonate structures make organisms denser, increased sinking rate is therefore an unavoidable consequence of calcification in planktonic organisms that are unable to swim. This includes the most abundant, non-flagellated (flagellates are used in propulsion) stages of coccolithophores, and planktonic foraminifera, because calcite is denser than other components of the organisms. This argument also applies to the aragonite-depositing pteropods after they have died and can no longer swim. It is not clear what competitive advantage this increased sinking caused by calcification might offer and therefore it is difficult to conclude how it might have evolved (Raven and Waite 2004). However, regardless of the evolutionary basis for calcification, a reduction in calcification decreases the amount of ballast available for the sedimentation of organic matter and  $\text{CaCO}_3$ , which has implications for the operation of the biological pump (Sections 2.2.2 and 5.2).

Since the functions of calcification are not fully understood, the long-term implications of reduced calcification on the physiological and ecological fitness of calcifying organisms are unknown.

### 3.5.5 *Influence of increased $\text{CO}_2$ on calcification*

Because of the dissimilarities in the calcification process, it is surprising to find a rather narrow range of

sensitivities to CO<sub>2</sub> in different calcifying groups. Recent laboratory and field studies reveal that the degree of carbonate supersaturation has a profound effect on the calcification rates of individual species and communities in both planktonic and benthic habitats. Published data on corals, coccolithophores and foraminifera all suggest a reduction in calcification by 5–25% in response to a doubling of atmospheric CO<sub>2</sub> from pre-industrial values (from 280 to 560 ppm CO<sub>2</sub>) (Feely et al 2004). This reduced calcification rate also occurs even when the carbonate saturation level was well above one (at values below one, CaCO<sub>3</sub> dissolves) (Section 2). This response holds for intracellular as well as extracellular calcification and across both aragonite and calcite forms.

However, it should be noted that research on the sensitivity of calcifying organisms to CO<sub>2</sub>-related changes in seawater chemistry have so far been limited mostly to short-term studies with single strains of organism. It is unknown whether the observed responses can be extrapolated to the genetically diverse populations that prevail in the natural environment and to what extent calcifying organisms can acclimatise or adapt to these changes. The rather uniform sensitivity to CO<sub>2</sub> and pH may also be biased by selective testing of species and clones dominant under (and therefore best adapted to) present-day CO<sub>2</sub> levels. In a recent study, calcification in a clone of the coccolithophore, *Coccolithus pelagicus*, proved to be insensitive to increased CO<sub>2</sub> (decreased pH) in the growth medium (Langer personal communication). Another species, *Calcidiscus leptoporus*, showed a decline in calcification rate and an increase in coccolith malformations at CO<sub>2</sub> concentrations above and below present-day levels (Langer personal communication). These results suggest that the previously derived simple relationship between pH and calcification may become more complex as new species and clones are tested.

It is currently unknown to what extent calcifying organisms are able to adapt to decreasing carbonate saturation states. Thus the extent to which physiological or genetic diversity may contribute to the resistance to the acidification process is unknown.

### **3.6 Potential adaptation and evolution resulting from the surface ocean CO<sub>2</sub> increase and acidification**

As described in Section 2 the high rate of increase in CO<sub>2</sub> concentration means that organisms are being exposed to changes that are faster than they have encountered in their recent evolutionary past. Few experiments have so far been conducted for long enough to indicate whether organisms will be able to genetically adapt to these changes.

Most of our evidence comes from short-term exposures, within the lifetime of the organism or, for more rapidly

reproducing organisms, several (fewer than 100) generations. Few experiments have gone on long enough for genotype selection to be significant (Burkhardt et al 1999; Gervais & Riebesell 2001; Collins & Bell 2004). The only published work for longer-term experiments was carried out on the freshwater microscopic alga *Chlamydomonas* (Collins & Bell 2004). Grown at almost three times the present atmospheric CO<sub>2</sub> concentration, the cells acclimatised to the change but did not show any genetic mutations that could be described as adaptation. However, several mutants were obtained which grew very poorly when returned to CO<sub>2</sub> at just above the present atmospheric level. Work of the type carried out on *Chlamydomonas* is needed for marine phytoplankton species to determine if they show 'adaptation' to growth at higher CO<sub>2</sub>.

Although the work on *Chlamydomonas* represents a very promising start, much more work is needed on a range of marine organisms representing different trophic levels, with different generation times and breeding systems, to provide information on the possibilities of long-term evolutionary adaptations. Ideally, such work would also consider the effects on particularly sensitive stages in the life cycle. Investigations should also include inter-species interactions, such as the effect of any changes in the chemical composition of primary producers (Section 3.2.1) on consumer organisms, such as grazers.

There is a very limited database from which to draw conclusions about the possibility of adaptation of organisms to the present rapid change in ocean surface CO<sub>2</sub>. Further investigation of this topic is very important. However, this could be particularly time consuming if organisms with long generation times are studied.

### **3.7 Possible impact of ocean acidification on the structure of marine communities**

With or without genetic change in relation to increased CO<sub>2</sub> at the species level, there is clearly also the possibility of changes in the relative abundance of species as CO<sub>2</sub> increases in the oceans. This is not an easy topic to address on the basis of available data from the oceans, because the effects are nonlinear and complex. But such changes of species composition are likely as CO<sub>2</sub> increases, given the growing evidence of potential effects of increased CO<sub>2</sub> on growth and reproduction differing among organisms (Denmen et al 1996; Boyd & Doney 2003).

Contradictory results have been obtained for the effect of CO<sub>2</sub> on species representation in phytoplankton communities. Experiments on samples of surface seawater on ship-borne microcosms in the tropical Pacific and mesocosms in Norwegian coastal waters showed a shift towards calcifying coccolithophores (such as *Emiliania huxleyi*) at low or present-day CO<sub>2</sub>, and towards diatoms at high CO<sub>2</sub> (Tortell et al 2002; Martin-Jézéquel et al 2004). However, a decrease in diatoms and an increase

in other phytoplankton organisms were observed at increased CO<sub>2</sub> and temperature in ship-borne microcosm incubations carried out in the Bering Sea (Hutchins personal communication). These contradictory results indicate that the impact of rising CO<sub>2</sub> on phytoplankton species composition may be community- or regime specific and is hence likely to differ seasonally and geographically.

For many ecosystems the impact that such changes in species composition would have on their productivity and the services that they provide is unclear. It is possible that different species may dominate and fill the gap in the food web left by those that are adversely affected by ocean acidification.

### **3.8 Conclusions**

#### ***Effects of ocean acidification on micro-organisms***

The evidence considered in Section 3.2 suggests that the increase of CO<sub>2</sub> in the surface oceans expected by 2100 is unlikely to have any significant direct effect on photosynthesis or growth of most micro-organisms in the oceans. Changes in elemental composition of the cells also appear to be small and variable. More work is needed before these negligible, or small, effects of increased CO<sub>2</sub> can be generalised and applied with confidence to the oceans as an indication of future trends. Moreover, much of the work that has been done relates to the acclimatisation of cells to increased CO<sub>2</sub> and has not been conducted for long enough to determine whether the organisms will be able to evolve, through natural selection, to the changed environment.

Changes in CO<sub>2</sub> concentrations and pH will lead to changes in nutrient concentrations and speciation. Insufficient data is currently available to identify the indirect impacts these changes might have.

A substantial increase in information is required if we are to arrive at widely applicable conclusions on the effect of increased surface ocean CO<sub>2</sub> on the functioning of non-photosynthetic micro-organisms in the oceans.

#### ***Effects of ocean acidification on multicellular animals***

In the short term (20–40 years), projected increases in atmospheric CO<sub>2</sub> will produce minor impacts on multicellular marine animals. Climate change scenarios that involve three- to fourfold increases in atmospheric CO<sub>2</sub> are more likely to stress their physiology and may reduce their growth. Increased CO<sub>2</sub> in the seawater may also increase mortality, particularly for organisms with high metabolic rates such as squid. Reproduction of multicellular animals is strongly influenced by CO<sub>2</sub> at the very high concentrations tested. However, much more

work is needed to establish the effects of the changes in surface ocean CO<sub>2</sub> concentrations expected over the next century. In particular, we need to examine the effects of increased CO<sub>2</sub> on the complete life cycle of multicellular animals to determine the validity of the suggestion that the gametes and juvenile (larval) stages are more sensitive to high CO<sub>2</sub> and low pH than is the adult stage.

The influence of ocean acidification on marine organisms other than those exerted through calcification, could include decreased reproductive potential, slower growth or increased susceptibility to disease. These responses could have cascading effects through food webs, with possible consequences for ecosystem structure and elemental cycling.

#### ***Effects of ocean acidification on calcification***

From our understanding of ocean chemistry and available evidence, it is clear that increasing the acidity of the oceans will reduce the concentration and therefore the availability of carbonate ions. It is expected that calcifying organisms will find it more difficult to produce and maintain their shells and hard structures. However, the lack of a clear understanding of the mechanisms of calcification and its metabolic or structural function means that it is difficult, at present, to reliably predict the full consequences of CO<sub>2</sub>-induced ocean acidification on the physiological and ecological fitness of calcifying organisms. What is clear is that any decrease in calcification, as a result of increased CO<sub>2</sub>, is likely to have significant consequences such as the weakening of coral skeletons and reef structures generally (Section 4.2). The widespread use of calcification in the oceans suggests that it is an essential aspect of the biology and ecology of many calcifying organisms. As outlined in Section 2, any changes in calcification will also have important implications for the global carbon cycle.

Organisms will continue to live in the oceans wherever nutrients and light are available, even under conditions arising from ocean acidification. However, from the data available, it is not known if organisms at the various levels in the food web will be able to adapt or if one species will replace another. It is also not possible to predict what impacts this will have on the community structure and ultimately if it will affect the services that the ecosystems provide. Without significant action to reduce CO<sub>2</sub> emissions into the atmosphere, this may mean that there will be no place in the future oceans for many of the species and ecosystems that we know today. This is especially likely for some calcifying organisms.

It is unclear how direct effects of increasing CO<sub>2</sub> interact with those of other environmental changes occurring simultaneously, such as those of climate and nutrient supply, the extent of oxygenation of sediments, surface ocean mixing and stratification. Independent of these

uncertainties it is possible to say with some confidence that that various groups of marine organisms will experience significant alterations in their geographical ranges (Boyd & Doney 2003).

Having evaluated the possible effects of ocean acidification on species and communities of organisms, in the following section we look at the wider picture and consider which marine ecosystems may be most vulnerable to the projected changes in ocean chemistry.



## 4 Ecosystems most at risk from the projected changes in ocean chemistry

### 4.1 Introduction

Section 2 shows that ocean chemistry is being, and will increasingly be, altered by rising atmospheric CO<sub>2</sub> levels. As the CO<sub>2</sub> concentration in the surface oceans increases, this raises their acidity (reduces their pH), and importantly for organisms that calcify, lowers the carbonate saturation status of the surface oceans. The extent and rate of change to ocean chemistry that is predicted to occur by 2100 has no precedent for at least hundreds of thousands of years and possibly much longer. Section 3 demonstrates that, while the effects of these changes in ocean chemistry on marine organisms are not well understood, significant effects are expected, especially for some calcifying organisms. Based on the conclusions in Section 3, here we examine the likely impacts of these changes in ocean chemistry on the ecosystems that are most likely to be at risk.

### 4.2 Impact of ocean acidification on benthic systems

#### 4.2.1 Coral reefs

Photosynthetic coral reefs require calcified structures to survive. Considerations of changes in ocean chemistry in the tropics and subtropics suggest that these systems are liable to significantly decline as a result of surface ocean acidification.

Coral reefs cover an estimated 1.28 million square kilometres of the world's tropical and subtropical oceans (Spalding et al 2001). They occur primarily in well-lit and shallow waters, characterised by low water-column turbidity (Spalding et al 2001). In contrast to cold-water corals, warm-water reef-building corals are symbiotic with single-celled dinoflagellate algae (Table 2). High rates of calcification allow the building of a scaffolding or framework, which becomes home to hundreds of thousands of other species that dwell in coral reefs (Reaka-Kudla 1996). Without the presence and activities of reef-building corals, coral reefs would be vastly different from the diverse and productive ecosystems that typify shallow tropical and subtropical oceans today. Despite representing less than 1.2% of the world's continental shelf area, coral reefs are critical resources to people and industries in many countries (Spalding et al 2001). The socio-economic value of coral reefs is considered in Section 6.

Warm-water coral reefs generally exist within a narrow environmental envelope defined largely by sea temperature, light and the aragonite saturation state (Kleypas et al 1999a). The growth of coral reefs is minimal outside this envelope. Climate change, through its effect on ocean temperature and aragonite saturation state

(Section 2.7.1), has already had an impact on the world's coral reefs (Hoegh-Guldberg 1999). Almost 30% of warm-water corals have disappeared since the beginning of the 1980s, a change largely due to increasingly frequent and intense periods of warm sea temperatures. High ocean temperatures cause corals to bleach (ie lose their pigmented dinoflagellate symbionts and, if conditions are warm enough for long enough, die). The increase in atmospheric CO<sub>2</sub> is compounding this effect, by lowering the aragonite saturation state of seawater, making carbonate ions less available for calcification (Section 2.7). Gattuso et al (1999) and Kleypas et al (1999b) have proposed that the calcification rates of corals would decrease by 10–30% under a doubling of atmospheric CO<sub>2</sub> concentrations. Ample evidence now indicates that coral calcification is directly proportional to the aragonite saturation (Gattuso et al 1999; Marubini & Atkinson 1999; Langdon et al 2000, 2003; Leclercq et al 2000, 2002; Marubini et al 2001, 2002). These studies, done in laboratory or mesocosm settings, reveal that doubling atmospheric CO<sub>2</sub> causes a 3–54% decrease in carbonate production.

Some studies have suggested that the decrease due to declining concentrations of carbonate ions will be more than offset by increases in calcification due to the increase in ocean temperature (Lough & Barnes 2000; McNeil et al 2004). These assessments are based on the assumption that calcification increases in direct proportion to temperature, despite the fact that all studies so far have shown that coral calcification reaches a maximum at or just below current-day temperatures. For this and other reasons, these theoretical counter-perspectives have been regarded as 'seriously flawed' (Kleypas et al 2005). Other suggestions that coral reefs may expand significantly to higher latitudes as seas warm have been countered by the observation that carbonate ion concentrations decrease towards the poles and will reach even lower values at high latitudes than is the case now as atmospheric CO<sub>2</sub> increases (Kleypas et al 2001). This, and the fact that light for photosynthesis also decreases at higher latitudes, suggests that the latitudinal limit for coral reefs will remain within a few hundred kilometres of where it is today.

The synergistic interaction of elevated sea temperature and atmospheric CO<sub>2</sub> is likely to produce major changes to coral reefs over the next few decades and centuries. Under most IPCC emission scenarios (IPCC 2000), corals are unlikely to remain abundant on reefs and could be rare on tropical and subtropical reefs by the middle of this century if CO<sub>2</sub> doubles or triples above present levels. Over longer timescales, reef frameworks that are critical for the protection of coastlines across tropical and subtropical regions may start to disappear as the rate of erosion starts to exceed calcification rates (Burke 2004).

The protection offered by coral reefs played a key role in reducing the energy of wave impacts during the Southeast Asian tsunami (in December 2004). In this case coastlines that did not have well-developed coral reefs suffered greater damage to infrastructure and saw greater loss of life as waves battered the coastal towns and cities (Brown 2004).

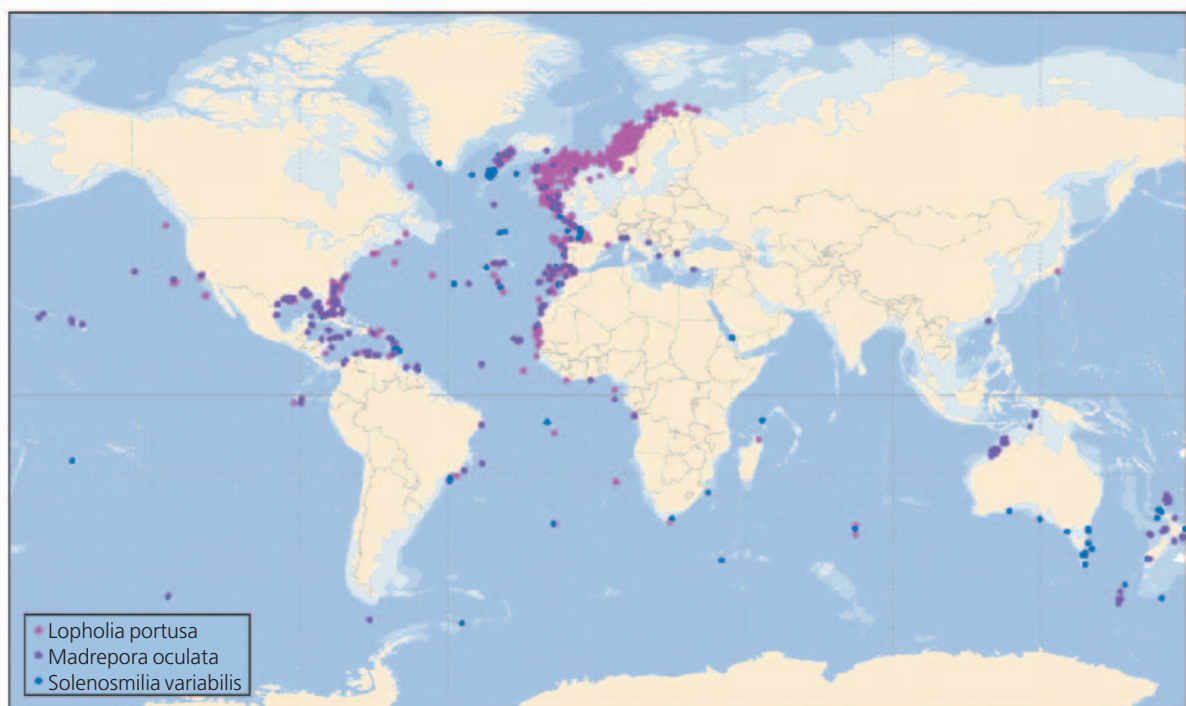
The changes projected for coral reefs are likely to have major ramifications for their biodiversity and function and those of associated ecosystems (sea grass, mangrove). The implications of these changes for people and industries that depend on coral reefs are likely to be significant (Section 6).

#### 4.2.2 Cold-water coral reefs

Non-symbiotic cold-water coral reefs have only been studied intensively for about a decade, when scientists gained access to increasingly sophisticated instrumentation to explore deep-water environments. The use of advanced technology has challenged conventional wisdom that coral reefs are confined to shallow and warm tropical and subtropical regions. Our knowledge of the biology and ecology of cold-water corals, their geographical distribution and spatial coverage, and their role in the marine ecosystem is still rudimentary. Decreasing surface ocean pH may have a significant impact on these systems before they have been fully explored.

Cold-water coral systems have been found in almost all the world's oceans and seas: in fjords, along the edge of the continental shelf, and around offshore submarine banks and seamounts (Freiwald et al 2004). Although frequently referred to as 'deep water' corals, they occur over a wide depth range, from a few tens of metres to over 1 000 m. Their distribution is probably mainly determined by temperature, as is reflected by some occurrences in shallow water at high latitudes and exclusively deep-water occurrences in tropical and subtropical waters. The full extent of the area covered by cold-water coral ecosystems is unknown, but recent studies indicate that it could equal, or even exceed, that of warm-water reefs (Freiwald et al 2004). Numerous new species were recently discovered in cold-water coral ecosystems; others found in association with them were previously thought to be extinct (Freiwald personal communication). Living primarily in dark, deep waters, cold-water coral ecosystems have no light-dependent symbiotic algae but depend on organic matter supplied from above. They are long lived, slow growing and fragile. Radioactive dating techniques have shown cold-water coral banks and reefs to be up to 8 000 years old. Geological records show that they have existed for millions of years. Cold-water reefs are derived from several systematic groups, with colonial stony corals (order Scleractinia), true soft corals (subclass Octocoralia), black corals (order Antipatharia) and calcifying lace corals (class Hydrozoa) being the most important taxonomic

Figure 9. Global distribution of cold-water coral reefs: points on the map indicate observed reefs, but not the actual area covered. The three most common cold-water corals are identified: *Lophelia pertusa*, *Madrepora oculata* and *Solenosmilia variabilis*. The high density of reefs shown in the North Atlantic most probably reflects the intensity of research in this region. Further discoveries are expected worldwide, particularly in the deeper waters of subtropical regions. (Reprinted from Freiwald et al (2004) with permission from UNEP-WCMC.)



groups. By far the most common cold-water coral is the cosmopolitan stony coral *Lophelia pertusa*, a habitat-forming, reef-building species which occurs in dense girdles stretching from the southwestern Barents Sea along the eastern Atlantic continental margin down to West Africa. Evidence is emerging of a similar belt along the western margin of the Atlantic off Nova Scotia to the Florida Straits and into the Gulf of Mexico. Other groups with global distribution include the genera *Madrepora* and *Solenosmilia* (Figure 9). Cold-water reefs and structures harbour a distinct and rich ecosystem, providing niches and nursery grounds for a variety of species, including commercial fish species.

So far, there are no studies on the sensitivity of cold-water corals to CO<sub>2</sub>-related changes in seawater chemistry. However, because of the comparatively uniform response of all calcifying organisms tested so far, it is reasonable to expect that calcification of cold-water corals will also be reduced as carbonate supersaturation declines. Because the carbonate saturation state generally decreases with latitude and water depth, the conditions in waters typically inhabited by cold-water corals are less favourable for calcification to start with. This may cause cold-water corals to be affected earlier and more strongly by CO<sub>2</sub>-related ocean acidification than their warm-water counterparts. Model calculations, based on a situation where CO<sub>2</sub> emissions continue on current trends, indicate that the aragonite saturation horizon (the depth below which aragonite dissolves) will rise closer to the oceans' surface) by several hundred metres for most of the ocean, and may reach the surface in the Southern Ocean by 2100 (Caldeira & Wickett in press). Thus, not only is the ocean-wide decrease in the aragonite saturation level likely to decrease cold-water coral calcification, large areas of the oceans may also become completely uninhabitable for cold-water corals as the impacts of increased CO<sub>2</sub> are greater at higher latitudes.

If CO<sub>2</sub> emissions continue on current trends, ocean acidification will threaten the existence of cold-water corals before we have even started to understand and appreciate their biological richness and importance for the marine ecosystem.

#### 4.2.3 *Shallow sediments and benthic organisms*

Sediment-dominated habitats, which occupy a large fraction of the area of the oceans, play a crucial role in several key ecosystem functions and processes in shelf sea environments. For example, in shallow (less than 50 m) coastal areas productivity in the overlying water column relies on the sediment system, with up to 80% of the nitrogen required by phytoplankton coming from the bacterial regeneration of organic matter within the seabed (Dale & Prego 2002). Phytoplankton are the main marine primary producers upon which the whole marine food chain depends, so the supply of nutrients for their growth from the sediment is essential for sea shelf productivity. This benthic–pelagic (bottom dwelling –

surface living) coupling is two way, with the sediment receiving the 'fall-out' of organic matter from the overlying primary production, by the biological pump (Section 2.2.3). This material acts as the primary food resource for benthic organisms, which in turn support a benthic food web with demersal fish (such as cod and plaice) being at the top. Hence both bottom dwelling and pelagic fisheries in shelf seas are dependent on a healthy sediment ecosystem and on benthic–pelagic coupling. Changes to the biological pump, and therefore the supply of food to the sediment-dwelling organisms, will affect the benthic food web and the benthic–pelagic coupling.

Ocean acidification has many potential implications for benthic organisms and their ecosystems. This section focuses on benthic systems, particularly those concerning animals living in soft mud or on the sandy floor. This excludes temperate and tropical reefs (considered benthic) which are considered above (Section 4.2); and muddy or sandy bottoms occupied by seagrass beds, which have been mentioned in Section 3.3.

Sediments in unmixed settings are characterised by strong geochemical gradients. For example, the pH at depths of 30 cm or so can be as much as one unit lower than the pH of the sediment surface and overlying water (Fenchel & Riedl 1970). In the face of such geochemical variability it is difficult to conceive how benthic sediment systems could be affected by the relatively small pH changes expected from surface ocean acidification. A number of processes in the surface layers of sediments (typified by pH values that are closer to overlying seawater) may be affected by changes expected under ocean acidification. By considering some of the potential changes to the distribution and activities of sediment-dwelling organisms, it is possible to identify areas where these small changes could have potentially large consequences for sediment communities and biogeochemical processes.

The communities of benthic sediments are strongly stratified, with different species characteristically occupying different depths (Barnes & Hughes 1988). The surface layer is the most densely inhabited and is home to most of the animals, whereas only those species capable of oxygenating their immediate environment are able to dwell below the depth where the rate at which oxygen diffusion from overlying water is inadequate to supply the respiratory requirements of organisms (Furukawa 2001). Microbial communities and the functions they perform (for example nitrification and denitrification) also differ considerably in their ability to tolerate oxygen and hence in where they are situated between the surface sediments and the deeper layers devoid of oxygen. The presence of these depth-constrained niches means that although benthic systems as a whole are already subject to a relatively large range in pH, many of the organisms and processes that exist within them are not. Although most larger animal species are restricted to the upper oxic (oxygen-containing) layers, others are able to inhabit the

deeper sediment layers. They do so by the creation of permanent burrows through which they are able to draw down oxygenated water from above. The burrows created by these larger animals experience significant oscillation in pH (as much as two pH units) and dissolved oxygen concentration (between saturation and near anoxia (absence of oxygen)), generated by the periodic ventilation of burrows (Furukawa 2001). Such oscillation is absent at the water–sediment interface. Consequently, animals that inhabit permanent burrows may have a greater tolerance to changes in pH than those that do not build burrows. This potential difference in pH tolerance between benthic species could lead to the selection of more tolerant species and thereby substantial changes in the structure and function of sediment communities in the face of changing levels of pH. Recent work has already identified significant variability in pH sensitivity for several different benthic groups (Shirayama et al 2004). Even among organisms that depend on CaCO<sub>3</sub> structures, variability in tolerance has been observed with echinoderms showing less tolerance to pH change than molluscs (Shirayama et al 2004). Such variability in sensitivity could have considerable implications for the diversity and functioning of sediment communities in shallow seas with declining pH.

It has long been recognised that organisms living within the sediment have the ability to alter the physical and chemical characteristics of their immediate environment, contributing significantly to the rate of nutrient fluxes at the sediment–water interface (Banta et al 1995; Nedwell & Walker 1995; Widdicombe & Austen 1998) and the maintenance of biodiversity (Widdicombe & Austen 1998; Widdicombe et al 2000). In soft sediment habitats the single most important mechanism by which nutrients are exchanged with and released from the sediments is bioturbation: the disturbance and mixing of the sediments by animals as they go through them (Rhoads & Young 1970). Any factor that alters the rate of bioturbation will have considerable implications for the functioning of marine ecosystems and, as some bioturbating species rely on calcareous structures, an increase in the acidity of coastal seas would be such a factor. Two of the most important groups of bioturbating organisms are the burrow-forming thalassinidean crustaceans (such as some shrimps) and the highly mobile subsurface echinoderms. Although both groups actively bioturbate the sediment, the mechanisms by which they do this are very different, which has important implications for their impact on the sediment environment. Burrowing shrimps create a permanent system of tunnels which enables oxygen and other water-borne substances to penetrate deep into the sediment. This has been shown to significantly increase the uptake of nitrate and the release of ammonium, as well as stimulating the process of denitrification by microorganisms (Howe et al 2004). Conversely, burrowing urchins ‘bulldoze’ through the surface sediment, creating a deep, uniform oxic layer which decreases the flux of nitrate into the sediment

(Widdicombe & Austen 1998). Organisms that create permanent burrows (for example thalassinidean shrimps) are already exposed to low and variable levels of pH whereas those species that inhabit the upper few centimetres of the sediment and do not create permanent burrows are not (for example burrowing urchins). In addition, the body structure of echinoderms would seem to make them particularly susceptible to changes in pH as they rely on a calcareous skeleton and have more ready exchange of CO<sub>2</sub> between ambient seawater and the internal body cavities than is the case for other marine animals of a similar size. This potential vulnerability of echinoderms to changes in pH is supported by the small amount of evidence currently available, which indicates that echinoderms are significantly impacted by a pH decrease of as little as 0.3 units (Shirayama et al 2004).

Most benthic animals have a pelagic larval stage to enhance their distribution. Bivalve larvae that are settling from the pelagic to the benthic phase have an extremely high mortality (greater than 98%) in the first days and weeks. This has been linked to undersaturation of carbonates which makes calcification difficult and weakens the shells (Green et al 2004).

Such major differences in the potential response of organisms from different taxa and functional groups to reduced pH could have a considerable impact on the functioning of marine sediments and the ‘goods and services’ they provide. Consequently, whilst changes in seawater pH may have a direct effect on sediment and seawater chemistry through changes in nutrient speciation, this effect may be exacerbated by changes in the type and intensity of megafaunal bioturbation.

### **4.3 Impact of ocean acidification on pelagic systems**

#### **4.3.1 Coastal and open ocean pelagic ecosystems**

Calcified organisms are very significant components of pelagic ecosystems and any changes in the functioning of these calcified components in response to surface ocean acidification would have large implications on the functioning of the ecosystem. Pelagic ecosystems supply the organic carbon used by organisms deeper in the oceans and are important in the interactions of the surface oceans with the atmosphere, such as in the exchange of CO<sub>2</sub>.

A diverse and often abundant community of coccolithophores, foraminifera and pteropods inhabits the sunlit (euphotic) zone of all open and coastal ocean areas, with the exception of the Southern Ocean (Section 4.3.2) (south of the polar front) and the Arctic Ocean. Massive blooms of coccolithophores, which can cover hundreds of thousands of square kilometres of surface oceans and can each produce up to one million tonnes of calcite (Holligan et al 1993), are seen from satellites in

temperate and subpolar latitudes (Iglesias-Rodriguez et al 2002). However, even outside these blooms, which are predominantly formed by only one species, *Emiliana huxleyi*, coccolithophores are a common and often dominant component of the phytoplankton community (for example in subtropical circulation currents). Although the spatial and temporal distributions of coccolithophores are consistent with a requirement for high-calcite saturation states (Tyrrell and Merico 2004), which is also reflected by their absence in low calcite saturation areas as such as the polar oceans, it is not clear what role this factor plays for the occurrence of this group. Laboratory and field experiments show that calcification of coccolithophores decreases with decreasing saturation state (Riebesell et al 2000; Zondervan et al 2001).

Ocean acidification is likely to also affect calcification of foraminifera, a group of calcite-producing protists. As with other calcifying organisms, changes to the distribution and abundance of these protists could have significant effects on the global carbon cycle.

As saturation states decline globally, it might be expected that calcifying organisms in near-polar areas, where saturation state is the lowest, will be affected first. Owing to the higher solubility of aragonite, pteropods, that produce  $\text{CaCO}_3$  in its aragonite form, will be more strongly affected than the coccolithophores and foraminifera which produce the calcite form. If  $\text{CO}_2$  emissions continue on current trends the aragonite saturation horizon will rise to the surface of the oceans before the end of this century, making aragonite skeletons unstable throughout the water column over the entire Southern Ocean (Section 4.2.1). The highest-latitude coccolithophore blooms are currently in the Barents Sea at more than  $70^\circ$  N. Satellite images suggests that these blooms are probably more, rather than less, numerous today than during the 1980s and early 1990s (Smyth et al 2004). Changes other than ocean acidification, such as global warming and related enhanced stratification at these high latitudes, may have favoured the northward extension of coccolithophore blooms in recent years.

The shift from coccolithophore to a diatom-dominated phytoplankton community, or *vice versa*, can have strong impacts on the entire ecosystem of the region where it occurs. In the eastern Bering Sea such a regime shift occurred in the late 1990s. Although previously dominated by diatoms, extensive blooms of *Emiliana huxleyi* have occurred throughout the eastern Bering Sea between 1996 and 2000 (Merico et al 2003). This change in the dominant primary producer was correlated with a restructuring of the region's ecosystem at all trophic levels. One of the results of this was a strong decline in salmon catches during these years.

The finding that coccolithophore blooms are now occurring at high latitudes shows that there are significant factors determining the abundance of coccolithophores other than the calcite saturation state.

However, it seems very likely that calcified planktonic organisms, including coccolithophores, will decline as  $\text{CO}_2$  in the surface oceans increases, with important implications for trophic interactions and ecosystem function (Section 5). It is important to note that we have much less understanding of the factors determining the occurrence of coccolithophore blooms than of the determinants of diatom blooms (Flynn 2001).

#### 4.3.2 Southern Ocean food webs

Southern Ocean food webs are of particular concern (Section 2.7.1). Calcifying organisms in the Southern Ocean will be among the first to be affected from ocean acidification. Aragonite-producing pteropods are the dominant calcifiers in the Southern Ocean. These pelagic molluscs account for a significant proportion of the biological pump of the Antarctic polar front, and in the Ross Sea (Section 2.2.2, Gardener et al 2000; Seibel & Dierssen 2003). Pteropods have a global distribution, but reach their highest abundances (up to 1 000 individuals per cubic metre) in polar and subpolar waters. These pelagic molluscs are an important food source for marine predators in the Antarctic food web and sometimes replace krill as the dominant zooplankton group in parts of the Southern Ocean. The response of pteropods to increased  $\text{CO}_2$  has not yet been tested. However, it is likely to be consistent with the other biogenic carbonate producers (Seibel & Fabry 2003). If pteropods are restricted to aragonite-saturated waters, then their habitat will become increasingly limited latitudinally and vertically as the aragonite saturation horizon moves closer to the oceans' surface.

In the event that pteropods were eliminated from the Southern Ocean, there would be a reduction in the biological pump to the deeper oceans of particulate inorganic and organic carbon in the region. Although pteropods contribute to the diet of carnivorous zooplankton, North Pacific salmon, mackerel, herring, cod and baleen whales (LeBrasseur 1966; Takeuchi 1972), most of these would probably be able to switch to other prey types. However, this could result in greater predation pressure on juvenile fishes. Gymnosomes, the shell-less planktonic molluscs that are believed to prey exclusively on pteropods, would probably shift their geographical distribution with that of their pteropod prey (Lalli and Gilmer 1989). Decreasing carbonate saturation state will impact the depth ranges of pteropods in several other regions of the world's oceans, such as the subarctic Pacific, where saturation levels are already low, as well as upwelling areas associated with the Benguela Current, the western Arabian Sea and the Peru Current, where pteropod abundances can be high (Fabry 1990; Hitchcock et al 2002).

Over the next few centuries, as the aragonite saturation horizon moves progressively closer to the surface of the oceans in these regions, and the calcite saturation state of the euphotic zone decreases, the trophic dynamics and

other ecosystem processes, including the cycling of  $\text{CaCO}_3$  and organic matter will be affected (Feely et al 2004).

#### **4.4 Conclusions**

According to the evidence available, changes in ocean chemistry will present severe challenges to some of the components of these vast and important ecosystems

considered in this section. Changes to important coastal ecosystems such as coral reefs, to the carbon cycle of the Southern Ocean and to deep-water reef ecosystems will have large-scale ramifications for this and other interconnected ecosystems. That said, we recognise that there are large gaps in our knowledge of how these processes might be affected and the outcome of the changes being exerted on them.

## 5 Interaction with the Earth systems

### 5.1 Introduction

Modelling of aspects of the effect of future climate change on the oceans has incorporated physical and biological processes. Such studies have considered the ability of the oceans to absorb CO<sub>2</sub> (see, for example, Sarmiento et al 1998; Sarmiento & LeQuere 1996) and on the emission of gases, such as dimethyl sulphide (DMS), from the ocean (Bopp et al 2003). However, these studies have generally not addressed the role of pH change.

In this section, we address the possible direct effects of enhanced ocean acidification by CO<sub>2</sub> on the Earth systems. In particular we look at the exchange of gases between the oceans and atmosphere, which is important for the chemistry of the atmosphere and which might affect global climate change. The processes behind each of these feedback effects are very complex, understanding the overall impact on the Earth systems is a significant challenge.

### 5.2 Feedback effects of reduced calcification

One can expect that the effect of lowered pH on the amount of CO<sub>2</sub> absorbed by the oceans will be very dependent on any changes that may occur in the composition of species within surface ocean communities. For example, if the amount of calcification is reduced by the lower pH (as discussed in Sections 3 and 4), there will be a net increase in CO<sub>2</sub> uptake as a result of a reduced return flux of the gas released from the calcification reaction (as discussed in Section 2). Model calculations indicate that if CO<sub>2</sub> concentrations continue to increase at current levels, the projected decrease in calcification would lead to a reduction in atmospheric CO<sub>2</sub> of 4–10 ppm by 2100 (Zondervan et al 2000; Heinze 2004). Making global ocean calcification proportional to the declining calcite saturation state causes a reduction of 19 ppm in atmospheric CO<sub>2</sub> by 2100 (Klepper & de Haan 1995).

A reduction and possibly regional cessation of calcification by organisms in the oceans would strongly affect ecosystem regulation and the flow of organic material to the seafloor. As discussed in Section 2, the biological pump removes carbon from the surface waters. It has been suggested that CaCO<sub>3</sub> acts as a mineral ballast for the export of organic carbon, such as plankton cells and other particulate matter, in the biological pump (Section 3.2.1) (Klaas & Archer 2002). Any reduction in CaCO<sub>3</sub> production will reduce the amount of ballast available to the biological pump and may therefore diminish the flow of carbon to the deep oceans. However, because any link between the flow of this mineral 'ballast' and the flow of organic matter is unknown, the significance of this effect remains uncertain (Passow 2004).

Another potential effect of ocean acidification may be the disappearance of coccolithophore blooms (Section 4.3.1). These massive blooms add to the albedo affect of the Earth. This means that they quantifiably increase the amount of sunlight that is reflected back into space, which cannot then contribute to global warming. It has been projected that the loss of these blooms could reduce the global albedo by up to 0.13%, and could therefore enhance global warming (Tyrrell et al 1999).

### 5.3 Other feedbacks within the Earth systems

As discussed in Section 3, it is unclear what impact rising atmospheric CO<sub>2</sub> will have on the physiology of phytoplankton (such as diatoms and flagellates). As a result it is uncertain whether it will lead to greater productivity and therefore draw down more CO<sub>2</sub> or reduce productivity thus absorbing less.

Apart from the CO<sub>2</sub>, the climate is affected by a number of other gases that are produced by marine organisms, including the greenhouse gases nitrous oxide (N<sub>2</sub>O) and methane (CH<sub>4</sub>). In addition, some groups of plankton produce DMS, a gas that when oxidised in the atmosphere produces cloud-forming particles which can lead to climatic cooling. Changes in DMS production under elevated CO<sub>2</sub> conditions, as with the preceding discussion on calcification, will be very dependent on which plankton species are most affected by the changed conditions. For example, it is well established that there is wide variation in the ability of different groups of phytoplankton to produce DMS from its biochemical precursor, dimethylsulphoniopropionate (DMSP). For example in the phytoplankton, diatoms form little DMSP whereas the alga *Phaeocystis* and coccolithophores are prolific producers (Liss et al 1994). Changes in the abundance of these groups would affect the size of the feedback.

Notwithstanding this uncertainty, a recent modelling study (Gunson, personal communication) suggests a considerable climatic sensitivity to changes in DMS emissions from the oceans. These models indicate that a relatively small (two-fold) increase in DMS emission, if occurring globally, would produce an atmospheric temperature decrease in the order of 1–2°C. Such a cooling would clearly be significant and changes in DMS emissions of this size are certainly possible. However, it should be stressed that there are considerable uncertainties in the modelling, including the mechanisms of particle and cloud formation on oxidation of DMS in the atmosphere, as well as in the representation in models of the variations in DMS production by different plankton species.

In this context it is important to note that organisms forming CaCO<sub>3</sub> plates, such as the coccolithophores, are major producers of DMS. This means that a decline in

coccolithophore productivity may also reduce DMS-related cloud formation (Malin & Steinke 2004) and so have a feedback effect on climate. In some recent laboratory and mesocosm studies it was found that under elevated CO<sub>2</sub> conditions the amounts of DMS and DMSP produced by the phytoplankton were halved (Avgoustidi personal communication). However, it needs to be stressed that such studies are very short-term (days to weeks in duration) and that the organisms are subject to rapid change in CO<sub>2</sub> level compared with what will happen in the real-world situation of relatively slow pH change.

Other gases formed by marine organisms can affect air quality; these include organo-halogens, non-methane hydrocarbons and oxygenated organics. Once released from the oceans into the troposphere (lower atmosphere), these gases can affect the formation of particles and destroy oxidants in the atmosphere. These oxidants, such as ozone, are important for improving air quality by breaking down organic pollutants.

In addition, other gases are emitted that affect the acidity of atmospheric particles and precipitation; these include ammonia, sulphur dioxide, and other products of DMS oxidation.

#### **5.4 Conclusions**

In the case of the gases N<sub>2</sub>O, CH<sub>4</sub> and DMS, which can affect atmospheric chemistry, there is not enough information about how their emission to the atmosphere might change as the ocean pH decreases. This uncertainty is increased by the current lack of understanding of the processes controlling their production in marine surface waters.

There are potentially important interactions between changes in the state of the oceans (including their pH) and changes in the global climate and atmospheric chemistry. Our knowledge of these impacts and effects is currently poor and requires urgent consideration as part of the broader drive to understand Earth Systems processes.



## 6 Socio-economic effects of ocean acidification

### 6.1 Introduction

It is clear that the full range and magnitude of the biological and biogeochemical effects of acidification of the surface oceans are still so uncertain that a reliable and quantitative estimate of the likely socio-economic effects is not yet possible. However, some general indications of the possible size of such effects can be obtained for at least some of the aspects discussed above, and a preliminary attempt to set such effects in context, by estimating at least the economic value of the resources at risk, even if the extent of damage is uncertain, is given below.

### 6.2 Effects on coral reefs

The likely effects of ocean acidification on coral reefs (Section 4.2.1) are probably the best understood and documented of those considered in this report. These alone are sufficient to give rise to serious concern. Coral reefs support many millions of people globally through subsistence food gathering. Many more people are supported through industries, such as tourism and fisheries that bring in billions of dollars annually (Hoegh-Guldberg & Hoegh-Guldberg 2004). The projected impacts and the implications for the ecosystems associated with the coral reefs (sea grass, mangrove) are likely to have adverse effects on tourism and fisheries, both of which are extremely important for the economic welfare of local populations, particularly in areas where alternative economic opportunities are scarce.

Research into the socio-economic effects of coral reef degradation has focused on damage to corals as a result of global warming. Studies in this area have not yet included the effects of ocean acidification on corals, such as declining calcification rates. However, they provide indicative values on socio-economic impacts of the loss of coral reefs from adverse environmental changes. As ocean acidification has not been included, these studies have to be considered conservative in terms of potential global impacts.

Potential socio-economic impacts of reef health have been explored for the world's largest coral reef ecosystem, the Great Barrier Reef. Hoegh-Guldberg & Hoegh-Guldberg (2004) assessed how climate-driven changes on the mortality of coral reefs would affect the industries of local coastal Queensland. The study developed a new measure of the importance of 'reef-interested' tourism for the five regions of coastal Queensland – a measure that considerably increases previous estimates. In terms of contribution to the regional economies (gross regional product, GRP), the estimated reef-interested component accounts for 68% of the total – AU\$1.4 billion (about £58 000 million, using the exchange rate in May 2005). The reef-

proportion of the interested component is highest in Far North Queensland (AU\$800 million of a total tourism GRP of AU\$900 million in 1999). The authors then calculate the diminishing effect of the tourist appeal of the Great Barrier Reef as the bleaching and mortality of corals (and the associated organisms) changes with increases in temperature. This effect was calculated using the possible future greenhouse gas emission scenarios developed by the IPCC (2000). Even under a modest emission scenario, leading to an atmospheric concentration of CO<sub>2</sub> of about 600 ppm by 2100, climate change is predicted to cost local economies substantially—a minimum of AU\$2.5 billion over 19 years to 2020. Under scenarios in which global greenhouse emissions continue to grow rapidly (IPCC 2000), leading to an atmospheric concentration CO<sub>2</sub> of over 800 ppm by 2100, losses for the coastal economies of Queensland rise to over AU\$14 billion.

The World Resources Institute (Burke et al 2004) has estimated that in 2000, Caribbean coral reefs alone 'provided annual net benefits in terms of fisheries, dive tourism, and shoreline protection services with an estimated value between US\$3.1 billion and US\$4.6 billion' (about £2 000 million and £3 000 million, using the exchange rate in May 2005); and that the loss of income by 2015 from these degraded reefs may be several hundred million dollars per annum. As pointed out by several authors (see, for example, Hoegh-Guldberg & Hoegh-Guldberg 2004), these baseline estimates are minimal estimates of the economic value of coral reefs because they do not value indirect contributions that coral reefs make such as the stabilisation of coastlines and their role in creating the circumstances for other ecosystems such as mangroves and sea grasses to flourish. These, when considered with the future accumulated benefits, make the value of coral reefs significantly higher than those associated with the direct benefits to industry.

Coastal reefs in Hawaii have been estimated to generate almost US\$364 million each year in added value (Cesar et al 2002). Here 'added value' is the net business revenues (ie income minus costs), directly and indirectly from residents and tourists going snorkelling and diving on Hawaii's reefs. About 84% of this added value (US\$304 million) is generated from snorkelling and diving on reefs and emerges from US\$700–\$800 million in gross sales per year. Added value from property generates another US\$40 million each year. This number reflects the higher prices for homes and higher occupancy and room rates for commercial properties adjacent to healthy coral reefs. In addition, there is a 'non-use value' (US\$7 million), which estimates the amount of money residents, visitors and non-visitors are willing to pay to ensure active management of a healthy reef. Finally, the annual added value for near-shore fisheries within the main Hawaiian islands' coastal reefs is about US\$2.5 million per annum.

This amount reflects the revenues of fishermen minus their costs.

It is clear that globally the economic value of coral reefs is many billions of dollars per annum, and that the likelihood of significant degradation of reefs would be a sufficient cause for action to protect them.

### **6.3 Effects on marine fisheries**

Revenue from global capture fisheries in 2002 was around US\$78 billion, with marine capture fisheries accounting for about 90% of this (FAO 2004). Although the major adverse effect on marine fisheries at present is that of the mortality generated by large-scale fishing (Pauly et al 1998), any further adverse effect on their productivity would nevertheless lead to very substantial social and economic losses.

Direct effects on marine fish include physiological effects such as hypercapnia, which has been studied on some species of fish in elevated CO<sub>2</sub> levels (Section 3.4.1). There is insufficient information to predict whether future high levels of CO<sub>2</sub> will lead to significant adult fish mortality. Similarly, it is not possible to predict if there will be any changes in the reproductive success of marine organisms (Section 3.4.2), which would have wide-ranging impacts on marine fisheries.

One of the major indirect impacts on tropical coastal fisheries may be associated with the loss of coral. In addition to the effect on tourism of rising acidity on coral growth, the potential loss of coral-dominated reef systems in the tropics may lead to large-scale changes to the critical habitats of many commercial fish species. These organisms, many of which are completely dependent on coral for food and shelter, would be expected to undergo a major contraction as coral populations dwindle. Organisms that are associated with coral but not as dependent may be expected to be relatively unaffected. Several studies already support this proposal. The orange-spotted filefish (*Oxymonacanthus longirostris*), which is unable to survive without coral, rapidly disappeared from Okinawan reefs after the 1998 bleaching event (Kokita & Nakazono 2001). This particular species, like many others such as butterflyfish and angelfish, requires coral for food, larval settlement and shelter. Although this species is not of great commercial concern, it illustrates the likely impacts of large-scale changes to the habitat of tropical coastal fishes. Other fish associated with coral reefs may stand to benefit from reefs that change from coral domination to reefs that are mostly dominated by algal species. Herbivorous fish populations appear to have increased after the 1998 mass bleaching event on Tanzanian reef systems (Lindahl et al 2001). Similar conclusions have been seen at other sites by Chabanet (2002). Our understanding of the relationships between organisms on coral reefs is relatively scant; hence our ability to project

how changes in coral cover will affect overall species diversity and community structure on coral reefs is limited. However, the impact of the loss of carbonate structures along tropical coastal areas, and therefore this important habitat, could be substantial.

These considerations show that there could be very significant effects of increased ocean surface CO<sub>2</sub> on fisheries.

### **6.4 More general ecosystem effects**

As noted in previous sections, pH is such a fundamental variable for marine biogeochemical processes that pervasive effects on ecosystem structure and function are possible. The widespread effects on the ecosystem of the eastern Bering Sea caused by the coccolithophorid blooms (Section 4.3.1) in 1997 may serve as an example of the significant impacts on an ecosystem that can result from small changes in the Earth systems. In this case it was a change in temperature (Pitcher & Calder 2000), which caused an opposite effect on coccolithophores than would be expected with ocean acidification. Observations of the coccolithophorid blooms in 1997 showed a detrimental affect on the mortality of diving seabirds and the migration of sockeye salmon. The number of sockeye salmon migrating in Bristol Bay was so low – an estimated 5 million to 12 million animals failed to appear – that the fishery was declared a ‘commercial failure’ (Fisheries 1998).

### **6.5 Ecosystem services and vulnerability**

The oceans provide numerous ecosystem services that benefit human-kind (Millennium Ecosystem Assessment 2005). These services, such as fisheries contribute significantly to global employment and economic activity. Other services provided by the oceans, for example providing a site for the release of wastes and pollutants, and protection of coastal area by coral from wave energy, are not sufficiently accounted for by standard economic measures. Attempts to quantify some of these services have produced estimates of many billions of dollars (Millennium Ecosystem Assessment 2005). Therefore any significant degradation (even by a few per cent) of these services could have a considerable impact on the global economy.

The Millennium Ecosystem Assessment report highlights established but incomplete, evidence that changes made to an ecosystem increase the likelihood of further nonlinear changes to that ecosystem (Millennium Ecosystem Assessment 2005). These may include accelerated, abrupt and potentially irreversible changes to ecosystem structure which would have significant consequences for human well-being. Owing to projected changes in ocean chemistry, marine ecosystems are likely to become less resilient to further change and more

vulnerable to other environmental impacts (for example climate change, coastal deforestation, large-scale fishing and pollution).

## 6.6 Corrosion

Corrosion of metals in seawater is a major economic issue for industries involved in shipping and fixed marine structures. Increase in water acidity has the potential to increase rates of metal corrosion. However, the pH decreases discussed in previous sections (a decrease of 0.5 pH units by the year 2100) are unlikely to be sufficient to lead to a significant direct increase in corrosion rate. This is because the rate of corrosion at pH values around those found in the oceans (about pH 8.2) is largely unaffected by small changes in pH. Corrosion is also likely to be limited by the rate of diffusion of oxygen to the metal surface. A further possible effect arises because metal surfaces in seawater tend to acquire an inorganic coating of which the major component is  $\text{CaCO}_3$  (Laque 1975). The formation of these coatings is enhanced where the metal surface has been treated with another metal to form cathodic protection; which induces a small protective electric current between the two metals in seawater to inhibit the rate of corrosion. Such inorganic coatings have a beneficial effect in slowing corrosion, but if they are subject to dissolution due to decreased pH then this might increase the rate of corrosion. However, we have been unable to find quantitative information on this effect and how significant a pH decrease of 0.5 units might be; it would appear to be a suitable topic for future study.

## 6.7 Conclusions

The likely adverse effects of ocean acidification on coral reef ecosystems projected in this report would have significant consequences for the human livelihoods, such

as tourism, that are based on them. This may lead to economic losses of many billions of dollars per year, and major socio-economic impacts on the vulnerable societies that depend upon them. In addition, changes to the stability of coastal reefs in tropical and subtropical parts of the globe may lead to serious decreases in coastal protection over longer timescales. These changes could fundamentally change the nature of entire coastlines and the resources available to human societies that depend on them. Future planning, especially in vulnerable coastal societies in developing countries, should include strategies that incorporate these potentially damaging effects of ocean acidification.

Ocean acidification may have significant impacts on the life cycles (including the reproductive success) of some marine fish and shellfish species, putting at risk some unknown fraction of the global economic value of these resources (about \$100 billion). It may well cause a significant perturbation of the whole marine biogeochemical system and the ecosystem services (valued at billions of dollars per year) which it provides, to an extent and in ways that at present cannot be foreseen.

However, estimates of the economic consequences of ocean acidification are uncertain, as they do not take into account large non-monetary effects that are outside the scope of formal economic assessments. Some off-setting beneficial effects may also occur to some components of the ecosystem, although there are invariably significant costs involved in adapting to change of any sort. Moreover, as future ocean acidification may involve a significant rate of change of pH, and the oceans and organisms in the past have evolved with much slower rates of change, it would be prudent to expect that the greater the rate and scale of change due to the present ocean acidification, the more adverse the impacts will be on the marine ecosystem.



## 7 Engineering approaches to mitigation of ocean pH change

This section considers the practicality of some of the engineering approaches that have been suggested as ways to mitigate the chemical effects on the oceans of increased atmospheric CO<sub>2</sub> concentrations.

There are many approaches to preventing the emissions of CO<sub>2</sub> to the atmosphere (for example improved efficiency, renewable energy, carbon sequestration). A discussion of these approaches is beyond the scope of this report; however, the Royal Society has commented in detail on the national and international implementation of these methods in previous reports (for example, Royal Society & Royal Academy of Engineering 1999; Royal Society 2002, 2003, 2005).

Some of the approaches to reduce the accumulation of CO<sub>2</sub> emissions to the atmosphere, for example direct injection of CO<sub>2</sub> into the deep oceans or fertilization of the upper oceans with iron (Coale 1996; Boyd et al 2000), have the potential to exacerbate chemical changes to the oceans. These chemical changes may have a range of important biological consequences, including some potentially negative impacts, and require further consideration.

It has been suggested that some of the chemical effects of CO<sub>2</sub> addition could be mitigated with the addition of alkalinity to the oceans (Kheshgi 1995; Rau & Caldeira 1999). However, this mitigation would be at best partial. If enough alkalinity were added to restore the mineral saturation state of ocean carbonate, only half of the pH change would be mitigated (Annex 1). If enough alkalinity were added to restore ocean pH, the oceans would become more saturated with carbonate minerals (Caldeira & Wickett in press). This in itself could potentially lead to ecosystem level changes. A major concern relating to this approach is the ecological damage from the amount of limestone mining that would be required (see below).

The challenges in achieving mitigation at a global scale, or even a local scale are formidable. Alkalinity could be

provided by highly soluble minerals such as magnesium hydroxide, Mg(OH)<sub>2</sub> (Kheshgi 1995). Unfortunately, such minerals are relatively rare and probably could not be obtained at the required scale. Thus, most attention has focused on carbonate minerals (for example limestone). The scale of the mining and transportation operation that would be required for a global effort appears to be prohibitively large and would also require a great deal of energy. This energy is likely to come from fossil fuel sources and would increase rates of greenhouse gas emissions. To counteract the changes in acidity caused by today's ocean uptake of roughly 2 Gt C per year (IPCC 2001) would require roughly 20 Gt CaCO<sub>3</sub> per year (Caldeira & Rau 2000), which, for a limestone layer 100 m thick, would require the removal of roughly 60 km<sup>2</sup> each year. This limestone would need to be coastally located, or transportation costs would likely be prohibitive (Rau & Caldeira 1999). Thus, features such as the white cliffs of Dover could be rapidly consumed. Therefore the introduction of limestone to offset ocean acidification would raise a host of additional environmental problems. Furthermore, limestone does not dissolve in surface waters, so additional processing, and energy, would be needed (Kheshgi 1995; Rau & Caldeira 1999).

Although the vast amounts of carbonate minerals needed may make this approach infeasible at the scale required to mitigate global changes in ocean chemistry, this approach is widely used by salt-water aquarists to promote coral growth in fish tanks. Thus, it might be possible to use alkalinity addition to save specific coral reefs (Rau & Caldeira 2002), but such ideas have never been tested *in situ* and therefore must be regarded as speculative.

Reducing the scale of future changes to the chemistry and acidity of the oceans is only possible by preventing the accumulation of CO<sub>2</sub> in the atmosphere. Alternative solutions, such as adding chemicals to counter the effects of acidification, are likely to be only partly effective and only at a very local scale.



# 8 Conclusions and recommendations

## 8.1 Conclusions

- 1 **The oceans are absorbing CO<sub>2</sub> produced from human activities from the atmosphere and this is causing chemical changes which make them more acidic (ie there is a decrease in the pH of the oceans).**
    - a **Ocean acidification, like global warming, is a predictable response to those human activities that increase the atmospheric concentration of CO<sub>2</sub>. The magnitude and rate of the acidification of the oceans can be predicted with more confidence than the rise in temperature due to global warming, as they are less dependent on climate-system feedbacks.**
    - b Predictions of the consequences of CO<sub>2</sub> emissions must take into consideration the close chemical and physical coupling between the oceans and the atmosphere. For example, changes in the chemistry of the oceans will affect its ability to absorb additional CO<sub>2</sub>, which will in turn affect the rate and scale of global warming. Rising sea temperatures caused by global warming also affect ocean chemistry, as well as other physical and biological processes.
    - c The oceans are currently taking up about one tonne of human-derived CO<sub>2</sub> per year for each person on the planet. Almost a half of the CO<sub>2</sub> produced in the past 200 years from burning fossil fuels and cement manufacture has been absorbed by the oceans. Calculations based on measurements of the surface oceans and our understanding of ocean chemistry indicate that this uptake of CO<sub>2</sub> has already reduced surface seawater pH by about 0.1 units, which corresponds to an increase of about 30% in the concentration of hydrogen ions.
    - d As CO<sub>2</sub> continues to enter the atmosphere from human activity, a proportion will be taken up by the oceans. If CO<sub>2</sub> emissions are not regulated, this could result in the pH decreasing by 0.5 units by the year 2100. This is beyond the range of current natural variability and probably to a level not experienced for at least hundreds of thousands of years and possibly much longer. Critically, the rate of change is also probably at least 100 times higher than the maximum rate during this time period. These changes are so rapid that they will significantly reduce the buffering capacity of the natural processes that have moderated changes in ocean chemistry over most of geological time.
  - e The chemical changes in the oceans caused by increases in the concentration of CO<sub>2</sub> in the atmosphere will include a lowering of the pH, an increase in dissolved CO<sub>2</sub>, a reduction in the concentration of carbonate ions, and an increase in bicarbonate ions. All of these will affect the organisms and processes in the oceans.
  - f **There appears to be no practical way to remove this additional CO<sub>2</sub> from the oceans after it has been absorbed, nor any realistic way to reverse its widespread chemical and probable biological effects.** It will take many thousands of years for natural processes to remove this excess CO<sub>2</sub> and return the oceans to a level close to their pre-industrial state. Thus, it appears that the only practical way to minimise long-term consequences for the oceans is to reduce CO<sub>2</sub> emissions to the atmosphere.
- 2 **These changes in ocean chemistry will impact on marine organisms and ecosystems.**
    - a Seawater pH is a critical variable in marine systems; even small changes will have a large impact on ocean chemistry. These changes are likely to alter the biodiversity of marine ecosystems, and may affect the total productivity of the oceans. The impacts will be greater for some regions and ecosystems. However, apart from a few ecosystems such as coral reefs and the Southern Ocean, the direction and magnitude of these impacts are very uncertain. Most of the available evidence suggests that these changes are likely to reduce the resilience of marine ecosystems.
    - b The best scientific information currently available suggests that these changes in ocean chemistry will almost certainly have major adverse effects on corals and the reefs they build in tropical and subtropical waters. This will affect the stability and longevity of the structures supporting these ecosystems with implications for the biodiversity and their ecological sustainability. Cold-water coral reefs are also likely to be adversely affected, before they have been fully explored.
    - c Future changes in ocean chemistry, resulting from enhanced atmospheric CO<sub>2</sub>, specifically the likely reduction in the concentration of carbonate ions, will make it more difficult for animals to produce hard structures such as carbonate skeletons and shells. The evidence available suggests that this will probably adversely affect most of these organisms. For

example many coastal animals and specific groups of phytoplankton and zooplankton will be affected.

- d Increased CO<sub>2</sub> and the associated reduction in seawater pH may be particularly stressful for organisms with a high metabolism such as squid. Some studies indicate that the physiology of other large marine animals may also be affected, possibly restricting their growth, reproduction or both.
- e Ecosystems near the ocean floor, especially on the seabed of shallow waters, provide an essential service for other organisms in the surface oceans: receiving food from the sunlit waters above in the form of sinking particles, they also recycle nutrients from the sediments, which are required for the growth of other organisms. Differences in the response of these diverse organisms to reduced pH could have a considerable impact on the functioning of marine sediments and the 'ecosystem goods and services' they provide.
- f Organisms will continue to live in the oceans wherever nutrients and light are available, even with ocean acidification. However, from the data available, it is not known if organisms at the various levels in the food web will be able to adapt or if one species will replace another. It is also not possible to predict what impacts this will have on the community structure and ultimately if it will affect the services that the ecosystems provide. Without significant action to reduce CO<sub>2</sub> emissions into the atmosphere, this may mean that there will be no place in the future oceans for many of the species and ecosystems that we know today.

### **3 Oceans play a very important role in the global carbon cycle and Earth's climate system.**

- a There are potentially important interactions between changes in the state of the oceans (including their pH) and changes in the global climate and atmospheric chemistry. Our knowledge of these impacts and effects is currently poor and requires urgent consideration.
- b Both ocean acidification and climate change result from increasing atmospheric CO<sub>2</sub> emissions. Effects of climate change, particularly increases in ocean temperature, will impact on marine ecosystems. Occurring at the same time, the impacts of climate change will be additional to (and possibly synergistic with) those due to increased CO<sub>2</sub> and ocean acidification.

### **4 The socio-economic effects of ocean acidification could be substantial.**

- a Serious damage to coral reef ecosystems, and the human activities that are based on them, such as fisheries and recreation, could amount to economic losses of many billions of dollars per year. This will have very serious impacts on the vulnerable societies that depend upon these ecosystems.
- b Ocean acidification is likely to have significant impacts on some marine fish and shellfish species. It is very hard to determine the economic value of many of these impacts, but would present a risk to some unknown fraction of the global economic value of these resources (about \$100 billion per year).
- c Ocean acidification will probably cause significant changes in the whole marine biogeochemical system and the ecosystem services that it provides, to an extent and in ways that cannot at present be foreseen.
- d Changes to the stability of coastal reefs in tropical and subtropical parts of the globe may lead to serious decreases in coastal protection over longer time periods. These changes could fundamentally change the nature of entire coastlines and the resources available to human societies that depend on these coastal reefs.

### **5 Reducing the scale of future changes to the chemistry and acidity of the oceans is only possible by preventing the accumulation of CO<sub>2</sub> in the atmosphere.**

- a Solutions other than preventing CO<sub>2</sub> emissions reaching the atmosphere, such as adding chemicals to counter the effects of acidification, are likely to be only partly effective and only at a very local scale. It would be impossible at a regional or global level, and could also cause damage to the marine environment.
- b There are many possible approaches to preventing the accumulation in the atmosphere of CO<sub>2</sub> produced by human activities: for example improved energy efficiency, use of renewable energy and carbon sequestration in geological reservoirs. Some approaches, such as direct injection of CO<sub>2</sub> into the deep oceans, have the potential to further exacerbate chemical changes to the oceans.
- c **Unless significant reductions are made in global emissions of CO<sub>2</sub> (to ensure atmospheric CO<sub>2</sub> concentration is under twice its current levels by 2100) the entire**



**depth of the Southern Ocean will become undersaturated for aragonite, which is required by some organisms to make carbonate skeletons and shells.** Further increases in atmospheric concentration of CO<sub>2</sub>, above this doubling, would make the impacts progressively worse for the oceans as a whole.

- 6 We conclude on the basis of current evidence that ocean acidification is an inevitable consequence of continued emissions of CO<sub>2</sub> into the atmosphere, and the magnitude of this acidification can be predicted with a high level of confidence. However, its impacts, particularly on marine organisms, are much less certain and require a substantial research effort.**
  - a Research into the impacts on ocean with a high CO<sub>2</sub> concentration is in its infancy and needs to be developed rapidly. Among the priority areas for further research are: the identification of those species, functional groups and ecosystems that are most sensitive to increased surface ocean CO<sub>2</sub>, and the rate at which organisms can adapt to these changes; the interaction of increased CO<sub>2</sub> in the surface oceans with other factors such as temperature, the carbon cycle, sediment processes, and the balance of reef accretion and erosion; feedbacks of increased ocean surface CO<sub>2</sub> on air–sea exchange of CO<sub>2</sub>, dimethylsulphide and other gases important for climate and air quality; and larger-scale manipulation experiments on the effect of increased CO<sub>2</sub> on biota in the surface oceans.
- 7 Ocean acidification is a powerful reason, in addition to climate change, for reducing global CO<sub>2</sub> emissions.**

## 8.2 Recommendations

- 1 **There is a clear risk of significant adverse effects of ocean acidification.** We recommend that this risk should be taken into account by policy makers and other relevant national and international bodies (perhaps including the United Nations Framework Convention on Climate Change) at all discussions and negotiations about climate and other global changes.
- 2 **Any targets set for CO<sub>2</sub> emission reductions should take account of the impact on ocean chemistry and acidification as well as climate change.** We recommend that if the risk of irreversible damage arising from ocean acidification is to be avoided, particularly in the Southern Ocean, the cumulative future emissions of CO<sub>2</sub> from human activities to the atmosphere must be considerably less than 900 Gt C by 2100.
- 3 Ocean acidification and its impacts on the oceans needs to be taken into account by the Intergovernmental Panel on Climate Change and kept under review by international scientific bodies such as the Intergovernmental Oceanic Commission, the Scientific Committee on Oceanic Research and the International Geosphere-Biosphere Programme.
- 4 Tackling ocean acidification cannot be done by any country alone. We believe that the UK could and should take a lead internationally on both policy and research. However, it will only be able to do so by developing and extending its research activity and its international scientific networks.
- 5 Marine ecosystems are likely to become less robust as a result of the changes to the atmosphere outlined in this report and will probably to be more vulnerable to other environmental impacts (for example climate change, deteriorating water quality, coastal deforestation, fisheries and pollution). **This increased fragility and sensitivity of marine ecosystems needs to be taken into consideration during the development of any policies that relate to their conservation, sustainable use and exploitation, or effects on the communities that depend on them.**
- 6 Research into ocean chemical changes needs additional investment. Given the potential impacts of these changes, we recommend that a major internationally coordinated research effort (including monitoring) should be launched. The scale of this needs to be commensurate with that on the effects of climate change arising from enhanced greenhouse emissions. The impacts of ocean acidification are additional to, and may exacerbate, the effects of climate change. For this reason, the necessary funding should be additional and must not be diverted from research into climate change.
- 7 International research collaboration should be enhanced, particularly on the questions associated with effects of enhanced atmospheric CO<sub>2</sub> on ocean chemistry and the resulting impacts on sensitive organisms, functional groups and ecosystems. These efforts need to focus on establishing a better understanding of the various metabolic processes at different parts of the life cycle and how these are expressed at an ecosystem level. Approaches required include global monitoring as well as laboratory, mesocosm and field studies. Models that include effects of pH over a range of scales from the level of the organism to that of the ecosystem will also be necessary. Greater understanding of the likely changes to the oceans resulting from acidification will help inform the management strategies by which human populations can mitigate or adapt to these changes, and can also be linked to climate change models to predict synergistic impacts. The existing research projects of the Surface Ocean–Lower Atmosphere Study (SOLAS) and the Integrated Marine Biogeochemistry and Ecosystem Research Project (IMBER) should be part of any new initiative.
- 8 **Action needs to be taken now to reduce global emissions of CO<sub>2</sub> to the atmosphere to avoid the risk of large and irreversible damage to the oceans. We recommend that all possible approaches be considered to prevent CO<sub>2</sub> reaching the atmosphere. No option that can make a significant contribution should be dismissed.**

# Annex 1 A brief account of measures of acidity such as pH, and the acid–base chemistry of the CO<sub>2</sub>–carbonate system in the sea

## A1 The meaning of pH

The term pH describes the acidity of a liquid. It is defined as:

$$\text{pH} = -\log_{10} [\text{H}^+] \quad (1)$$

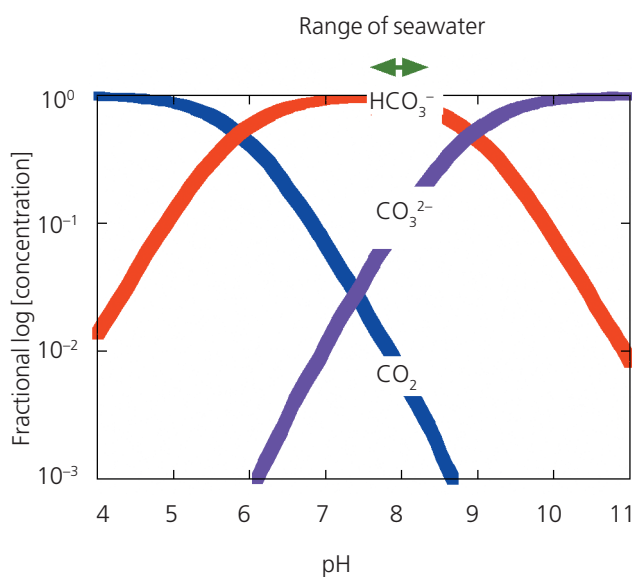
This negative logarithmic dependence on hydrogen ion concentration, [H<sup>+</sup>], in moles per litre means that if [H<sup>+</sup>] increases 10-fold then pH decreases by 1 unit. The square brackets refer to the concentration of H<sup>+</sup> and subsequently for the concentration of other substances.

Water has the formula H<sub>2</sub>O. Only a small proportion of the water molecule splits up into H<sup>+</sup> and OH<sup>-</sup>. In pure water, the amounts of [H<sup>+</sup>] and [OH<sup>-</sup>] are equal and the concentration of each is 10<sup>-7</sup> in the units mole per litre. This means that a neutral solution has pH = 7. Acid solutions have an excess of [H<sup>+</sup>] and a pH less than 7. Alkaline (basic) solutions have an excess of [OH<sup>-</sup>] and pH greater than 7, up to 14.

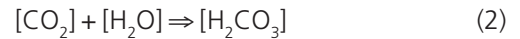
## A2 Dissolved inorganic carbon in seawater

As CO<sub>2</sub> dissolves in seawater, it reacts with seawater to produce H<sup>+</sup> and various negatively charged forms of dissolved carbon (see Figure A). Carbon dioxide dissolved in seawater first reacts with the water molecule (H<sub>2</sub>O) to form carbonic acid (H<sub>2</sub>CO<sub>3</sub>). Not all the CO<sub>2</sub> dissolved in seawater reacts to make carbonic acid and therefore seawater contains dissolved gaseous

Figure A. Relative proportions of the three inorganic forms of CO<sub>2</sub> dissolved in seawater. Note the ordinate scale (vertical axis) is plotted logarithmically.



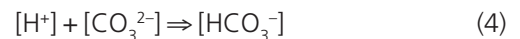
CO<sub>2</sub>; a point that is easily appreciated from a familiarity with carbonated drinks (which are solutions of carbonic acid). According to Henry's Law, in a simple aqueous solution we would expect the concentration of CO<sub>2</sub> in the air to be proportional to that in the solution of carbonic acid.



Carbonic acid is an acid because it can split up into its constituents, releasing an excess of H<sup>+</sup> to solution and so driving pH towards lower values. Carbonic acid splits up by adding one H<sup>+</sup> to solution along with HCO<sub>3</sub><sup>-</sup> (a bicarbonate ion):

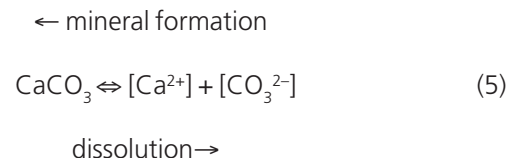


This increase in H<sup>+</sup> causes some CO<sub>3</sub><sup>2-</sup> (called carbonate ion) to react with H<sup>+</sup> to become HCO<sub>3</sub><sup>-</sup>:



Thus, the net effect of the dissolution of CO<sub>2</sub> in seawater is to increase concentrations of H<sup>+</sup>, H<sub>2</sub>CO<sub>3</sub> and HCO<sub>3</sub><sup>-</sup>, while decreasing concentrations of CO<sub>3</sub><sup>2-</sup>.

The decrease in carbonate ion concentration [CO<sub>3</sub><sup>2-</sup>] has important consequences for the chemistry of carbonate minerals commonly used by marine biota to form shells or skeletons. The formation and dissolution of carbonate minerals can be represented as:



Because the dissolution of CO<sub>2</sub> in seawater decreases [CO<sub>3</sub><sup>2-</sup>], this reaction moves to the right, impeding the formation of carbonate minerals and promoting their dissolution. Dissolution of carbonate minerals (Equation 5) provides carbonate ions that can react to consume H<sup>+</sup> according to Equation 4. Thus, the dissolution of carbonate minerals tends to decrease [H<sup>+</sup>] (increase pH), counteracting some of the pH effects of added CO<sub>2</sub> (see A3).

## A3 The carbonate buffer and seawater pH

The term 'carbonate buffer' is used to describe how the dissolved inorganic carbon system in seawater acts to diminish changes in ocean H<sup>+</sup> concentration, and thus pH. If a process, such as CO<sub>2</sub> dissolution (Equations 2 and 3), adds H<sup>+</sup> to seawater, some of the added H<sup>+</sup> reacts with

carbonate ( $\text{CO}_3^{2-}$ ) ion to convert it to bicarbonate ( $\text{HCO}_3^-$ ) (Equation 4). Because initially most of the added  $\text{H}^+$  would be consumed in this way, the change in pH is much less than it would otherwise be. But this process also consumes some carbonate ion; therefore this pH-buffering capacity would diminish as  $\text{CO}_2$  concentrations increase. Because  $\text{CO}_2$  is absorbed at the sea surface, it is the surface oceans that are most affected.

On the longer time scales of ocean mixing, interaction with  $\text{CaCO}_3$ -rich sediments tends further to buffer the chemistry of the seawater so that changes in pH are lessened. For example, if the deep oceans start to become more acidic such as through the addition of  $\text{CO}_2$ , which decreases concentrations of  $\text{CO}_3^{2-}$ , some carbonate ion will be dissolved from sediments (Equation 5).

The carbonate buffer acts to stabilise the average pH of seawater at approximately  $\text{pH} = 8$  because of the following two processes: (i) uptake of  $\text{CO}_2$  from the atmosphere (for example from volcanoes and now, importantly, from fossil fuel burning) and (ii) interaction of seawater with oceanic sediments composed of  $\text{CaCO}_3$ . Because  $\text{CaCO}_3$  is abundant in sediments, the pH of the deep oceans cannot change by large amounts over timescales of 10 000 years. However, over historical

timescales, significant changes in surface and near surface ocean pH can occur.

#### **A4 The calcium carbonate saturation horizon**

As discussed in this report, small organisms living in open ocean waters construct shells or plates of  $\text{CaCO}_3$  that, on death of the organism, fall to the sea floor. Their preservation in sea floor sediments depends on the solubility of  $\text{CaCO}_3$  in seawater and on the concentration of carbonate ions.

There is a critical concentration of carbonate ions in seawater (the saturation concentration) below which  $\text{CaCO}_3$  will start to dissolve. Because  $\text{CaCO}_3$  solubility increases with decreasing temperature and increasing pressure, the critical concentration occurs at a depth, the 'saturation horizon', below which seawater is under-saturated and  $\text{CaCO}_3$  will tend to dissolve and above which seawater is super-saturated and  $\text{CaCO}_3$  will tend to be preserved. Because the  $\text{CaCO}_3$  mineral calcite is less soluble than the form aragonite, the aragonite saturation horizon is shallower. Because added  $\text{CO}_2$  decreases the carbonate ion concentration, the saturation horizons will become shallower with increasing releases of human-derived  $\text{CO}_2$  to the atmosphere.

## Annex 2 List of respondents

To inform the study we issued an open call for evidence in August 2004. We are very grateful to those who responded to this call and to those who provided additional information at the request of the Working Group.

<b><i>Name of submitter</i></b>	<b><i>Organisation</i></b>
Dr Martin Angel	Southampton Oceanography Centre
Ms Valia Avgoustidi	University of East Anglia
Dr Richard Bellerby	University of Bergen, Bjerknes Centre for Climate Research
Dr Jelle Bijma	Alfred Wegener Institute
Dr Philip Boyd	University of Otago
Dr J S Burnell-Gray	Institute of Corrosion
Dr Victoria Fabry	California State University San Marcos
Dr Richard Feely	NOAA, USA
Prof André Freiwald	Friedrich Alexander Universität Erlangen Nürnberg
Dr Jim Gunson	The Hadley Centre
Prof G Fogg FRS CBE	Personal submission
Dr Jason Hall-Spencer	University of Plymouth
Dr Peter Haugan	University of Bergen
Dr Donald Hawthorn	Personal submission
Prof Christoph Heinze	University of Bergen
Prof Dave Hutchins	University of Delaware
Dr Ian Joint	Plymouth Marine Laboratory
Prof Les Kaufman	Boston University Marine Program
Dr Dan Laffoley	English Nature
Dr Martina Langenbuch	Alfred Wegener Institute
Prof G Langer	Alfred Wegener Institute
Dr Ben McNeil	University of New South Wales
Dr Douglas Mills	Institute of Corrosion
Dr Corinne Le Quéré	Max-Planck-Institut für Biogeochemie
Dr Tim McClanahan	World Conservation Society
Prof Paul Pearson	Cardiff University

Prof Andy Ridgwell	Department of Earth and Ocean Sciences, University of British Columbia
Dr Chris Sabine	NOAA, USA
Prof Yoshihisa Shirayama	Seto Marine Biological Laboratory, Kyoto University
Dr Taro Takahashi	Lamont-Doherty Earth Observatory of Columbia University
Dr Toby Tyrell	Southampton Oceanography Centre
Dr Ed Urban	Scientific Committee on Oceanic Research
Prof Dieter Wolf-Gladrow	Alfred Wegener Institute

## Annex 3 Abbreviations and glossary

Albedo	Proportion of sunlight reflected by the Earth back into space. A reduction or increase of the Earth's albedo has an impact on global warming
Algae	Photosynthetic organisms lacking characteristic features of land plants, including phytoplankton and seaweeds
Anoxic	Without oxygen
Aragonite	Form of $\text{CaCO}_3$ with orthorhombic (crystal system based on three unequal axes at right angles to each other) symmetry in its crystal structure
Archaea	Single-celled creatures that, with bacteria, make up a category of life called the prokaryotes (organisms composed of a cell having no nuclear membrane)
Bacteria	Single-celled creatures that, with archaea, make up a category of life called the prokaryotes (organisms composed of cells having no nuclear membrane)
Benthic	Bottom dwelling
Bioturbation	The disturbance and mixing of the sediments by animals as they move through them
$\text{CaCO}_3$	Calcium carbonate. Compound used in the formation of shells and plates of marine organisms
Calcite	Form of $\text{CaCO}_3$ with a trigonal (rhombohedral) symmetry in its crystal structure
CCS	Carbon capture and storage
Cephalopoda	A class of molluscs including squids, cuttlefish and octopuses
Cetacea	An order of large aquatic mammals including whales, dolphins and porpoises
$\text{CH}_4$	Methane
$\text{CO}_2$	Carbon dioxide
$\text{CO}_3^{2-}$	Carbonate ion
Coccolithophore	Calcifying planktonic algae
Demersal	Living near the bottom of the sea
DIC	Dissolved inorganic carbon
Dinoflagellate	Members of the algal class Dinophyceae, occurring as members of the marine phytoplankton and as photosynthetic symbionts in some benthic marine foraminifera and invertebrates
Dissociation	The capacity for certain compounds to form ions including $\text{H}^+$ ; this causes, and is caused by, pH changes
DMS	Dimethylsulphide, a breakdown product of DMSP which is volatile and can, in the atmosphere, be chemically transformed to compounds that can increase cloud formation
DMSP	Dimethylsulphoniopropionate a compound produced by some marine phytoplankton organisms, and whose breakdown produces DMS in globally significant quantities.
Euphotic zone	Zone of the sea where light penetration is sufficient for photosynthesis

Foraminifera	An order of protozoans, the members of which have a shell that is usually calcareous
GLODAP	Global Data Analysis Project
GRP	Gross regional product
Gt	Gigatonne ( $10^9$ tonnes)
Gymnosomata	Carnivorous marine planktonic molluscs which feed exclusively on pteropods
Halocarbon	A compound in which the hydrogen of a hydrocarbon is replaced by halogens
Halogen	Any of the group of elements fluorine, chlorine, bromine, iodine and astatine
$\text{HCO}_3^-$	Bicarbonate ion
$\text{H}_2\text{CO}_3$	Carbonic acid
$\text{H}_2\text{O}$	Water
IPCC	Intergovernmental Panel on Climate Change
Krill	A small shrimp-like planktonic crustacean of the order Euphausiacea, important as food for fish, and for some whales and seals
Henry's Law	The concentration of a solute gas in a solution at a given temperature and salinity is directly proportional to the partial pressure of that gas above the solution
Hypercapnia	$\text{CO}_2$ -induced acidification of body fluids
LLNL	Lawrence Livermore National Laboratory
Mesocosm	Experimental apparatus or enclosure designed to approximate natural conditions for tonnes of seawater, and in which environmental factors can be manipulated
Microcosm	Experimental apparatus or enclosure designed to approximate natural conditions for kilograms of seawater, and in which environmental factors can be manipulated
$\text{Mg}(\text{OH})_2$	Magnesium hydroxide
Orthorhombic	Crystal structure based on three unequal axes at right angles to each other
$\text{N}_2\text{O}$	Nitrous oxide
Oxic	Containing oxygen
Pelagic	Living in the middle depths and surface waters of the sea
pH	A measure of the acidity of a solution; a pH below 7 indicates acidity, and above 7 denotes alkalinity
Planktonic	Of plankton, floating or drifting organisms
Protist	A member of the Protista, a group of unicellular organisms regarded as intermediate between, or more properly distinct from, plants and animals.
Protozoan	A member of the Protozoa, a group of protists with animal-like features



Pteropods	Planktonic marine molluscs with wing-like extensions to the foot, commonly called sea butterflies. The herbivorous Thecosomata typically have an aragonitic shell and are the organisms referred to in the text as Pteropods. The carnivorous Gymnosomata lack a shell and are sometimes considered to be pteropods
Saturation horizon	A natural boundary in seawater, above which $\text{CaCO}_3$ can form, and below, it dissolves. The boundary forms through the interplay of several variables, including pH
Speciation	In the context of this report, it is the chemical form of an element in seawater
Surface ocean	Near surface waters where exchange of $\text{CO}_2$ occurs
Symbionts	Partners in a symbiotic association
Symbiosis	Close spatial and functional association of different organisms over much or all of their lives
Thecosomata	Herbivorous planktonic marine molluscs with an aragonitic shell, considered in the text to be equivalent to pteropods
Trigonal	Three-sided; having three fold symmetry
UNFCCC	United Nations Framework Convention on Climate Change
Upwelling	Bulk movement of water from the deep ocean to the surface as part of global ocean circulation or, on a smaller scale, as part of other upward water movements



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