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# Ocean Acidification

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**Please cite this document as:**

Turley, C., C. Brownlee, H.S. Findlay, S. Mangi, A. Ridgwell, D.N. Schmidt, and D.C. Schroeder (2010) Ocean Acidification in MCCIP Annual Report Card 2010-11, MCCIP Science Review, 27pp. [www.mccip.org.uk/arc](http://www.mccip.org.uk/arc)

**EXECUTIVE SUMMARY**

The oceans are an enormous store of carbon, substantially greater than on land or in the atmosphere and hence play a key role in the global carbon cycle, especially in helping regulate the amount of CO<sub>2</sub> in the atmosphere. The oceans are important because they have taken up around 28-34% of the CO<sub>2</sub> produced by humankind through the burning of fossil fuels, cement manufacturing and land use changes since the industrial revolution. Whilst this has somewhat limited the historical rise of CO<sub>2</sub> in the atmosphere, thereby reducing the extent of greenhouse warming and climate change caused by human activities, this has come at the price of a substantial change to ocean chemistry. In particular, and of great concern, is the 30% decrease in ocean pH and 16% decrease in carbonate ion concentration between pre-industrial days and today. These changes are known as 'ocean acidification'. Our understanding of the impact of CO<sub>2</sub> on the carbonate chemistry is such that we know with very high certainty that ocean acidification will continue, tracking future CO<sub>2</sub> emissions to the atmosphere.

Evidence from experiments and observations are raising concern that future ocean acidification may be a threat to many marine organisms. This is mainly due to the rate at which ocean carbonate chemistry is changing which may exert pressure on marine organisms to respond. Responses can come in many forms. Marine organisms may migrate to alternate habitats, while others may simply be able to acclimatize to changes in their environment. Those that cannot may not survive these rapid changes to ocean chemistry. These different scenarios will have wider implications on food webs and ecosystem function. Moreover, the scale and direction of impacts due to ocean acidification on biogeochemical cycling of carbon, nutrients and climate reactive gases and other potential feedbacks to climate is largely unknown. Here, ocean acidification events in the Earth's past may help interpret the future of our oceans in a world of unabated CO<sub>2</sub> emissions. No exact geological analogue exists for society's activities today as the rate of acidification today is faster than at any time in the last 65 Ma years and the oceans chemistry is different today than during large parts of Earth's history. For example, past oceans contained higher calcium ion concentration, which helped stabilize calcium carbonate minerals in marine organisms' skeletons. The most comparable example is the ocean acidification and warming during the Palaeocene-Eocene Thermal Maximum (PETM) 55 Ma ago. Based on the observed biotic reaction at the PETM recorded in the geological record, the extent of future acidification, particularly in the deep ocean, raises the possibility of similar extinctions. After the PETM, recovery of the deep sea benthic marine ecosystems from this event took more than a hundred thousand years. The much faster rate of future changes in the surface ocean may challenge the ability of some key calcifying organisms to adapt or migrate.

At present, the socio-economic impacts of ocean acidification are difficult to predict. However, the goods and services provided by the marine environment to the UK are important, for example, multi million pound fisheries, fish meal and aquaculture industries employing tens of thousands of people and if impacted by ocean acidification could have a direct economic impact. Globally coral reefs have been valued at \$30 billion providing food, tourism and shore protection so any threat to them will be important for the economics of some of UK's overseas territories.

Ocean acidification is a global scale threat but impacts will be felt at the local and regional scale. It is therefore likely that UK coastal waters, ecosystems and habitats will be impacted this century as CO<sub>2</sub> emissions continue to rise. The only way of reducing the impact of ocean acidification is the urgent and substantial reduction of these emissions.

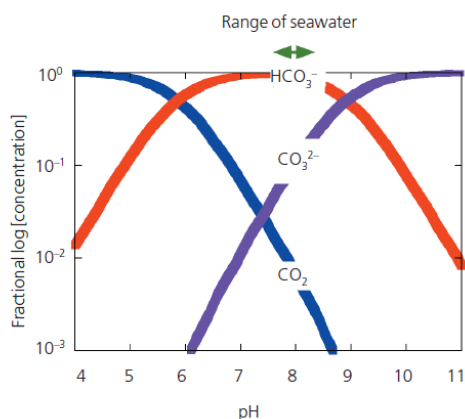
## FULL REVIEW

### 1. What is already happening?

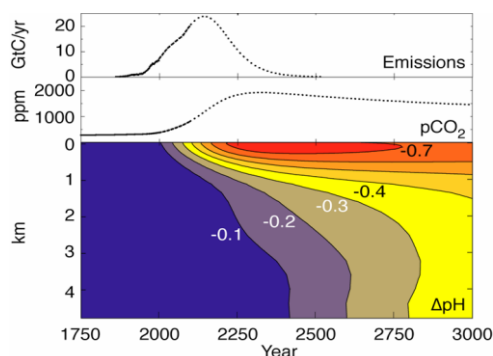
#### Ocean Carbonate Chemistry

##### *The ocean carbon reservoir and changes to ocean chemistry*

The oceans are a major part of the Earth's carbon cycle, with estimates of the pre-industrial ocean carbon reservoir of ~38000 PgC (petagrams, 10<sup>12</sup> kg, of carbon; 1 PgC equals and is sometimes written as 1 Gt carbon), compared with ~700 PgC in the atmosphere and <1170 PgC in the terrestrial biosphere (reviewed in Royal Society, 2005). Oceans act as an important carbon sink, absorbing more CO<sub>2</sub> than they release into the atmosphere. About a quarter of all anthropogenic CO<sub>2</sub> released into the atmosphere since the beginning of the industrial revolution has been absorbed by the World's oceans (Sabine *et al.*, 2004). Ocean uptake of anthropogenic CO<sub>2</sub> has therefore buffered climate change by restricting the rate of rise in atmospheric concentration of this greenhouse gas. However, when the CO<sub>2</sub> reacts with seawater the concentration of the bicarbonate ion (HCO<sub>3</sub><sup>-</sup>) increases, while the amount of carbonate ions (CO<sub>3</sub><sup>2-</sup>) and pH of the surface ocean waters decrease (Figure 1). This has already had a significant impact on ocean chemistry, with estimates of mean surface ocean pH decrease of ~0.1 (equivalent to a ~30% increase in hydrogen ion (H<sup>+</sup>) concentration), starting from a value of ~8.18 around the time of the industrial revolution (Caldeira & Wickett, 2003; Figure 2). This pH drop is significantly larger than the seasonal pH variability of 0.03 to 0.04 due to changes in temperature and photosynthesis (Keeling *et al.*, 2004; Santana-Casiano *et al.*, 2007). Long term oceanographic time series stations corroborate this model and observed, after removal of seasonal variability, an annual rate of decline in surface ocean pH of 0.0019 ± 0.00025 a<sup>-1</sup> over the last two decades (IPCC, 2007; Doney *et al.*, 2009).



**Figure 1.** Relative proportions of the three inorganic forms of CO<sub>2</sub> 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. From Royal Society (2005).



**Figure 2.** Projected changes in ocean pH from a model scenario of continued use of all known fossil fuel reserves. From Caldeira & Wickett (2003).

### *Changes to aragonite and calcite saturation*

Along with temperature and salinity, the concentration of  $\text{CO}_3^{2-}$  directly influences the saturation state, and consequently the rate of dissolution and formation of calcium carbonate ( $\text{CaCO}_3$ ) minerals in the ocean. The saturation state ( $\Omega$ ) is used to express the degree of  $\text{CaCO}_3$  saturation in seawater. The three main mineral forms of  $\text{CaCO}_3$  produced by organisms are, in order of least soluble to most soluble: calcite, aragonite and magnesium-calcite. The solubility differences lead to different saturation states geographically at the ocean surface. Today, the vast majority of the surface ocean is supersaturated with respect to mineral  $\text{CaCO}_3$  ( $\Omega > 1$ ). The larger this value the easier it will be for organisms that produce  $\text{CaCO}_3$  shells, skeletons and liths (Where  $\Omega < 1$ , seawater is undersaturated and dissolves carbonates.) Increasing ocean acidification is lowering the carbonate ion concentration and hence magnesium-calcite, aragonite and calcite saturation states are all decreasing. The physiology of each organism will also be important in determining their vulnerability to decreasing saturation state (see below).

### *Shoaling of the saturation horizons*

The saturation state with respect to these minerals does not just vary from the poles to the tropics but also with water depth because solubility strongly depends on pressure. The depth at which these calcium carbonate minerals start to dissolve is known as the saturation horizon. Aragonite is more soluble than calcite and therefore the aragonite saturation horizon (ASH) is in shallower water than the calcite saturation horizon (CSH). Due to differences in ocean chemistry, the depths of these horizons naturally vary between the ocean basins. For instance, the ASH is <600m in the North Pacific but is over 2000 m deep in the North Atlantic (Guinotte *et al.*, 2006). As anthropogenic  $\text{CO}_2$  invades the ocean interior and carbonate ion concentrations are reduced, the saturation horizons will progressively shoal. Hence, locations on some continental slopes that were once bathed in super-saturated waters will find themselves in under-saturated conditions with carbonate minerals starting to dissolve.

### *Upwelling of $\text{CO}_2$ rich waters*

Intermediate waters from below the depth of the ASH, which are naturally rich in  $\text{CO}_2$ , can be seasonally upwelled onto the shelf seas of the western edge of continents. A recent study off the western coast of North America found that these undersaturated and low pH (7.6) waters bath the shelf from February to September (Feely *et al.*, 2008). A further reduction of ocean pH due to anthropogenic  $\text{CO}_2$  addition will extend the duration of exposure of the shelf biota to these corrosive waters. Other upwelling regions that do not currently experience undersaturated conditions at any time of the year may start to do so seasonally. This first, seasonal incidence of under-saturated conditions will occur before the often annual predictions of large scale ocean models.

### *Coastal waters*

The limited information available regarding seawater chemistry on coastal shelf seas has indicated that there is a greater range of pH nearshore than in open oceans as a result of terrestrial influences such as river run-off and nutrient enrichment as well as large temperature and salinity fluctuations (Hinga, 2002; Blackford & Gilbert, 2007). This large natural variability may mean that organisms from the coastal shelf sea are less susceptible to changes in pH than open ocean organisms as they may have a greater ability and potential for adaptation.

### **Impacts to Marine Organisms**

#### *Acid based regulation*

Marine organisms use ions obtained from the surrounding seawater in a number of important biological processes, including formation of mineral structures like shells or skeletons, as well as in key physiological processes. Internal pH for marine animals is normally regulated at a particular level (e.g. haemolymph pH 7.4 – 7.9 depending on species). Organisms have adapted a number of mechanisms that can, on short timescales, buffer changes in pH thereby preventing damage to internal processes and functioning.

#### *Calcification*

Three major calcifying groups of organisms, the coccolithophores, foraminifera and corals account for the bulk of calcification on a global scale. These groups calcify by significantly different mechanisms that involve different degrees of complexity and organization. In the coccolithophores calcite is produced in an intracellular compartment – the coccolith vesicle which is isolated from the rest of the cell and from the external medium. The mature calcite coccoliths are secreted to the external cell surface. Impacts of changes in external pH on the calcification mechanism in coccolithophores are therefore likely to be indirect via effects on cellular mechanism of cellular pH regulation. Foraminifera produce calcite shells or tests in an extracellular compartment that is isolated from the bulk external medium. The mechanisms, by which the calcifying cells are able to exert control over the composition of this calcification space, are the subject of numerous studies (e.g. de Nooijer et al, 2008). In corals, a more complex organization of transport processes occurs at a multicellular level with spatial separation of inorganic carbon and calcium transporters in different cell types (Tambutté et al, 1996; Brownlee, 2009). Calcifying organisms are not only vulnerable through impacts on their physiology, but additionally by dissolution of their  $\text{CaCO}_3$  structures. The mineralogy is species specific, and hence their susceptibility to dissolution will depend on the mineral form as well as the relative biological control that they exert on carbonate formation (reviewed by Kleypas *et al.*, 2006). While coccolithophores and foraminifera produce calcite, corals produce the more soluble aragonite, as do the pteropod molluscs, certain macroalgae and some other molluscs. Amorphous calcite is laid down by some species, particularly in early development stages, as the basis for carbonate formation and may be particularly susceptible to dissolution, even more so than aragonite and calcite.

## 2. What could happen in the future?

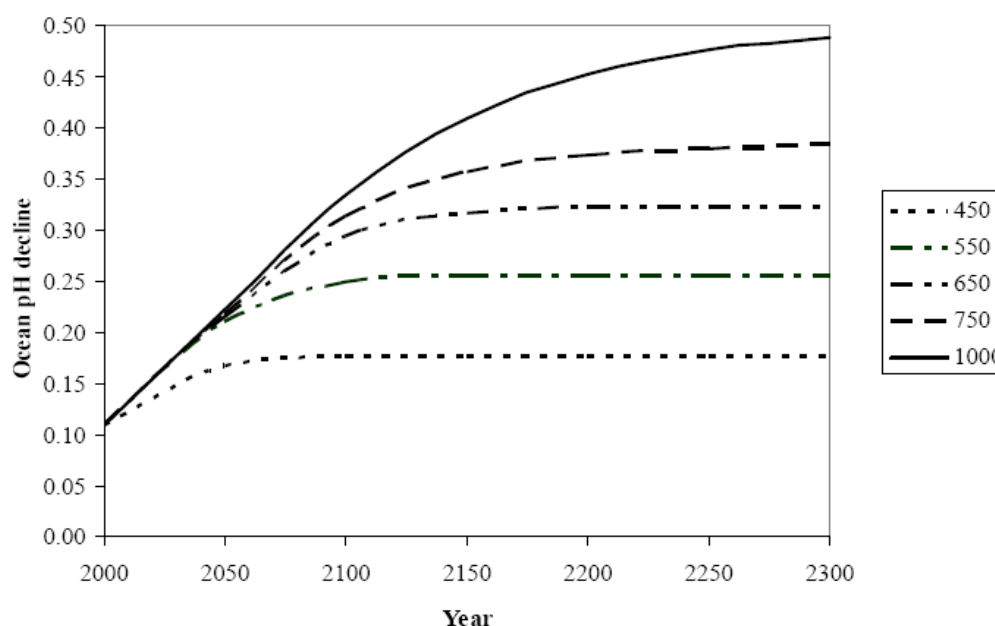
### Ocean Carbonate Chemistry

#### *Around UK waters*

Projection of future seawater pH around UK coastal and shelf waters is generally consistent with global projections but variability and uncertainties are greater due to riverine inputs and geochemical interactions between ocean and underlying sediments (Blackford & Gilbert, 2007).

#### *Ocean acidification and relationship to climate change mitigation options*

The degree of changes to ocean chemistry, including ocean pH, will depend on the mitigation or emissions pathway society takes (Figure 3). For example, by 2100, atmospheric CO<sub>2</sub> concentrations could reach >800 ppm without any mitigation of emissions causing an additional surface water pH decrease of ~0.4 pH units. Stabilizing at atmospheric CO<sub>2</sub> concentrations lower than 800 ppm would restrict the additional pH decline. For example, CO<sub>2</sub> concentrations commensurate with a desired maximum of 2°C of global warming (~450 ppm) would produce less than an additional 0.1 pH unit decline (Figure 3). Conversely, continuing unrestricted fossil fuel use past 2100 could potentially lead to a total maximum ~0.77 pH unit fall at around 2300 (Caldeira & Wickett, 2003: Figure 2).



**Figure 3.** Trajectories for surface ocean pH decrease calculated for different atmospheric CO<sub>2</sub> concentration profiles leading to stabilization from 450-1000 ppm. These were calculated from the model predictions by Caldeira & Wickett (2003). From Turley (2006).

#### *Changes to aragonite and calcite saturation*

Global ocean models unanimously project reduction in calcium carbonate saturation throughout all oceans and undersaturation with respect to aragonite occurring in polar and sub polar surface waters within several decades (Orr *et al.*, 2005). However there is still much uncertainty at a regional scale, as many of the models cannot resolve processes well at for example freshwater boundaries or upwelling areas, as discussed below.

#### *Shoaling of the saturation horizons*

Continued uptake of anthropogenic CO<sub>2</sub> by the ocean is moving the ASH towards the surface of the ocean at a rate of more than 1m per year, although this varies with



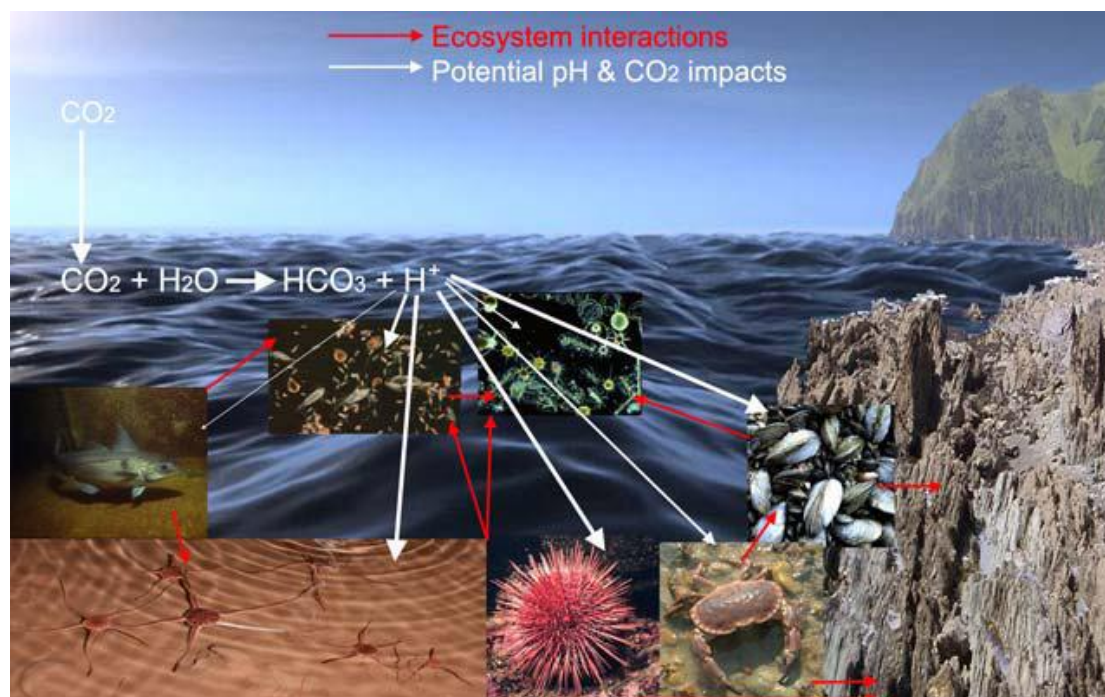
location. This means that, for example, in the Southern Ocean with naturally low saturation, the saturation horizon will have shoaled by more than 700 m and reach the ocean surface by the end of the century under an IS92a emissions scenario (Orr *et al.*, 2005).

#### *The long term legacy of CO<sub>2</sub> emissions on ocean chemistry*

It will take tens of thousands of years for the changes in ocean chemistry to be buffered through neutralization by calcium carbonate from sediments and hundreds of thousands for the weathering of rocks on land to eventually restore ocean pH completely (Archer & Brovkin, 2008; Archer *et al.* 2009). The only way of reducing the impacts of ocean acidification on a global scale and in a societally-relevant time-frame is through urgent and substantial reductions in anthropogenic CO<sub>2</sub> emissions.

#### **Potential Impacts to Marine Organisms**

Changes in seawater chemistry caused by ocean acidification threaten to disrupt the mechanisms organisms have adapted to buffer changes in pH in order to prevent damage to internal processes and function. It is unclear how long these compensation mechanisms can function, particularly as they are energetically costly. Experiments at CO<sub>2</sub> levels equivalent to those predicted for the next 100 to 300 years have significantly impacted survival, growth and development of many marine organisms (Fabry *et al.*, 2008). Many marine organisms play important roles within ecosystems so that changes to their diversity or efficiency of function could affect the ecosystems and food webs within them (Figure 4).



**Figure 4.** Simple schematic of some ecosystem interactions between example organisms living in open water (fish, zooplankton, phytoplankton), coastal water (crabs, shellfish, urchins) and the sediment (brittlestars and urchins) together with arrows denoting the potential CO<sub>2</sub> impact on the organism (large width arrows denote higher vulnerability based on authors judgement from information taken from the literature).

#### *Sea bed dwelling organisms*

The UK's regional seas provide a variety of important habitats for many benthic organisms (animals and plants that live on and in rocks, sand, mud, shingle, etc.), including commercially important species such as lobsters, crabs and shellfish (see section 5.1). There have been limited investigations into the response of key

organisms from these ecosystems to realistic future ocean acidification scenarios. Current investigations are limited to a number of species from a few taxonomic groups. These species have been chosen primarily because they are key model species which are well studied and much is known about their biology and ecology. They are often important for either food web dynamics or for ecosystem functioning.

Studies on sea urchins and brittlestars showed they were unable to compensate for medium-length experimental changes in seawater pH. Sea urchins were unable to maintain their internal pH balance for longer than seven days at pH 7.4 (year 2300 continued emission scenario) resulting in loss of normal body functions (Miles *et al.*, 2007). In experiments at (UKCP09) low emissions levels urchins exhibited reduced growth and survival rates over several months (Shiryama & Thornton, 2005). Other experiments on brittlestars showed muscle wastage in their arms as a trade-off attempt to increase their calcification at (UKCP09) high emissions levels (Wood *et al.*, 2008). In contrast, a recent study on starfish revealed no significant decreases in calcification and an increase in feeding and growth rates resulting from ocean acidification during a medium-term experiment (70 days) at (UKCP09) high emissions levels (Gooding *et al.* 2009).

Mussels and oysters show a decrease of shell and body growth by 55% at pH 7.3 (just below the pH in year 2300 under a scenario of continued emissions) (Michaelidis *et al.*, 2005). Net calcification decreased by 25% (at UKCP09 low emissions) and 37% (at UKCP09 high emissions) in mussels and 10% (UKCP09 low emissions) and 15% (UKCP09 high emissions) in oysters (Gazeau *et al.*, 2007). Other impacts from ocean acidification found in molluscs include reduced immune response (Bibby *et al.*, 2008) and altered behaviour in relation to predatory cues (Bibby *et al.*, 2007), although these occurred at much lower pH levels than projected for the next century. Natural analogues have also been described for molluscs in estuarine systems which have a declining pH gradient along the estuary (Marshall *et al.* 2008). Marine snails were shown to have a correlating increase in shell erosion but there was a continued presence of these organisms at low pH (as low as pH 6.8) suggesting that populations persist by reducing their size and perhaps changing their metabolic processes (Marshall *et al.* 2008).

Crustaceans (crabs, lobsters, barnacles) have been shown to be somewhat more able to compensate for changes in pH (Spicer *et al.*, 2007; Pane & Barry, 2007) however they are still subject to dissolution impacts and their early life stages are proving more vulnerable (McDonald *et al.* 2009; Arnold *et al.* 2009; Findlay *et al.* 2009). Other organisms also appear to be less vulnerable, such as sediment-dwelling organisms (*Neries* worms), which may be periodically subjected to low pH in their current environment and therefore have compensation mechanisms (Widdicombe & Needham, 2007).

Aspects of early-life development, including fertilisation, larval growth and development, as well as juvenile success, have been documented to be affected by ocean acidification at pH levels projected for the end of the century (UKCP09 high emissions level) in molluscs, echinoderms, crustaceans and fish (Havenhand *et al.*, 2008; Dupont *et al.*, 2008; Findlay *et al.* 2009; Arnold *et al.* 2009; Ellis *et al.*, 2009; McDonald *et al.*, 2009; Munday *et al.*, 2009; Checkley *et al.*, 2009). However, as has been shown in adults, conflicting results exist within and between species, and no clear patterns have yet been established. Many responses occur at sub-lethal levels, such as reduced development rate, reduced calcification rates, lowered growth rates. These present difficulties when making predictions as to how these impacts will alter populations, communities and the wider ecosystem.



These benthic organisms are not only commercially important, but also play important roles in the cycling of nutrients between the sediment and the water column (Figure 4), and as “ecosystem engineers”. Sea urchins, for example, in soft sediments are bioturbators and efficiently mix the sediments; on rocky shores they modify the habitat by grazing algae and allowing diverse communities to develop. Lowered fitness of these animals could change nutrient and carbon cycling (Fernand & Brewer, 2008), potentially altering the availability of nutrients for other organisms as well as disrupting ecosystem dynamics of rocky shores or in sediments. Recent studies have shown that ocean acidification impacts nutrient fluxes from sediments: Wood *et al.* (2009) found a reduction in nitrate uptake by sediments, while Widdicombe *et al.* (2009) found an increased uptake of nitrate and a decreased uptake of phosphate by sediments as well as an increased release of ammonium and a decreased release of nitrite by sediments. Community studies in the field have shown that changes in community occur in correlation with decreasing pH (Wootton *et al.*, 2008) but major changes only occurred at pH levels much lower than expected from ocean acidification resulting from uptake of CO<sub>2</sub> from the atmosphere (Dashfield *et al.*, 2008; Widdicombe *et al.*, 2009). Coralline algae, important for habitat formation, particularly for settling larvae, showed reduced calcification rates and increased levels of mortality under lowered pH conditions (UKCP09 high emissions level) (Martin *et al.* 2008; Martin & Gattuso, 2009).

Cold-water or deep-water corals are found throughout the world's oceans, including the European continental shelf and the UK coastline (e.g. cold-water coral, *Lophelia*). They can form large reef frameworks that persist for millennia and are biodiversity hotspots that play an important role as refuges, feeding grounds and nurseries for deep-sea organisms, including commercial fish (Guinotte *et al.*, 2006; Roberts *et al.*, 2006). Future projections of global aragonite saturation state and the depth of the ASH indicate that 70% of cold-water corals are likely to experience undersaturation this century and in some places as early as 2020 (Orr *et al.*, 2005; Guinotte *et al.*, 2006). Maier *et al.* (2009) report that calcification rates are slower during short-term incubations of cold-water corals (*Lophelia*) under (UKCP09) low and high emission scenarios, however individuals were still able to calcify. Over longer time periods however it is unknown how cold-water corals will respond to ocean acidification and it is likely that their aragonitic skeletons will experience dissolution in these corrosive waters, potentially leading to breakdown of reef structure and loss of habitat for other organisms (Turley *et al.*, 2007).

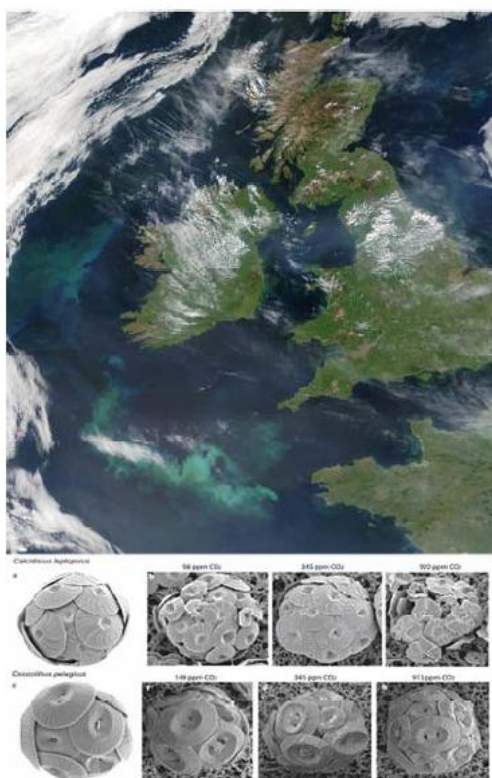
Warm water coral reefs do not grow around the UK, but are important in many of UK's Overseas Territories (e.g. Anguilla, British Virgin Islands, etc.) located in warm, sunlit, aragonite rich waters. Coral reefs harbour an immense biodiversity and are important for shore protection. Decreasing aragonite saturation is reducing rates of coral calcification so much so that if this continues their rate of erosion will outpace calcification resulting in loss of coral structural integrity (Kleypas *et al.*, 2006; Manzello *et al.*, 2008; Silverman *et al.*, 2009).

#### *Pelagic organisms*

Pelagic organisms, including phytoplankton, zooplankton and other organisms living in the upper water column may also be vulnerable to ocean acidification. Major migration events have occurred over the last five decades amongst plankton organisms due to rapid climatic changes. Warm-water/subtropical species were observed to move into more temperate areas and this trend seems to be accelerating over recent decades (Edwards *et al.* 2009).

Coccolithophores, planktonic algae which produce blooms so large they are visible from space (Figure 5), produce calcitic liths or plates. Experiments indicate highly

species specific and strain-specific reactions, with some species (e.g. *Emiliania huxleyi* and *Gephyrocapsa oceanica*) experiencing decreased rates of calcification by 16% at (UKCP09) low emissions scenario and 30% at (UKCP09) high emission scenario (Riebesell *et al.*, 2000). Other species have shown no response (Langer *et al.*, 2006) or even an apparent increase in calcification (Iglesias-Rodriguez, *et al.*, 2008), although when normalized to cell organic production no experiments has shown a relative increase in calcification (Ridgwell *et al.*, 2009). These variable responses are indicative of the nature of these organisms, i.e. certain species are continually adapting in response to their rapidly changing environment over these relatively short time-scales. This scenario is likely to be most important for species that have large population sizes and rapid generation times, so that the genetic variation required for adaptive evolution can be readily supplied. Langer *et al.* (2009) demonstrates this point clearly as they show that sensitivity of different strains of *E. huxleyi* to changes in carbonate chemistry differs substantially. As natural populations are genetically diverse, strain-specific responses to carbonate chemistry changes may lead to a high degree of adaptive potential of the species.



**Figure 5.** MODIS Satellite image of UK regional seas showing phytoplankton and coccolithophore blooms (whitish green blue swirls). From NASA Visible Earth [http://visibleearth.nasa.gov/view\\_rec.php?id=2119](http://visibleearth.nasa.gov/view_rec.php?id=2119) Credit: Jacques Descloitres, MODIS Land Rapid Response Team, NASA/GSFC). Two images of coccolithophores showing some of the more extreme malformations found in experiments (CO<sub>2</sub> concentrations were 920 ppm, equivalent to ca. year 2100 scenarios). From Langer *et al* (2006).

Copepods, which make up a large proportion of the zooplankton, have been found to have reduced survival in their early life stages (Kurihara *et al.*, 2004) but longer term studies on several life stages and generations showed no impact on subsequent impacts from ocean acidification at levels much higher than projected for the next century (Kurihara & Ishimatsu, 2008). Planktonic pteropods, important grazers in areas of the polar oceans, have been found to be highly susceptible to dissolution (Fabry, 1990). Furthermore a recent experimental study illustrated a decrease in net calcification of an important pteropod in the Arctic Ocean (Comeau *et al.*, 2009) which is likely to experience undersaturation with respect to aragonite in the next 30 years (Steinacher *et al.*, 2009).

#### Nutrients

In addition to direct impacts on marine organisms, the lower pH expected over the next hundred years could theoretically impact the speciation of biologically important nutrients (e.g. nitrogen, phosphate and silica) and micronutrients (e.g. iron, cobalt, manganese etc). A decrease in pH of 0.3 units (UKCP09 high emissions scenario) could reduce the fraction of ammonium by around 50% (Raven, 1986), however, at the moment there is no direct evidence for this. Nitrification has also been shown to be pH sensitive, with rates reduced by ~ 50% at pH 7 (Huesemann *et al.* 2002). This may result in a reduction of ammonia oxidation rates and an accumulation of ammonia instead of nitrate. Over a shelf sea ecosystem model this has been predicted to result in a 20% decrease in pelagic nitrification by year 2100 (Blackford & Gilbert, 2007). Laboratory results have also shown changes in nutrient sediment flux rates with decreasing pH; different nutrients show different responses and results vary depending on the sediment fauna. Changes in nutrient fluxes most likely result from changes in microbial communities; although these changes are less obvious at pH levels expected from ocean acidification over the next 100 years (Widdicombe & Needham, 2007; Widdicombe *et al.*, 2009, Wood *et al.*, 2009). Ocean acidification may also increase the proportion of soluble iron, which might be beneficial to areas of the oceans where iron is thought to limit primary production, although the UK shelf is not one of these iron-limited regions (Royal Society, 2005). Additionally, the nutritional quality of plankton may also change with increasing acidification, by reducing particle size and phytoplankton community structure (Engel *et al.*, 2008), changing C:N:P stoichiometry of community production, and/or a loss of carbon (Riebesell *et al.*, 2007; Bellerby *et al.*, 2007; Thingstad *et al.*, 2008). Changes in phytoplanktonic assemblages either caused by changes to calcification, nutrients or to different CO<sub>2</sub> uptake rates by different species (Tortell *et al.* 2008) are difficult to predict. A loss of organic carbon or an increase in C: N ratio lowers the nutritional value of primary-produced organic matter, which in turn affects the quality of food available for zooplankton, and hence lowers growth and reproduction.

Unabated CO<sub>2</sub> emissions may result in changes to species biogeography as they track their habitat. Some species may fill the abandoned niches, changing the structure of the ecosystem. For example, non calcifiers and alien species are found instead of calcifiers in areas of low pH around the CO<sub>2</sub> vent in Mediterranean (Hall Spencer *et al.*, 2008) and may give us a future view of the regime shifts that might occur in a future high CO<sub>2</sub> ocean.

#### *Sensitivity to multiple stressors*

Many organisms in coastal and shelf seas are additionally impacted by other climate factors (changing temperature, salinity, wind, waves and currents) and non-climate factors (invasion of non-native species, over-fishing, pollution (particularly acid run-off and atmospheric deposition), diseases, and nutrient and sediment load (Jackson, 2008)). The majority of studies so far on ocean acidification have been at ambient (and often optimal) conditions that organisms are found in. If an organism is increasingly stressed by temperature or pollution then ocean acidification could compound these impacts preventing them from adapting or recovering (see review by Pörtner *et al.*, 2005). Investigations on the combined effects of temperature and ocean acidification on marine organisms, to date, are limited to just a handful of studies (e.g. Metzger *et al.*, 2007; Feng *et al.*, 2008; Martin & Gattuso, 2009; Parker *et al.*, 2009; Gooding *et al.*, 2009). Metzger *et al.* (2007) focussed on short-term physiological implications of CO<sub>2</sub> acting on thermal tolerance and demonstrated that high levels of CO<sub>2</sub> (10,000 ppm) enhanced heat sensitivity which led to a narrowing of the thermal tolerance range of crabs. Martin & Gattuso (2009) demonstrated that temperature and ocean acidification acted synergistically on coralline algae to reduce net calcification and survival. Parker *et al.* (2009) found that oyster embryo

development was more severely affected by both elevated temperature and lowered pH under (UKCP09) high emissions scenarios. Conversely, Gooding *et al.* (2009) showed that temperature and ocean acidification appeared to enhance growth in sea stars. While Feng *et al.* (2008) demonstrated that changes in UV and temperature together with ocean acidification affect the calcification ability of coccolithophores to differing extents depending on the combination of stressors. Hence at this time, few generalisations can be made about the relative impact of temperature and ocean acidification on marine organisms and more research is required.

### **Learning about the future from Earth's distant past**

The rate of change of oceanic pH projected this century may be the most rapid change experience by marine organisms for 65 million years. For example, changes in CO<sub>2</sub> levels over the last 800,000 years (linked to shifts from glacial to interglacial periods) have been in the order of 70 to 90 ppmv, and have happened over timescales of thousands of years (EPOCA community members, 2006) in contrast to the rapid change in atmospheric CO<sub>2</sub> happening at the moment (~90 ppm in 100 years). An examination of the geological record for such acidification events may give us an understanding of potential adaptation and scale of recovery.

#### *Considering the geological record for an analogue for today's ocean acidification event*

Experiments use rather abrupt changes in pH and are relatively brief compared to the generation times of some of these organisms. Therefore cultures can not fully assess adaptation potential which demands long time series covering large numbers of generations. The geological record, stored in the sediment at the bottom of the ocean, encapsulates both past records of ocean acidification and the biological reaction. The global distribution of marine sediments therefore allows the investigation of ecosystem shifts and their impact on biogeochemical cycles as well as the timescales of recovery after ocean acidification events.

No geological event could ever be a perfect analogue for future ocean acidification. Ideally, the analogue would be during a time with similar climates, configuration of continents and ecosystems. It is important to keep in mind though, that most modern organisms alive in the ocean today are likely to have never experienced such a large change in their evolutionary history. For instance, during no point in the last 800,000 years did the atmospheric CO<sub>2</sub> concentration reach a value anywhere near current concentrations (Siegenthaler *et al.*, 2005) and hence nor would pH have been so low. Furthermore, none of the ocean acidification events in the past ~65 million years, e.g. at the Palaeocene Eocene boundary appear to have been as rapid as the projected changes happening in the next decades (Ridgwell and Schmidt, 2010).

#### *The Pliocene warmth, 3.3 to 3 million years ago*

Most likely, the last time that CO<sub>2</sub> levels have been as high as those found today was during the Pliocene, three million years ago (Seki *et al.* 2010). The higher CO<sub>2</sub> led globally to a three degree warming over several millennia which regionally was amplified to twice this temperature change (Dowsett *et al.*, 1996) making it an ideal analogue for future climate (Solomon *et al.*, 2007). Ecosystems during this time were very similar to present. The climate change led to poleward migration of organisms, likely as a response to the warming both on land and in the ocean, but did not cause large scale extinctions. This highlights that comparatively slow changes in CO<sub>2</sub>, temperature and pH over several millennia did not permanently alter ecosystems. Estimates of rates of pH change during the Pliocene warmth could provide constraints for CO<sub>2</sub> mitigation targets but the CO<sub>2</sub> change is not large enough to determine adaptation potential and ecosystem responses.



### *The late Cretaceous, 99.6 to 65.5 million years ago*

An example of a period during Earth history with CO<sub>2</sub> as high as the projections for non mitigation scenarios is the late Cretaceous (Bice *et al.*, 2006). Intriguingly, although CO<sub>2</sub> was high for millions of years during this period, the coastline of Britain, for example the White Cliffs of Dover, documents vast carbonate deposition by coccolithophores whose descendants are still important carbonate producers today and who can be affected by ocean acidification (e.g. Langer *et al.*, 2006, Riebesell *et al.*, 2000). However, there are two major differences between then and today, which make this comparison flawed. Firstly, the Cretaceous ocean had about a 2-fold higher calcium concentration, meaning that low pH and low carbonate ion concentrations could still result in super-saturation of the surface ocean which is the product of both calcium and carbonate ion concentrations. Secondly, gradual increases of CO<sub>2</sub> and decreases in pH over millions of years would have provided enough time for genetic adaptation and evolution to high CO<sub>2</sub> conditions. Therefore, credible analogues for future ocean acidification need to have similar rates as well as magnitudes of CO<sub>2</sub> change as those predicted for the next century and millennium.

### *Palaeocene-Eocene Thermal Maximum, 55.5 million years ago*

The best current analogues for ocean acidification are the Palaeocene hyperthermals, a series of events between 58 and 52 millions years ago. Sediments deposited during these events (Figure 6) are characterised by a high degree of dissolution of carbonates and record a geochemical signature of a massive input of carbon associated with a transient temperature rise (Dickens *et al.*, 1995). The best studied of these events is the Palaeocene-Eocene Thermal Maximum (PETM) 55.5 million years ago. The geological signature of this event is not just restricted to the deep sea but is also recorded in the North Sea and the shelf sediments of the Mediterranean (Speijer *et al.*, 1997). The biotic response is very different in the deep sea benthic than in the planktonic ecosystem.



**Figure 6.** Sedimentary evidence of an ocean acidification event 55.5 million years ago (Palaeocene-Eocene boundary) from the South Atlantic (Ocean Drilling Leg 208, Walvis Ridge). The arrow indicates the boundary visible by a sharp contrast between white carbonates and red clays. The red clay shows that the carbonate saturation horizon shoaled and all carbonates in the sediment dissolved.

The planktonic ecosystem did not experience a comparable extinction. The composition of the marine fossilised plankton changed, the most important of which was the occurrence of a massive dinoflagellate bloom (Sluijs *et al.*, 2005). Several other planktonic assemblages, such as foraminifers, and coccolithophorids, showed major compositional changes as a reaction to changing nutrient and temperature



conditions (see Sluijs *et al.*, 2007 for a review). This highlights that adaptation to these climatic changes was possible if the organism had a habitat they could track. However, new computer simulations show much higher (order of magnitude) rates of environmental change for the surface ocean for the future than the Palaeocene–Eocene thermal maximum, which could potentially challenge the ability of plankton to adapt (Ridgwell and Schmidt, 2010).

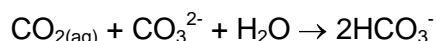
While planktonic organisms reacted to the environmental change with migration to higher latitudes, thereby tracking their ideal temperature, benthic organisms in the deep sea, mainly benthic unicellular organisms called foraminifers, faced 40% extinction. The extinction is much larger amongst the calcifying benthic foraminifers than amongst those building their shells out of sand grains and organic material suggesting that the ability to calcify was severely affected. This hypothesis is further corroborated by the fact that the surviving benthic foraminifers and ostracods, small crustaceans, are small and thin-walled suggesting low saturation conditions (Thomas, 2007).

### **Global carbon cycling and climatic consequences**

UK coastal waters will depend on global scale cycling of carbon and feedback to climate.

#### *The oceanic atmospheric CO<sub>2</sub> buffer*

With the continued dissolution of anthropogenically-sourced CO<sub>2</sub> in surface ocean waters, the capacity of the ocean to absorb further CO<sub>2</sub> emissions diminishes. This is because carbonate ions in the ocean in effect scavenge CO<sub>2(aq)</sub> to form bicarbonate, in the reaction:



As the carbonate ion concentration of the ocean declines, so does the capacity of seawater to buffer atmospheric CO<sub>2</sub>, encapsulated in the ‘Revelle Factor’ (Zeebe & Wolf-Gladrow, 2001). Hence with continuing CO<sub>2</sub> emissions, the fraction of each mole of CO<sub>2</sub> emitted that is taken up by the ocean declines and a greater fraction will remain in the atmosphere, producing a positive feedback on global warming in which warming is expected to be approximately linear with cumulative CO<sub>2</sub> emissions (Goodwin *et al.*, 2009). However, the reduction in the strength of the ocean carbon sink with increasing cumulative CO<sub>2</sub> emissions is no more a consequence of ocean acidification than ocean acidification is a consequence of reduced buffering – both are closely related consequences of the dissolution of CO<sub>2</sub> from the atmosphere and both involve decreases in carbonate ions. We thus focus here on the specific impacts of ocean acidification, but noting that the progressive weakening of the seawater CO<sub>2</sub> buffer is arguably the most fundamental single impact on the ocean of fossil fuel combustion.

#### *Direct effects of ocean acidification on atmospheric CO<sub>2</sub>*

By precipitating calcium carbonate (CaCO<sub>3</sub>) from sea-water, marine organisms affect the global carbon cycle and climate system. In the chemical reaction for creating carbonate shells and skeletons:



dissolved inorganic carbon in seawater in the form of HCO<sub>3</sub><sup>-</sup> cannot interact directly with the atmosphere, but via calcification it is converted into dissolved CO<sub>2</sub> (CO<sub>2(aq)</sub>), that can leave solution and escape to the atmosphere as gaseous CO<sub>2</sub>. Thus, ignoring questions of whether CaCO<sub>3</sub> particles are important to the fate of organic carbon (‘ballasting’ – see below), the process of calcification acts to increase the

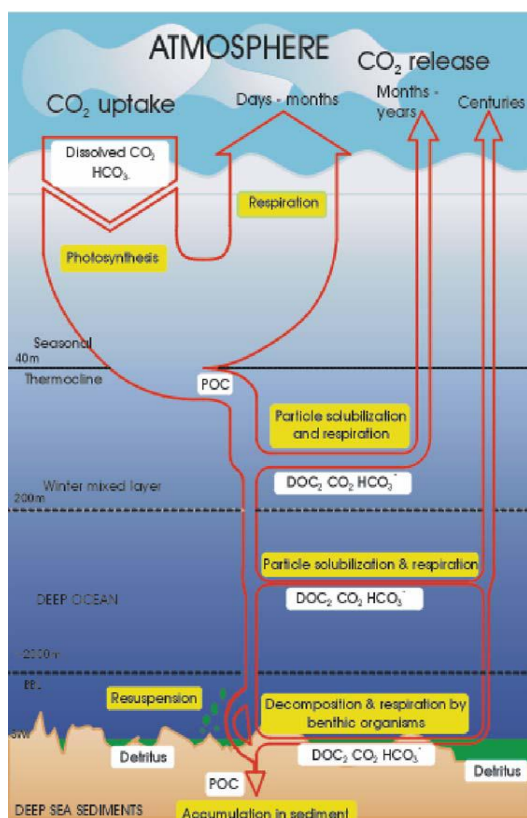
concentration of  $\text{CO}_{2(\text{aq})}$  at the ocean surface and acts as a brake on the transfer of fossil fuel  $\text{CO}_2$  from the atmosphere into the ocean. Reducing the rate of calcification globally then accelerates the rate of uptake of fossil fuel  $\text{CO}_2$  from the atmosphere – a negative feedback for climate change.

Only a few global models have so far been applied in quantifying the importance of changing pelagic carbonate production on the oceans ability to sequester  $\text{CO}_2$ . Predictions for the additional quantity of fossil fuel  $\text{CO}_2$  taken up by the ocean by the year 2100 fall in the range 5.9 and 18 PgC (Gehlen *et al.*, 2007; Heinze, 2004; Ridgwell *et al.*, 2007). An alternative approach to this question is to use a single model, but run as a large ensemble of differing experiments which explicitly take into account the broad range of calcification responses observed in laboratory manipulation experiments. The uncertainty from model ensembles spans 5.4 PgC to 25.7 PgC, with an ensemble mean  $\text{CO}_2$  uptake of 17.2 PgC (Ridgwell *et al.*, 2007). This range is broadly comparable to that existing between different models, suggesting that the current uncertainty in the species calcification response in conjunction with their relative importance for carbonate production dominates the overall uncertainty in model predictions of fossil fuel  $\text{CO}_2$  uptake by the ocean.

Better experimentally-based understanding of acidification impacts at both the organism and ecosystem level and how this translates to the global scale is needed for improvements to be made in model predictions of future fossil fuel  $\text{CO}_2$  uptake. However, it should be recognised that the direct impact on atmospheric  $\text{CO}_2$  is relatively small compared to emissions and other carbon cycle feedbacks. For instance, currently yearly emissions of  $\text{CO}_2$  from fossil fuels and cement production of  $7.2 \text{ PgC yr}^{-1}$  (IPCC, 2007) are of a comparable magnitude to the 100-year integrated impact of reduced calcification. The year 2100 model predictions of a 5-25 PgC repartitioning of  $\text{CO}_2$  from atmosphere to ocean is also dwarfed by the likely anthropogenic  $\text{CO}_2$  inventories of the ocean and atmosphere, which even in 1994 stood at 118 and 165 PgC, respectively. There are also important gaps in our understanding of fundamental aspects of the workings of the marine carbon cycle (see below).

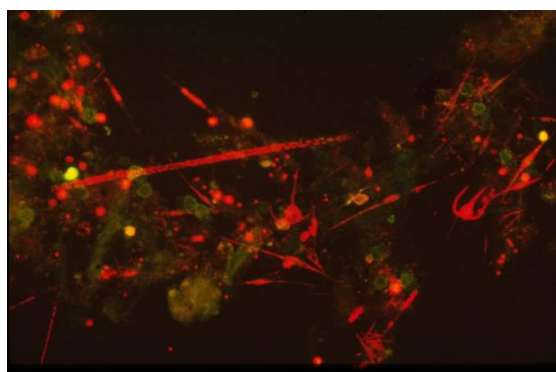
#### *Indirect impacts of ocean acidification on atmospheric $\text{CO}_2$*

How some of the organic matter produced by plankton at the ocean surface manages to reach the deep ocean without first being completely degraded by bacteria along the way may be sensitive to changes in calcification and thus ocean acidification (Figure 7). This is important because the continual transfer of particulate organic matter and its associated carbon to the deep sea creates a chemical gradient in the ocean with lower concentrations of dissolved  $\text{CO}_2$  at the surface than at depth. Any reduction in the fraction of organic matter reaching the deep ocean would reduce the surface-to-deepwater dissolved  $\text{CO}_2$  gradient, resulting in a higher concentration of  $\text{CO}_2$  in the atmosphere.



**Figure 7.** Schematic diagram showing the biological pump and the flux of carbon through the oceanic water column to the deep sea sediments and approximate return times dependent on depth of remineralisation. From Turley (2000).

Because the  $\text{CaCO}_3$  shell material produced by marine calcifiers (Figure 5) is much denser than the soft body parts of plankton, its presence in aggregates with organic matter (Figure 8) may play an important role in accelerating the rate of sinking (Armstrong *et al.*, 2002). Any reduction in calcification by plankton at the ocean surface due to ocean acidification would then increase the time that organic matter was suspended in the warm upper ocean and increase the likelihood of its being consumed by bacteria. The consequence would be an increase in the rate of recycling of both nutrients and  $\text{CO}_2$  back to the surface. While this may result in an increase in primary production by plankton due to greater nutrient availability, the faster rate of return of dissolved carbon would drive atmospheric  $\text{CO}_2$  higher overall.



**Figure 8.** Epifluorescent photomicrograph of a macroaggregate from the surface waters in the NE Atlantic, showing a range of red autofluorescing (excitation at 450-490 nm) phytoplankton cells containing chlorophyll. Scale bar = 200  $\mu\text{m}$ . From Turley (2000).

The limited number of global models that have assessed the potential importance of  $\text{CaCO}_3$  in the ‘ballasting’ (density-dependent sinking) of aggregates with organic matter, suggest that reduced  $\text{CaCO}_3$  ballasting could cut the ca. 6–18 PgC direct impact of acidification-driven changes in calcification on fossil fuel  $\text{CO}_2$  uptake by 80% (Heinze, 2004). It is possible that the sign of the net  $\text{CO}_2$  impact could be reversed, resulting in more fossil fuel  $\text{CO}_2$  overall residing in the atmosphere (Barker *et al.*, 2003). However, the importance of mineral ballasting in the transport of organic

matter to depth is currently uncertain, partly because of the technical and logistical difficulties of observing and experimenting on the aggregation (and dis-aggregation) processes in the ocean interior.

Aside from potential changes in the efficiency of recycling of organic matter and its associated nutrients, higher ambient concentrations of dissolved CO<sub>2</sub> and acidification have been observed in the laboratory to result in a greater production of organic matter per cell in phytoplankton (Riebesell *et al.*, 2007, Bellerby *et al.*, 2007, Zondervan *et al.*, 2002). Increased photosynthetic fixation of carbon and subsequent removal from surface waters as sinking particulate organic matter would decrease the concentration of dissolved CO<sub>2</sub> at the ocean surface and thus accelerate the uptake of fossil fuel CO<sub>2</sub> from the atmosphere. However, for this phenomenon (i.e., increased photosynthetic fixation of CO<sub>2</sub> and organic matter export) to be effective there must be sufficient nutrients. A commensurate decrease in the amount of nitrogen and phosphorus required per unit quantity of carbon fixed would facilitate this, an effect which the results of mesocosm experiments supports (Riebesell *et al.*, 2007, Bellerby *et al.*, 2007). The uncertainties of acidification impacts on cellular organic matter composition are large and no global models yet routinely incorporate this effect in predicting future atmospheric CO<sub>2</sub> concentrations. Additional feedbacks as nutrient-to-carbon ratios change may also become important and limit productivity (Thingstad *et al.*, 2008).

Whether the supply of organic matter to the deep ocean decreases due to decreased carbonate ballast production, and/or increases due to physiological impacts of higher CO<sub>2</sub>, there may be important impacts on the organisms and communities living at the ocean floor because organic matter derived from the surface waters is their main food resource (Turley, 2000). Changes in the supply of organic matter to the deep ocean however it occurs will have implications for the degree of oxygenation of the deep ocean as the bacterial metabolism of this material consumes O<sub>2</sub> throughout most of the modern ocean and surface sediments of the deep sea.

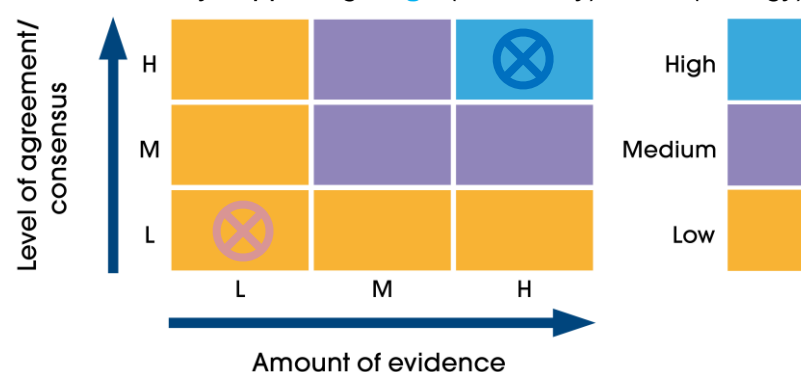
#### *Impacts of ocean acidification on climate (other than via CO<sub>2</sub>)*

Blooms of coccolithophores (Figure 5) can modify the surface optical properties of the ocean because the coccolith platelets that are shed in the water column are efficient at scattering sunlight. Any reduction in the number, mass, or shape of coccoliths as a result of ocean acidification (Figure 5) could thus potentially alter the surface energy budget in regions of the ocean where coccolithophorid blooms are common. However, estimates of the total contribution of coccolithophorid blooms to the surface energy budget suggest that even the complete loss of all coccolith production globally would have a radiative forcing (warming) impact of just 0.22 Wm<sup>-2</sup> (Tyrrell *et al.*, 1999), equivalent to no more than 10% of that due to the historical increase in CO<sub>2</sub> alone (IPCC, 2007).

Coccolithophores are also major producers of dimethyl sulphide (DMS) which may have a role in climate regulation via the production of cloud condensation nuclei (Charlson *et al.*, 1987). A reduction in the occurrence of coccolithophore blooms that occur in large areas of the global oceans, often of 100 000s km<sup>2</sup> (Figure 5) could lead to a reduced flux of DMS from the oceans to the atmosphere and hence to further increases in global temperatures via cloud changes. Mesocosm experiments have shown changes in DMS production at CO<sub>2</sub> concentrations different to current concentrations (e.g. Vogt *et al.*, 2008, Hopkins *et al.*, 2010). However, the existence of global climate impacts via acidification and DMS production should be considered highly uncertain at present.

### 3. Confidence in the science

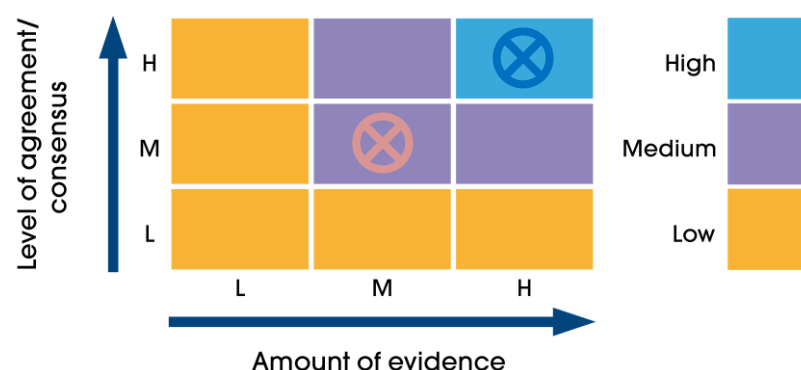
What is already happening: **High** (Chemistry) / **Low** (Biology)



The chemical changes (blue X) are measurable and happening now, the chemistry is known so certainty is high. There is little evidence for current biological impacts (red X) of ocean acidification up to today (and therefore little agreement) but this may be because there are no long term data bases that look at this.

*Our overall assessment of confidence in the summary report card 'for what is already happening' is reported as 'high' where our need to understand what has happened is currently focussed upon changes in ocean chemistry.*

What could happen: **High** (Chemistry) / **Medium** (Biology)



Our assessment of what could happen in the future to ocean chemistry (blue X) is based on good understanding of ocean carbonate chemistry, general circulation models and dependant the rate of future CO<sub>2</sub> emissions to the atmosphere.

Our assessment of what could happen to biology in the future (red X) is based on recent models projections indicating vulnerability of the Arctic and coastal upwelling to carbonate undersaturation, further work highlighting the vulnerability of corals to decreasing saturation and other experimental evidence increasingly revealing that juveniles, reproduction, physiology etc. of different organisms may change as a result of ocean acidification, even if adults are not. Species specific reactions to ocean acidification experiments show the complexity of the biotic reaction and tradeoffs that might occur between different physiological processes. The great majority of the growing evidence from field work, experiments, modelling and geological record indicates that the consequences for the future could be very serious but there are still substantial knowledge gaps together supporting the continued Medium rating.

*Our overall assessment of confidence in the summary card for 'what could happen in the future' is reported as 'medium' where our need to understand what could happen in the future requires a broader view of the potential ecosystem level impacts as well as the changes in ocean chemistry.*



#### 4. Knowledge gaps

The top priority knowledge gaps that need to be addressed in the short term to provide better advice to be given to policy makers are:

1. Impact of future ocean acidification on global and UK coastal organisms and ecosystems taking into account the full life cycle and physiology of individuals and potential “adaptability”.
2. Biogeochemical feedbacks between ocean acidification and climate change and the impact of these global scale changes to local and regional scales
3. Impact of changing ocean chemistry on the goods and services provided by the marine environment.

#### 5. Socio-economic impacts

The UK's coastal and shelf sea environments and the biodiversity within them provide a wide range of goods and services that are essential for the maintenance of social and economic well being (Beaumont *et al.*, 2008). These goods and services can be defined as provisioning, regulating, cultural and supporting services (MEA, 2003), providing benefits at several levels (local, regional and global) and to different groups (individuals and public bodies).

##### Provisioning services (food provision, raw materials)

Globally over 1 billion people rely on fish as their main animal protein source, especially in developing nations (Pauly *et al.*, 2005). The UK population traditionally enjoys fish and although its own national industry has declined over recent decades, it is still an important industry. In 2008, the UK fishing industry had 6,573 fishing vessels utilising a mixture of gears and techniques to catch a broad variety of fish, such as mackerel, cod, scallops and mussels. Landings by UK vessels amounted to 588 thousand tonnes of sea fish with a total value of £629 million (Irwin and Padia, 2009). Shellfish (nephrops, crabs, mussels etc) comprised 42% of total harvest. The fleet comprised 12,761 fishermen with 80% of these being full time fishermen.

Analysis of the catch landings based on sea area showed that the Northern North Sea was the most productive region contributing 62.3% of the value of finfish and 31.3 % of shellfish (Figure 9). Due to its rocky coastline, the Northern North Sea region is valuable for pot fisheries for edible crabs and lobsters, and offshore fisheries for edible crab off the Yorkshire coast.



**Figure 9.** The value of (a) finfish, and (b) shellfish landed at the major ports by UK vessels in 2008 arranged into seven sea areas. The total value for the finfish landed was £260.4 million while the value of shellfish was £257.3 million. © Crown copyright 2010 Reproduced by permission of Cefas, Lowestoft.

Mounting evidence indicates that ocean acidification will likely impair calcification in animals with calcium carbonate shells and skeletons (e.g. Section 3, and reviews by Kleypas *et al.*, 2006; Gazeau *et al.*, 2007; Fabry *et al.*, 2008; Hoegh-Guldberg *et al.*, 2008). This includes commercially valuable molluscs, crustaceans and echinoderms. Further, most other commercially harvested species, such as finfish, prey on shellfish, echinoderms, crustaceans or their predators. Ocean acidification could therefore lead to degradation of marine resources which would result in a reduction in fish harvest and protein provision, and loss of revenue and jobs. For instance, using the Defra Sea Fisheries Statistics 2008 (Irwin and Padia, 2009), and assuming a 10-25% reduction in growth/calcification (with a doubling in atmospheric CO<sub>2</sub>, see section 3) results in 10-25% loss of shellfish landings that is equivalent to £26.4 - 66 million per year loss in value and around 1,200-3,100 potential job losses.

Two significant raw materials extracted from the UK marine environment are fishmeal and fish oil, and seaweed. Fishmeal and fish oil are key constituents of pelleted diets for the intensive production of carnivorous fish species. In 2004, 192,000 tonnes of fishmeal were consumed in the UK of which 50,000 were produced locally with the remainder imported. The total value of the fishmeal UK market in 2004 was £81 million (European Parliament Report, 2004). Reduction in availability of these raw materials could therefore impact the extent and/or market cost of UK finfish aquaculture. In 2004, England, Scotland and Wales had 613 fish and shellfish farming businesses operating on 1329 sites, employing 3,412 people. The main finfish species farmed are salmon (139 000 tonnes mainly in Scotland) and rainbow trout (16 - 17,000 tonnes) (Defra, 2008). There is also a limited production of other species, such as carp and brown trout, and relatively new species to aquaculture such as turbot, halibut, cod and Arctic char have produced encouraging results. Thus should acidification have significant impact on the production of these raw materials there could be socio-economic consequences on dependent industries.

Globally, warm water coral reefs are valuable marine ecosystems. They are important for nature and represent a very high value for humankind, supporting millions of people through provision of food and income. Cesar *et al.*, (2003) estimate that coral reefs provide nearly US\$ 30 billion each year in net benefits in goods and services to world economies, including tourism, fisheries and coastal protection. Increased stress on food production systems such as coral reefs, driven by climate change or ocean acidification, could thus have significant repercussion on food provision and/or security; particularly in developing countries where fish provide the major protein source (Pauly *et al.*, 2005).

Pearls are created naturally by shellfish through the secretion of aragonite but can also be cultured artificially in oysters. Currently, the global pearl farming industry is worth \$1.5 billion each year and is expected to grow into a \$3 billion per year industry by 2010 (International Pearl Convention 2007). A reduction in aragonite saturation may impact the rate of production and quality of both natural and cultured pearls and therefore the future pearl market. Less expensive “Mother of Pearl” used frequently in costume jewellery, button making and the arts and craft industry may also be impacted.

### **Regulating services (e.g. gas and climate regulation)**

In addition to physical processes such as ocean mixing, tides, current and air-sea exchange, the chemical composition of the atmosphere and ocean is maintained through a series of biogeochemical processes regulated by marine organisms. Their ability to fix CO<sub>2</sub> through photosynthesis and transfer a proportion of this to the deep sea via this biological pump is a key part of the global carbon cycle - essentially the oceans are buffering the effects of climate change through the removal of a large

proportion of the anthropogenic CO<sub>2</sub> (see sections 2 and 5). A recent study to value the role of marine biodiversity in gas and climate regulation found that the Isles of Scilly marine environment was fixing 136,495 tC y<sup>-1</sup> with a mean net present value of £47 million (Davis *et al.*, 2008), implying that on a UK scale the value would be £ billions. Any stressor reducing ocean productivity and the biological pump would have substantial environmental and economical impacts. The economic cost of replacing these natural processes with industrial processes would be exorbitant.

Sediments play a crucial role in a number of key ecosystem processes, in particular the microbial cycling of carbon and nitrogen (section 3, Figure 4). In addition, the behavioural characteristics of species that live in or/and on the sediment are important determinants of sediment biogeochemistry and element cycling, as their activities result in a release of dissolved and particulate nutrients from the sediment to the water column where they support primary productivity. Changes to this coupling, of sediment and pelagic biogeochemistry, through ocean acidification could have worrying knock-on consequences to shelf sea productivity and the food webs it supports, but this is highly uncertain.

### **Cultural services (e.g. leisure and recreation)**

A significant component of leisure and recreation in the UK depends upon coastal marine biodiversity (e.g. bird watching, sea angling, rock pooling and diving) which in turn supports employment and small businesses. The rapid growth of sea angling based on sustainable practices is recognized as a significant opportunity for the UK economy. If UK marine biodiversity declines as a result of ocean acidification and other drivers, the value of this sector will decrease, with a potential loss of revenue. In addition, the occurrence of harmful or unpleasant algal bloom can reduce the aesthetics of beach recreation, as has been experienced in the Adriatic over the last decade.

The enormous biodiversity supported by coral reefs underpins substantial tourist industries for many tropical countries, including UK entities, and often provide their main revenue. Countries with coral reefs attract millions of SCUBA divers every year, yielding significant economic benefits to the host country. Globally, tourism is estimated to provide US\$ 9.6 billion in annual net benefits (Cesar *et al.*, 2003) and a multiple of this amount in tourism spending. Coral reef biodiversity also has a high research and conservation value, as well as a non-use value, estimated together at US\$ 5.5 billion annually (Cesar *et al.*, 2003). Loss of coral reefs and their diversity would impact global tourism to these areas and their enjoyment by tourists, including those from the UK.

### **Supporting services (e.g. biologically mediated habitat)**

Maerl beds, mussel patches and cold-water corals are among the most important biologically mediated habitats in UK waters supporting a large number of species. This includes the provision of refuge and food for juvenile life stages of commercially important shellfish such as the queen scallop, Atlantic cod, saithe and pollack (Hall-Spencer *et al.*, 2003). Cold water corals grow in deep, CO<sub>2</sub> rich waters and may be even more vulnerable to ocean acidification through shoaling of the ASH than their tropical coral reefs (Roberts *et al.*, 2006; Guinotte *et al.*, 2006; Turley *et al.*, 2007). Around 70% of known locations of these old, slow growing corals may be in undersaturated, corrosive waters by the end of this century, with some affected even earlier, thereby impacting economically valuable species that take refuge and feed there (Guinotte *et al.*, 2006; Roberts *et al.*, 2006).

Globally, coral reefs and mangroves play an important role in shore protection and enhance local productivity and biodiversity. It is estimated that tropical coral reef

calcification rates will decrease with decreasing CaCO<sub>3</sub> saturation so that reef erosion will be greater than reef accretion in the next few decades depending on the location of the reef (Kleypas *et al.*, 2006). This protective function of reefs was valued at US\$ 9.0 billion per year by Cesar *et al.*, (2003) so any decline in this function will have a socio-economic impact either through loss of low lying land habitat and infrastructure or through a need for investment in shore protection.

In addition to these quantified values, reefs have drawn a mass of medical and pharmaceutical research interest in the pursuit of finding cures for human diseases. Any loss in these roles will have significant socio-economic impacts on the people that depend on these services.

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