University of Bristol School of Geographical Sciences

## An introduction to:

# 'Ocean acidification: The other fossil fuel CO<sub>2</sub> problem'

# GEOG16001 'World in Crisis?'



by Prof. Andy Ridgwell (andy@seao2.org)

Material adapted from a DEFRA publication authored by: Carol Turley, Helen S. Findlay, Stephen Mangi, Andy Ridgwell, and Daniela N. Schmidt.

### NOT FOR FURTHER DISTRIBUTION

#### **LEARNING GOALS**

- That a proportion of the CO<sub>2</sub> gas emitted to the atmosphere from the burning of fossil fuels (+ cement production and deforestation) dissolves in seawater.
- That inorganic carbon dissolved in seawater actually exists in more than one form  $-CO_{2(aq)}$ ,  $HCO_3^{-}$ ,  $CO_3^{-2^{-2}}$ .
- That dissolving CO<sub>2</sub> in seawater makes environmental conditions more acidic hydrogen ions are released, the concentration of which determine the *p*H of the water. (This is where the term 'ocean acidification' comes from.)
- That the surface ocean is acidified first, but that the circulation of the ocean will propagate the acidity to greater depths and eventually throughout the ocean.
- That dissolving CO<sub>2</sub> in seawater also reduces the carbonate ion (CO<sub>3</sub><sup>2-</sup>) concentration. (Think of CO<sub>2</sub> reacting with CO<sub>3</sub><sup>2-</sup> and destroying it.)
- That the concentration of  $CO_3^{2-}$  is important to the stability (solubility) of the mineral calcium carbonate (CaCO<sub>3</sub>).
- That a variety of marine organisms make either calcite or aragonite (which are the most common structural forms of the mineral calcium carbonate) shells or skeletons, organisms which laboratory experiments have demonstrated an impact of acidification on.
- That therefore, marine organisms and ecosystems may be adversely impacted and disrupted by fossil fuel CO<sub>2</sub> emissions and ocean acidification in the future, with an exciting range of possible economic and societal consequences.
- That there are geochemical (near) certainties about the occurrence of ocean acidification, but biological uncertainties as to the ecological consequences (although for a few organisms the future looks inescapably bleak).

#### WHAT THIS MEANS ...

Don't beat yourselves over the <u>exact</u> details of the chemical formulas and reactions. The key is to appreciate that  $CO_2$  forms a (weak) acid in seawater. Think of 'acid rain' if you like. Try and grasp the relationship between the concentration of hydrogen ions and pH – the essential thing to remember is that pH is a non-linear scale – i.e., a small change in reported pH equates to a large change in chemistry (e.g., from pH of 8.0 to 7.0 is a ten-fold increase in hydrogen ions!).

You do also need to appreciate that carbon dissolved in seawater comes in different forms. You will <u>not</u> be required to recall the exact details of these forms (charges etc), but it would be helpful if you could grasp that one form of dissolved carbon, the carbonate ion  $(CO_3^{2^-})$ , is 'special' and is 'destroyed' by dissolving  $CO_2$  in seawater.

Appreciate that whether calcium carbonate (CaCO<sub>3</sub>) dissolves and how easy it can be precipitated from solution is sensitive to the carbonate ion concentration. Simply from the formula – **CaCO<sub>3</sub>**, you can see that it involves a carbonate ion (CO<sub>3</sub><sup>2-</sup>). Hence, it should be intuitive that having very little CO<sub>3</sub><sup>2-</sup> in the surrounding seawater will encourage CaCO<sub>3</sub> to 'disintegrate' and dissolve (and release CO<sub>3</sub><sup>2-</sup> into the seawater).

If you have got this far, the rest is biology (and economics)! A variety of marine organisms make shells out of  $CaCO_3$ , which may be affected by fossil fuel  $CO_2$ . Remember the sorts of organisms that are affected – what it is about corals that endanger them (== skeletons made out of  $CaCO_3$ ); what is it about certain species of plankton (shells and protective platelets ('liths') made out of  $CaCO_3$ ). Do not worry about the Latin names of individual species! Just appreciate that there are major groups of organisms that are important in the food chain and economically valuable for a variety of reasons and that because they make shells and skeletons out of calcium carbonate they will likely be adversely impacted by ocean acidification.

#### **SUMMARY**

The problems faced by society as a result of the effects of increasing concentrations in the atmosphere of  $CO_2$  and other greenhouse gases, namely: surface warming, changes in precipitation patterns with both droughts and flooding likely to be exacerbated, and rising sea levels, are well appreciated. Of the  $CO_2$  that is released to the atmosphere through the burning of fossil fuels and cement manufacturing, since the industrial revolution nearly 50% has been absorbed by the oceans. Whilst this has somewhat limited the historical rise of  $CO_2$  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 dramatic and substantial change to ocean chemistry. In particular, and of great concern, is the demonstrable and measureable change in ocean pH – 'ocean acidification'. Our understanding of the impact of  $CO_2$  on the carbonate chemistry is such that we know with very high certainty that ocean acidification will continue, tracking future  $CO_2$  emissions to the atmosphere.

Evidence from laboratory experiments and observations overwhelmingly indicate that ocean acidification is a serious threat to many marine organisms and the food webs and ecosystems that depend on them. Of less certainty are the scale and direction of impacts on biogeochemical cycling of carbon, nutrients and climate reactive gases and other potential feedbacks to climate. Considering the valuable goods and services that the marine environment provides, there will likely be societal and economic consequences of ocean acidification. Because ocean acidification is a simple consequence of the sea-water chemistry of fossil fuel  $CO_2$  originally released to the atmosphere, the only way of reducing the impact of ocean acidification is the urgent and substantial reduction of  $CO_2$  emissions to the atmosphere.

This document provides an overview of '*Ocean acidification: The other fossil fuel CO*<sub>2</sub> *problem*'.

#### OCEAN UPTAKE OF CO2 AND SUBSEQUENT CHANGES TO OCEAN 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, compared with ~700 PgC in the atmosphere and < 2000 PgC in the terrestrial biosphere [*Royal Society*, 2005]. (1 PgC =  $10^{15}$  g carbon, which to put into perspective: current human emissions of CO<sub>2</sub> to the atmosphere from the burning of fossil fuels is over 7 PgC yr<sup>-1</sup> and remaining oil reserves amounting to ca. 340 PgC [*IPCC*, 2007].) Oceans act as an important carbon sink, annually absorbing more CO<sub>2</sub> overall than they release into the atmosphere. Nearly half of the CO<sub>2</sub> released into the atmosphere since the industrial revolution (118



**Figure 1.** Column inventory of anthropogenic  $CO_2$  in the ocean (mol m<sup>-2</sup>) [*Sabine et al.*, 2004]. Note how areas of high inventories and thus efficient fossil fuel  $CO_2$  uptake tend to be colder (colder water = higher  $CO_2$  solubility) as well as being areas of water mass formation (sinking in the North Atlantic and intermediate and mode water formation between  $30^{\circ}$  and  $50^{\circ}$ S).

PgC), both through the burning of fossil fuels and cement manufacture has been absorbed by the World's oceans (Figure 1) [*Sabine et al.*, 2004]. Ocean uptake of anthropogenic  $CO_2$  has therefore limited the current extent of climate change by reducing the atmospheric  $CO_2$ concentration that would have been reached in the absence of the ocean  $CO_2$ sink.  $CO_2$  forms a weak acid (carbonic acid,  $H_2CO_3$ ) when dissolved in seawater:

 $CO_{2(aq)} + H_2O \rightarrow H_2CO_3$ 

which does not hang around and promptly dissociates to release a hydrogen ion (H<sup>+</sup>):

 $H_2CO_3 \rightarrow H^+ + HCO_3^-$ 

where  $HCO_3^-$  is the bicarbonate ion.  $HCO_3^-$  can undergo a further dissociation reaction to form another hydrogen ion plus a carbonate ion  $(CO_3^{2^-})$ :

 $\mathrm{HCO}_{3}^{-} \rightarrow \mathrm{H}^{+} + \mathrm{CO}_{3}^{2-}$ 

The sum total of dissolved inorganic carbon species (ignoring H<sub>2</sub>CO<sub>3</sub> which is present only in minute amounts):  $CO_{2(aq)} + HCO_3^{-} + CO_3^{-2}$  is collectively termed *dissolved inorganic carbon* ('DIC'). The relative contribution of these different inorganic species is shown in Figure 2.



**Figure 2.** Relative distribution of the three main components of dissolved inorganic carbon (DIC) as a function of pH.

The net effect of dissolving CO<sub>2</sub> in seawater can be written:

#### $CO_2 + H_2O + CO_3^2 \rightarrow 2HCO_3^-$

with some of the bicarbonate undergoing dissociation to release hydrogen ions.

Although the chemistry of seawater is unfortunately rather messy and complicated by a host of other weak acids such as boric acid what interact with hydrogen ions, there are two main chemical consequences of dissolving  $CO_2$  in sweater. Most importantly – there is an increase in

the concentration of  $H^+$ . The concentration of  $H^+$  gives the *p*H of the water:

#### $pH = -log_{10}([H^+])$

such that a concentration of  $10^{-8}$  mol l<sup>-1</sup> of hydrogen ions equates to a *p*H of 8.0. (For most practical purposes the *p*H is also approximately equal to  $-\log_{10}([H^+])$ , where  $[H^+]$  is the concentration of hydrogen ions in units of mol kg<sup>-1</sup>.)

Historical burning of fossil fuels and deforestation has already had a significant impact on ocean chemistry, with estimates of a mean surface ocean pH decrease of ~0.1 (equivalent to a ~30%)



**Figure 3.** Monthly carbon-system parameters at two time-series stations in subtropical gyres: HOT (Hawaii Ocean Timeseries station) and BATS (Bermuda-Atlantic Time-series Station). [*Kleypas et al.*, 2006]

increase in hydrogen ion (H<sup>+</sup>) concentration), from a value of ~8.18 around the time of the industrial revolution [*Caldeira and Wickett*, 2003]. Long term oceanographic time series stations (Figure 3) indicate a decline in surface ocean pH of 0.0019  $\pm$  0.00025 yr<sup>-1</sup> over the last two decades.

If we continue burning fossil fuels unabated, ocean pH will continue to decline (Figure 4). Furthermore, the effect of acidification will progressively propagate throughout the entire ocean (Figure 5).





**Figure 5.** Assumed CO<sub>2</sub> emissions (top), predicted CO<sub>2</sub> concentrations from the emissions scenario (middle), and horizontally averaged changes in ocean pH (bottom). [*Caldeira and Wickett*, 2003]

**Figure 4.** Changes in ocean carbonate chemistry associated with increasing atmospheric  $CO_2$ . Top panel shows how different atmospheric CO2 concentrations equate to surface *p*H, while the bottom panel shows the speciation amongst the different dissolved carbon forms (and see Figure 2). [*Kleypas et al.*, 2006]

#### Changes to aragonite and calcite saturation

There is a second important consequence of the dissolution of  $CO_2$  in seawater – the concentration of carbonate ions  $(CO_3^{2^-})$  is reduced (see earlier equations). The mineral calcium carbonate  $(CaCO_3)$  has a crystal lattice motif comprising one calcium ion  $(Ca^{2^+})$  ionically bound to one carbonate ion  $(CO_3^{2^-})$  which can be configured in different polymorphic forms – the most common of which are **calcite**, a trigonal structure, and **aragonite**, which is orthorhombic. Whether CaCO<sub>3</sub> precipitates or dissolves depends on the relative stability of its crystal structure (calcite being more stable than aragonite) which can be directly related to the ambient concentrations (strictly, 'activities') of Ca<sup>2+</sup> and  $CO_3^{2^-}$  by the **saturation state** (also known as the solubility ratio)  $\Omega$  of the solution, defined:

$$\Omega = [\mathrm{Ca}^{2^+}] \times [\mathrm{CO}_3^{2^-}]/K_{\mathrm{sp}}$$

where  $K_{sp}$  is a solubility constant. The precipitation of calcium carbonate from sea-water is thermodynamically favourable when  $\Omega$  is greater than unity, and CaCO<sub>3</sub> will tend to dissolve in waters with  $\Omega < 1.0$ . A reduction in CO<sub>3</sub><sup>2-</sup> concentrations will thus lower the value of  $\Omega$ , leading to the potential for under-saturated conditions ( $\Omega < 1.0$ ) and thus CaCO<sub>3</sub> dissolution to occur (e.g., see Figure 6).

(To visualize why a reduction in  $[CO_3^{2^-}]$  will ultimately lead to the dissolution of CaCO<sub>3</sub>, think of Ca<sup>2+</sup>+CO<sub>3</sub><sup>2-</sup> pairs the surface of the crystal as in a dynamic equilibrium with free Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> ions in the surrounding solution. Solid CaCO<sub>3</sub> is in equilibrium ( $\Omega = 1.0$ ) with the solution when the rate of Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> ion pairs separating and leaving the surface is equal to the rate of ions attaching to the surface. By reducing the concentration of CO<sub>3</sub><sup>2-</sup> ions in solution you tip the balance to ion pairs leaving the surface at a faster rate to new ones attaching. Something like that anyway ...)

The thermodynamic stability of calcium carbonate minerals in seawater is important because aragonite and calcite (as well as high-magnesium containing calcite) are all used by many different marine organisms to make their shells, skeletons, and 'liths' (e.g., see Figures 7 & 8). The level of saturation ( $\Omega$ ) has a direct affect on the organism's ability to make these calcium carbonate structures, a process called calcification – the greater the saturation state the easier it will be for organisms to calcify. However, if waters become under-saturated ( $\Omega < 1.0$ ) with respect to these minerals, the calcium carbonate structures gradually dissolve until they disappear. Although carbonate ion saturation has decreased since pre-industrial days, currently most surface waters remain oversaturated, with the warm tropic waters having the highest saturation state and the colder polar and sub polar waters the lowest (Figure 6). Global ocean models unanimously project undersaturation with respect to the aragonite phase occurring in polar and sub polar surface waters within decades [Orr et al., 2005; Feely et al., 2004], shown in Figure 6. However, a recent study of North America found that these under-saturated, corrosive waters with pH of 7.6 bath the shelf from February to September. A reduction of ocean pH will extend the duration of exposure of the shelf biota to these corrosive waters [Feely et al., 2008]. This indicates that other up-welling regions as well as high latitude waters may be particularly vulnerable to the earlier onset of ocean acidification, at least earlier than that predicted by large scale General Circulation Models.

#### The extent of future ocean acidification

As illustrated in a 'worse case scenario' of CO<sub>2</sub> emissions with no mitigation (Figure 5), by 2100, atmospheric CO<sub>2</sub> concentrations could reach >800 ppm causing an additional surface water *p*H decrease of ~0.4 *p*H units. Average surface ocean *p*H could fall by a maximum of 0.77 pH units by ~2300. Any mitigation and/or reduction of CO<sub>2</sub> emissions will produce benefits for the marine environment.



Figure 6. Estimated aragonite saturation states of the surface ocean for the years 1765, 1995, 2040, and 2100. [*Kleypas et al.*, 2006]

#### POTENTIAL IMPACTS TO MARINE ORGANISMS

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 *p*H for marine animals is normally regulated at a particular level (e.g. haemolymph *p*H 7.4 – 7.9 depending on species). Organisms have adapted a number of mechanisms that can, on short timescales, buffer changes in *p*H thereby preventing damage to internal processes and functioning. Changes in seawater chemistry caused by ocean acidification threaten to disrupt these systems. It is unclear how long these buffering 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] and it may be that long-term critical thresholds of vulnerability will occur in this time period [*Turley and Findlay*, in press]. 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.

Calcifying organisms are not only vulnerable through impacts to their physiology, but additionally by dissolution of their CaCO<sub>3</sub> 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 shell formation (reviewed by *Kleypas, et al.* [2006]). Amorphous calcite is laid down by some species as the basis for carbonate formation and may be particularly susceptible to dissolution, even more so than aragonite and calcite.



**Figure 7.** Representatives of major benthic calcifiers: (a) coralline algae (**aragonite**); (b) Halimeda (**calcite**); (c) benthic foraminifera (**calcite**); (d) reef-building coral (*Dendrogyra cylindrus*) (**aragonite**); (e) deep-water coral (*Lophelia pertusa*) (**aragonite**); (f) bryozoan (**aragonite/calcite**); (g) mollusc (**aragonite**); (h) echinoderm (brittle star) (**high-Mg calcite**); (i) crustacean (lobster) (**calcite**). [*Kleypas et al.*, 2006]

#### Sea bed dwelling ('benthic') calcifiers

Regional seas and continental shelves provide a variety of important habitats for many benthic organisms (animals and plants that live on and in rocks, sand, mud, shingle, etc.), illustrated in Figure 7. There have been limited investigations into the response of key organisms from these ecosystems to realistic future ocean acidification scenarios. Studies on sea urchins and brittlestars showed they were unable to compensate for longer-term changes in ocean acidification. Sea urchins were unable to maintain their acid-base balance for longer than seven days at pH 7.4 (year 2250) [*Miles et al.*, 2007]. In experiments at CO<sub>2</sub> levels just 200 ppm higher than today (year 2050) they exhibited reduced growth and survival rates over several months [Shiryama & Throntron, 2005]. Other experiments on brittlestars showed muscle wastage in their arms as a trade-off attempt to increase their calcification at pH 7.7 (year 2100) [Wood et al., 2008]. Mussels and oysters show a decrease of shell and body growth by 55% at year 2300 levels [Michaelidis et al., 2005]. Net calcification decreased by 25% (at ×2 pre-industrial CO<sub>2</sub>, year 2050) and 37% (at ×3 pre-industrial CO<sub>2</sub>, year 2100) in mussels and 10% (×2 CO<sub>2</sub>) and 15% (×3 CO<sub>2</sub>) in oysters (reviewed by Guinotte and Fabry [2008]). Crustaceans (crabs, lobsters, barnacles) have been shown to be somewhat more able to compensate for changes in pH [Spicer et al., 2007; Pane and Barry, 2007] however they are still subject to dissolution impacts and their early life stages are proving vulnerable.

These organisms are not only commercially important, but also play important roles in the cycling of nutrients between the sediment and the water column, 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.

Cold-water (a.k.a. deep-water corals) corals are found throughout the worlds' oceans, including the European continental shelf and the UK coastline (Pink Sea fans, *Eunicella*). They 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



**Figure 8.** Representatives of major planktonic calcifiers: (a) the coccolithophore *Emiliania huxleyi* (phytoplankton which makes overlapping platelettes called 'liths' from **calcite**); (b) planktonic foraminifer (zooplankton which creates a multi-chambered shell out of **calcite**); and (c) the euthecosomatous pteropod *Cavolinia tridentata* ('sea butterfly' – has an **aragonite** shell). [*Kleypas et al.*, 2006]

[Guinotte et al., 2006, Roberts et al., 2006]. Future projections of the acidification of the deep ocean indicate that 70% of cold-water corals are likely to experience undersaturation ( $\Omega < 1.0$ ) with respect to aragonite this century and in some places as early as 2020 [Orr et al., 2005; Guinotte et al., 2006; Turley et al., 2007]. It is unlikely that coldwater corals will be able to calcify under these conditions as their aragonitic skeleton will experience dissolution in these corrosive waters, leading to breakdown of reef structure and loss of habitat for other organisms.

Warm water coral reefs harbour an immense biodiversity and are important for shore protection. Decreasing aragonite saturation (see: Figure 6) 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].



**Figure 9.** SeaWiFS satellite image of UK regional seas showing phytoplankton and coccolithophore blooms (whitish green blue swirls).

#### Pelagic calcifying organisms

Pelagic organisms, including phytoplankton, zooplankton and other organisms living in the upper water column (summarised in Figure 8), may also be vulnerable to ocean acidification, although results so far have shown there is high species-species variability. Coccolithophores, planktonic algae which produce blooms so large they are visible from space (Figure 9), produce calcitic liths (Figure 10). Experiments indicate that some species (e.g. Emiliania *huxleyi* and *Gephyrocapsa oceanica*) may experience decreased rates of calcification by 16% at  $\times$ 2 CO<sub>2</sub> and 30% at  $\times$ 3 CO<sub>2</sub> (Figure 10), although other species have shown no response. Copepods (Figure 8c), 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]. Planktonic pteropods, important grazers in areas of the polar Oceans, produce shells out of aragonite and have been found to be highly

susceptible to dissolution [*Fabry*, 1990]. Changes in planktonic assemblage or nutrient flows are complex and will likely result in a change in community structure, particularly with a decrease in abundance of calcified organisms. Unabated  $CO_2$  emissions may result in changes to species biogeography as they track their habitat. Habitat disappearance might lead to extinction for example in high latitudes. Some species may fill the abandoned niches, changing the structure of the ecosystem. For example, non calcifiers and alien species have replaced calcifiers in areas of low *p*H around the  $CO_2$  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  $CO_2$  ocean. Could we be eating jellyfish-and-chips from the local chippie in the future?



**Figure 10.** Two images of coccolithophores showing increased malformation at higher CO<sub>2</sub> concentrations (920 ppm is equivalent to ca. year 2100 scenarios). (From *Langer et al.* [2006].)

#### **GLOBAL CARBON CYCLING AND CLIMATIC CONSEQUENCES**

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

By precipitating calcium carbonate  $(CaCO_3)$  from sea-water, marine organisms affect the global carbon cycle and climate system. In the chemical reaction for creating carbonate shells and skeletons:

## $\mathrm{Ca}^{2^+} + 2\mathrm{HCO}_3^- \rightarrow \mathrm{Ca}\mathrm{CO}_3 + \mathrm{CO}_{2(\mathrm{aq})} + \mathrm{H_2O}$

dissolved inorganic carbon in seawater in its 'inert' form (HCO<sub>3</sub>.) which cannot interact directly with the atmosphere, 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  $CO_{2(aq)}$  at the ocean surface. Any reduction in calcification in the future thus has implications for atmospheric CO<sub>2</sub>. This is because the release of  $CO_{2(aq)}$  in surface waters by calcifying organisms acts as a brake on the transfer of fossil fuel CO<sub>2</sub> from the atmosphere into the ocean. Reducing the rate of calcification globally then accelerates the rate of uptake of fossil fuel CO<sub>2</sub> from the atmosphere.



**Figure 11.** 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].)

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 CO<sub>2</sub>. Predictions for the additional quantity of fossil fuel CO<sub>2</sub> 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]. This is comparable to the current emissions of fossil fuel CO<sub>2</sub> in just a single year (ca. 7 PgC [*IPCC*, 2007])! The direct impact of ocean acidification and reduced pelagic calcification of atmospheric CO<sub>2</sub> is therefore relatively unimportant.

# Indirect impacts of ocean acidification on atmospheric CO<sub>2</sub>

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. 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  $CO_2$  at the surface than at depth (Figure 11). Any reduction in the fraction of organic matter reaching the deep ocean would reduce the surface-to-deep dissolved  $CO_2$  gradient, resulting in a higher concentration of  $CO_2$  in the atmosphere.

Because the CaCO<sub>3</sub> shell material produced by pelagic calcifiers (Figure 8) is much denser than the soft body parts of plankton, its presence in aggregates with organic matter (Figure 12) may play an important role in accelerating the rate of sinking [*Armstrong et al.*, 2002]. Any reduction in



Figure 12. Image of a marine snow aggregate.

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  $CO_2$  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  $CO_2$  higher overall.

The limited number of global models that have assessed the potential importance of

CaCO<sub>3</sub> in the 'ballasting' (density-dependent sinking) of aggregates with organic matter, suggest that reduced CaCO<sub>3</sub> ballasting could cut the ca. 6-18 PgC direct impact of acidification-driven changes in calcification on fossil fuel CO<sub>2</sub> uptake by 80% [*Heinze*, 2004]. It is possible that the sign of the net CO<sub>2</sub> impact could be reversed, resulting in more fossil fuel CO<sub>2</sub> overall residing in the atmosphere [*Barker et al.*, 2003]. The implications of a reduction in organic matter supply for the organisms and communities living at the ocean floor is currently unknown but we do know that organic matter sinking in this way from the surface waters is the main food resource for the diverse group of organisms that live there [*Turley*, 2000]. However, because of the technical and logistical difficulties of observing and experimenting on the aggregation (and dis-aggregation) processes in the ocean interior, there is currently considerable uncertainty as to the importance of CaCO<sub>3</sub> in the transport of organic matter to depth.

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

Blooms of coccolithophores (Figure 9) 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 4) 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  $0.22 \text{ Wm}^{-2}$  [*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 9) 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, enriched for coccolithophore growth under different  $CO_2$  scenarios showed changes in DMS production at  $CO_2$  concentrations different to current concentrations. However, the existence of global climate impacts via acidification and DMS production should be considered highly uncertain at present.

#### SOCIETAL AND ECONOMIC CONSEQUENCES OF OCEAN ACIDIFICATION

The coastal and shelf marine environments provide a wide range of goods and services that are essential for the maintenance of social and economic well being. Such ecosystem services provide benefits at several levels (local, regional and global) and to different groups (individuals and public bodies). Ecosystem goods and services are also valuable for reasons not related to their use, for example in contributing to cultural and spiritual traditions. Ocean acidification is likely to impair calcification in animals with calcium carbonate shells and skeletons and will especially impact ecosystems and marine resources that depend in some way on the presence and correct functioning of marine calcifiers.

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 security. The substantial biodiversity supported by coral reefs underpin substantial tourist industries for many tropical countries 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].

Coral reefs (as well as mangroves) also play an important role in shore protection and enhance local productivity and biodiversity. This protective function of reefs was valued at US\$ 9.0 billion per year by *Cesar et al.* [2003]. 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.

Pearls are created naturally by shellfish through the secretion of aragonite but can also be cultured artificially in oysters. Currently, the global pearl farming is a \$1.5-bn industry. The global pearl industry is expected to grow into a \$3bn 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.

Maerl beds, mussel patches and cold-water coral reefs 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].

In general, ocean acidification could lead to a 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 2006 [*James*, 2007], and assuming a 10-25% reduction in growth/calcification due to ocean acidification results in 10-25% loss of shellfish landings that is equivalent to £24.4 - 61 million per year loss in value and around 1000-3000 potential job losses.

#### REFERENCES

- Armstrong, R.A., Lee, C., Hedges, J.I., Honjo, S. and Wakeham, S.G. (2002) A new, mechanistic model for organic carbon fluxes in the ocean: based on the quantitative association of POC with ballast minerals. Deep-Sea Res. II, 49, 219-236.
- Barker, S., Higgins, J. A. and Elderfield H. (2003) The future of the carbon cycle: review, calcification response, ballast and feedback on atmospheric CO<sub>2</sub>. Philosophical Transactions of the Royal Society, A, 361, 1977.
- Caldeira K, Wickett ME (2003) Anthropogenic carbon and ocean pH. Nature, 425, 365.
- Cesar, H., Burke, L. and Pet-Soede L. (2003) The economics of worldwide coral reef degradation. Cesar Environmental Economics Consulting (CEEC), 6828GH Arnhem, The Netherlands, 23 pp.
- Charlson, R.J., Lovelock, J.E., Andreae, M.O. and Warren, S.G. (1987). Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate. Nature, 326, 655-661.
- Fabry, V.J. (1990) Shell growth rates of pteropod and heteropod mollusks and aragonite production in the open ocean: implications for the marine carbonate system. J. Mar. Res., 48, 209–222.
- Fabry, V. J., Seibel, B. A., Feely, R. A. and Orr, J. C. (2008) Impacts of ocean acidification on marine fauna and ecosystem processes. ICES J. Mar. Sci., 65, 414-432.
- Feely RA, Sabine CL, Lee K, Berelson W, Kleypas J, Fabry VJ, Millero, FJ (2004) Impact of anthropogenic CO<sub>2</sub> on the CaCO<sub>2</sub> system in the ocean, Science, 305, 362–366.
- Feely, R.A., Sabine, C.L., Hernandez-Ayon, J.M., Ianson, D. and Hales, B. (2008) Evidence for Upwelling of Corrosive "Acidified" Water onto the Continental Shelf. Science, 22 May 1-4, 10.1126/science.1155676.
- Gehlen, M., Gangstø, R. Schneider, B. Bopp, L. Aumont, O. and Ethe, C. (2007) The fate of pelagic CaCO3 production in a high CO2 ocean: A model study, Biogeosciences Discuss., 4, 533-560.
- Guinotte, J.M., Orr, J., Cairns, S., Freiwald, A., Morgan, L. and George, R. (2006) Will human induced changes in seawater chemistry alter the distribution of deep-sea scleractinian corals? Front. Ecol. Environ., 4, 141–146.
- Hall-Spencer, J.M., Grall, J. and Moore, P.G. (2003) Bivalve fishing and maerl-bed conservation in France and the UK retrospect and prospect Atkinson. Aquatic Conservation: Marine and Freshwater Ecosystems, 13, 33-41.
- Hall-Spencer, J.M., Rodolfo-Metalpi, R., Martin, S., Ransome, R., Fine M., Turner, S.M., Rowley S.J., Tedesco D. and Buia, M.-C. (2008) Volcanic carbon dioxide vents show ecosystem effects of ocean acidification. Nature, doi:10.1038/nature07051.
- Heinze, C. (2004) Simulating oceanic CaCO3 export production in the greenhouse, GRL 13, doi:10.1029/2004GL020613.
- IPCC (2007) Climate Change 2007: The physical science basis. Summary for policymakers. Contribution of working group I to the fourth assessment report. The Intergovernmental Panel on Climate Change, http://www.ipcc.ch/SPM2feb07.pdf
- James E (ed) 2007. UK Sea Fisheries Statistics 2006. Department for Environment, Food and Rural Affairs, Defra, London 157pp.
- Kleypas, J.A., Feely, R.A., Fabry, V.J., Langdon, C., Sabine C.L. and Robbins, L.L. (2006). Impacts of ocean acidification on coral reefs and other marine calcifiers: a guide for future research. Report of a workshop held 18– 20 April 2005, St Petersburg, FL, sponsored by NSF, NOAA, and the US Geological Survey, 1-88.
- Kurihara, H. Shimode, S. and Shirayama, Y. (2004) Effects of raised CO<sub>2</sub> concentration on the egg production rate and early development of two marine copepods (*Acartia steueri* and *Acartia erythraea*). Mar. Poll. Bull., 49, 721-727.
- Langer, G., Geisen, M., Baumann, K.-H., Klas, J., Riebesell, U., Thoms, S., Young, J.R. (2006), Species-specific responses of calcifying algae to changing seawater carbonate chemistry, Geochemistry Geophysics Geosystems, 7, Q09006, <u>http://dx.doi.org/09010.01029/02005GC001227</u>.
- Michaelidis, B., Ouzounis, C., Paleras, A. and Pörtner, H.O. (2005) Effects of long-term moderate hypercapnia on acidbase balance and growth rate in marine mussels *Mytilus galloprovincialis*. Mar Ecol Prog Ser 293, 109–118.
- Miles, H., Widdicombe, S., Spicer, J.I. and Hall-Spencer, J. (2007) Effects of anthropogenic seawater acidification on acid-base balance in the sea urchin *Psammechinus miliaris*. Mar. Poll. Bull., 54, 89-96.
- Orr, J.C., Fabry, V.J., Aumont, O., Bopp, L., Doney, S.C., Feely, R.A., Gnanadesikan, A., Gruber, N., Ishida, A., Joos, F., Key, R.M., Lindsay, K., Maier-Reimer, E., Matear, R., Monfray, P., Mouchet, A., Najjar, R.G., Plattner, G.-K., Rodgers, K.B., Sabine, C.L., Sarmiento, J.L., Schlitzer, R., Slater, R.D., Totterdell, I.J., Weirig, M.-F., Yamanaka ,Y. and Yool, A. (2005) Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms. Nature, 437, 681-686.
- Pane, E.F. and Barry, J.P. (2007) Extracellular acid-base regulation during short-term hypercapnia is effective in a shallow water crab, but ineffective in a deep-sea crab. Mar. Ecol. Prog. Ser. 334, 1–9.
- Ridgwell, A., Zondervan, I., Hargreaves, J., Bijma, J. and Lenton, T. (2007) Assessing the potential long-term increase of oceanic fossil fuel CO<sub>2</sub> uptake due to 'CO2-calcification feedback', Biogeosciences 4, 481-492.
- Riebesell, U., Zondervan, I., Rost, B., Tortell, P. D., Zeebe, R. E., Morel, F. M. M.: Reduced calcification of marine plankton in response to increased atmospheric CO2, Nature, 407, 364–367, 2000.
- Roberts, J.M., Wheeler, A.J. and Freiwald, A. (2006) Reefs of the deep: the biology and geology of cold-water coral ecosystems. Science, 312, 543–547.

- Royal Society (2005) Ocean acidification due to increasing atmospheric carbon dioxide. Policy document 12/05 Royal Society, London. The Clyvedon Press Ltd, Cardiff
- Sabine CL, Feely RA, Gruber N, Key RM, Lee K, Bullister JL, Wanninkhof R, Wong CS, Wallace DWR, Tilbrook B, Millero FJ, Peng TH, Kozyr A, Ono T, Rios AF (2004) The oceanic sink for anthropogenic CO<sub>2</sub>. Science 305, 367– 371.
- Shirayama, Y. and Thornton, H. (2005) Effect of increased atmospheric CO<sub>2</sub> on shallow water marine benthos. J Geophys Res 110 C09S08.
- Spicer, J.I. Raffo, A. and Widdicombe, S. (2007) Influence of CO<sub>2</sub>-related seawater acidification on extracellular acidbase balance in the velvet swimming crab *Necora puber*. Mar. Biol. 227.
- Turley, C.M. (2000) Bacteria in the deep-sea benthic boundary layer and sediment water interface of the NE Atlantic: A Review. FEMS Microbiol. Ecol. 1154, 1-11.
- Turley, C.M., Roberts, J.M. and Guinotte, J.M. (2007) Corals in deep-water: Will the unseen hand of ocean acidification destroy cold-water ecosystems? Coral Reefs, 26, 445-448.
- Turley C.M. and Findlay, H.S. Ocean Acidification as an Indicator of Global Change. In: CLIMATE and GLOBAL CHANGE (Trevor Letcher, Ed) Elsevier (in press).
- Tyrrell, T., Holligan, P. and Mobley C. (1999), Optical impacts of oceanic coccolithophore blooms, J. Geophys. Res., 104(C2), 3223-3241.
- Wood, H.L. Spicer J.I. and Widdicombe, S. (2008) Ocean acidification may increase calcification rates, but at a cost. Proc. R. Soc. B., 275 1767-1773.
- Worm, B., Barbier E.B., Beaumont N., Duffy J.E., Folke C., Halpern B.S., Jackson J.B.C., Lotze H.K., Micheli F., Palumbi S.R., Sala E, Selkoe K.A., Stachowicz J.J. and Watzon R. (2006) Impacts of biodiversity loss on ocean ecosystem services. Science 314:787-790.