

# Calcium carbonate cycling in future oceans and its influence on future climates

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*In the last few years, evidence has accumulated that calcifying organisms are likely to be affected by ocean acidification. Therefore, the production of calcium carbonate will probably decline, although conversely global warming, increasing stratification and sea level rise may also stimulate increases in global calcification. As acidification reaches the deep ocean, it will cause pronounced shallowing of the lysocline depths for calcite and aragonite, leading most probably to an almost complete cessation of deep-sea calcium carbonate burial for some centuries. Here, I briefly review the consequences of these and other changes on future ocean calcium carbonate cycling, and the consequences of this for future climate. Associated climate impacts are not likely to be significant over the next few centuries, but will become increasingly important thereafter. After the carbonate compensation response to acidification has run its course, extra CO<sub>2</sub> is expected to be left behind in the atmosphere, protecting against future ice ages.*

## INTRODUCTION

Like many others I consider myself extremely fortunate to have worked with Patrick Holligan for many years, and to have benefited not only from his advice but also from being exposed to his great curiosity into the global operation of the Earth System. Patrick's global interests led him not only to carry out local process studies into globally important processes, such as the comprehensive study of biogeochemical cycling within a coccolithophore bloom (Holligan *et al.*, 1993), but also to his role in establishing and sustaining the Atlantic Meridional Transect (AMT) programme with its ability to probe biogeochemical processes through two hemispheres and through very many biogeochemical provinces. Patrick's enthusiasm for the global scale has always been inspiring.

In this paper, I revisit an earlier paper of Patrick's. In 1996, Patrick collaborated with Jane Robertson on a review paper "Significance of ocean carbonate budgets for the global carbon cycle" (Holligan and

Robertson, 1996). The title of my article is adapted from theirs, with the difference that I consider here how the ocean calcium carbonate cycle is likely to change in the future, and how these changes are likely to affect the global carbonate pump, atmospheric CO<sub>2</sub> and climate. Some of this was touched upon in their earlier paper (in a section titled "Anthropogenic perturbation of the carbonate pump"), and I attempt here to bring their earlier discussion up to date by incorporating recent work on ocean acidification and also recent work on long-term impacts of ocean acidification. In contrast to other reviews on the future of calcifying organisms, in this review I consider not just the next century but also much further into the future, up to a million years or so.

## ANTHROPOGENIC CHANGES AND EARTH SYSTEM RESPONSE

In this section, some of the key changes and feedback processes are described, of relevance to CaCO<sub>3</sub> cycling.

These include not only the changes that are arising rather directly from the insults we are inflicting on the Earth System at the current time, but also indirect impacts, such as those associated with feedbacks likely to be induced in response to anthropogenic changes.

The nature of future changes is difficult to predict with any precision. This is not only because of the great complexity of the Earth System, but also because future anthropogenic impacts depend on future carbon dioxide emissions and therefore on the degree to which the international community is able to agree on emissions cuts. To date we have burnt slightly less than one-tenth of the easily recoverable fossil fuels, ~300 Gt C out of about 4000 Gt C (Marland *et al.*, 2005), and in the process have increased the Earth's atmospheric CO<sub>2</sub> concentration from a pre-industrial value of 280 ppm to >380 ppm today. This increase of 100 ppm over pre-industrial is already large in comparison with the natural oscillation of ~100 ppm between ice ages (~180 ppm) and interglacials (~280 ppm).

In the following I generally assume that there will continue to be considerable emissions on into the future, for instance that cumulative emissions are likely to reach at least 2000 Gt C by the year 2300, and therefore that peak future atmospheric CO<sub>2</sub> will be at least several hundred parts per million higher than today's value (IPCC, 2007). If the political process results in a rapid transition to drastically lowered carbon usage, then the amplitude of impacts sketched out here will be necessarily lower. Likewise, if emissions continue but are countered by large-scale intervention to sequester CO<sub>2</sub> (e.g. by pumping down CO<sub>2</sub> into rocks beneath the earth's surface), then impacts will be smaller.

## OCEAN ACIDIFICATION

### Chemical consequences of ocean acidification

Although fossil fuel emissions are injected into the atmosphere, the CO<sub>2</sub> does not all stay there. In fact, nearly half of the emissions to date have by now diffused across the sea-surface and entered the ocean: the total oceanic absorption of anthropogenic CO<sub>2</sub> is calculated as  $118 \pm 19$  Gt C between 1800 and 1994 (Sabine *et al.*, 2004). Because of the slow overturning circulation of the ocean (order of 1000 years), most of the fossil fuel CO<sub>2</sub> now residing in the ocean is present in the surface layers, which are in intimate contact with the atmosphere. However, in locations where surface waters sink to depth, such as the high-latitude North

Atlantic, anthropogenic CO<sub>2</sub> is also penetrating into the deep ocean (Sabine *et al.*, 2004).

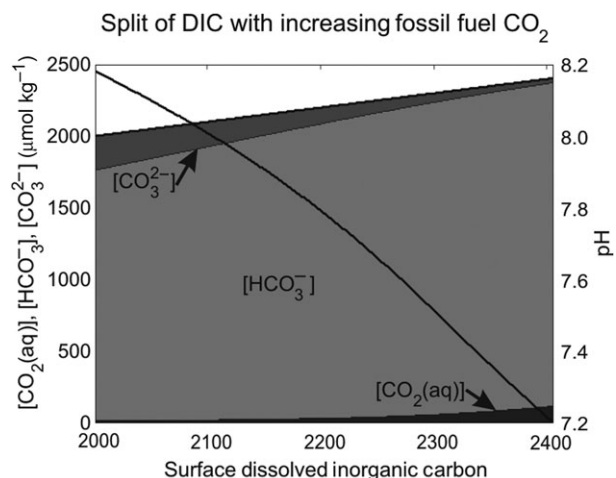
When CO<sub>2</sub> dissolves in water, it makes the receiving water more acidic. As the atmospheric CO<sub>2</sub> concentration continues to rise and the surface ocean absorbs ever greater amounts of CO<sub>2</sub> in response, its acidity increases. Surface ocean pH has already decreased by about 0.1 units from its pre-industrial average value of ~8.2 down to a present-day average of ~8.1, according to model reconstructions (Orr *et al.*, 2005). The pH value is expected to fall much further (in the absence of a strong curtailment of emissions, as just discussed), perhaps down to an average surface value of 7.9 by year 2100 (Orr *et al.*, 2005) followed by a fall to <7.5 (maximum reduction of -0.77 units) by the year 2300 (Caldeira and Wickett, 2003). Note however that while the term "ocean acidification" is used, seawater will nevertheless remain alkaline. Surface ocean pH is dropping and seawater is clearly shifting towards more acidic values, but pH is not predicted to fall below neutral values (7.0) as a result. It will remain alkaline in the future, although less so over time. The fall in seawater pH is not only a theoretical prediction, it has also been observed in direct measurements. For instance, a year-on-year decline averaging  $-0.0017 \pm 0.0004$  pH units year<sup>-1</sup> has been observed between 1995 and 2004 at the ESTOC time-series site in the Canary Islands (Santana-Casiano *et al.*, 2007).

These changes to pH have large implications for the distribution of dissolved inorganic carbon (DIC) in the ocean. DIC comprises three separate chemical species: bicarbonate ions (HCO<sub>3</sub><sup>-</sup>, typically about 90% of the total), carbonate ions (CO<sub>3</sub><sup>2-</sup>, typically about 10% of the total) and dissolved CO<sub>2</sub> gas (CO<sub>2</sub>(aq), typically about 1% of the total). Although total amounts of DIC are increasing, the concentration of CO<sub>3</sub><sup>2-</sup> is falling rapidly and is predicted to fall further in the future. Declining pH is predicted to lead to a halving of carbonate ion concentration by the year 2100, compared with pre-industrial levels, and therefore to a halving of CaCO<sub>3</sub> saturation state (Zeebe and Wolf-Gladrow, 2001; Caldeira and Wickett, 2005; Orr *et al.*, 2005) (Fig. 1).

The saturation state of seawater with respect to CaCO<sub>3</sub> is given by the formula:

$$\Omega = \frac{[\text{CO}_3^{2-}] \cdot [\text{Ca}^{2+}]}{K_{\text{sp}}},$$

i.e. the product of the carbonate ion and calcium ion concentrations divided by the value of the stoichiometric solubility product  $K_{\text{sp}}$ .  $K_{\text{sp}}$  is equal to the product of calcium and carbonate ion at saturation ( $\Omega = 1$ ), and



**Fig. 1.** Schematic of carbon chemistry changes due to invasion of fossil fuel CO<sub>2</sub> into the surface ocean. Changes are shown as a stacked plot for the three different components of DIC, with changes in pH (solid line) superimposed. X-axis corresponds to increasing fossil fuel carbon from left to right, as fossil fuel invasion increases surface ocean DIC from an assumed pre-industrial value of 2000  $\mu\text{mol kg}^{-1}$ . [HCO<sub>3</sub><sup>-</sup>] and [CO<sub>2</sub>(aq)] increase with addition of fossil fuel CO<sub>2</sub>, whereas pH and [CO<sub>3</sub><sup>2-</sup>] decline.

is sensitive to pressure, temperature, salinity and other factors. The sensitivity to pressure is particularly strong, leading to a large difference between surface ( $\sim 0.43 \times 10^{-6} \text{ mol}^2 \text{ kg}^{-2}$  at 10 m, for calcite) and deep ( $\sim 1.15 \times 10^{-6} \text{ mol}^2 \text{ kg}^{-2}$  at 5000 m, for calcite) values (Zeebe and Wolf-Gladrow, 2001). Because calcium is both extremely abundant (and therefore resistant to short-term change) and more or less invariant throughout the oceans, spatial and temporal changes in saturation state are mostly controlled by changes in [CO<sub>3</sub><sup>2-</sup>]. Pressure also has a strong effect on  $\Omega$ , through  $K_{\text{sp}}$ , leading to lower values of  $\Omega$  deeper in the ocean, but this pressure effect does not change with time. Anthropogenic effects on  $\Omega$  are therefore mostly through [CO<sub>3</sub><sup>2-</sup>]. Because there are two main polymorphs of CaCO<sub>3</sub> used by organisms, namely calcite (foraminifera, coccolithophores, etc.) and aragonite (corals, pteropods, etc.), and because they have different propensities for dissolution (different  $K_{\text{sp}}$  values), there are also two saturation states. The saturation state for aragonite always has lower values than that for calcite (aragonite is relatively more soluble in seawater).

The changes in  $\Omega$  value will not be geographically uniform, in part because anthropogenic CO<sub>2</sub> is not entering the ocean everywhere at the same rate, and in part because some areas of the ocean have naturally lower  $\Omega$  than others.  $\Omega$  tends naturally to higher values towards the equator, lower values towards the poles. It is predicted that the Southern Ocean will become

undersaturated with respect to aragonite by about the year 2050 (Orr *et al.*, 2005).

The impacts of ocean acidification on carbonate chemistry just described are well understood, despite a suggestion to the contrary (Loáiciga, 2006; rebutted by Caldeira *et al.*, 2007).

As well as impacting on the carbonate chemistry in a well understood way, ocean acidification will also impact on other aspects of marine chemistry (Raven *et al.*, 2005), for instance on trace metal speciation, giving rise to the possibility of other impacts on marine biology, for instance via changes in iron availability. However, little is presently known about other possible chemical and biological changes.

### Biological consequences of ocean acidification

The likely biological consequences have previously been reviewed in considerable detail by Raven *et al.* (Raven *et al.*, 2005) and Kleypas *et al.* (Kleypas *et al.*, 2006). Here I briefly review the evidence up to the present time, in less detail than the earlier reviews, and focussing primarily on those organisms calculated to be of most significance to the global production of CaCO<sub>3</sub>, notably scleractinian (stony) corals, coralline algae, coccolithophores and foraminifera (Milliman *et al.*, 1993). Although a number of experimental studies have found impacts of acidification on shellfish calcification (Michaelidis *et al.*, 2005; Shirayama and Thornton, 2005; Gazeau *et al.*, 2007), these impacts will not be considered further here because of their small quantitative contribution to global CaCO<sub>3</sub> production.

Nearly all experiments to date have focussed on measuring how acidification affects the rate of calcification. What is much harder to ascertain, although of possibly equal or greater significance to future global calcification rates, is how thinner shells and weaker skeletons (corals) will impact on competitiveness of calcifying organisms and therefore on future population abundances. For instance, although a recent study showed that naked coral polyps can survive perfectly well without skeletons in a laboratory tank (losing them as pH is adjusted down then rebuilding them as pH is returned back to normal levels; Fine and Tchernov, 2007), suggesting that coral polyps can survive long-term exposure to low pH in the natural environment (Stanley, 2007), such a conclusion completely ignores the probable vulnerability of unarmoured, tethered, soft-bodied polyps to grazing by fish. It is important to consider such impacts on organism viability as they live in their natural ecosystem (replete with competitors,

parasites and predators), in addition to the more easily studied physiological impacts.

Global calcification rate is likely to be doubly affected by acidification in future: (i) by diminished calcification rates per individual organism and (ii) by lower abundances of calcifying organisms in marine ecosystems. The two effects will multiply together, in terms of their impact on global  $\text{CaCO}_3$  production.

It appears that the effects of high  $p\text{CO}_2$  on calcifying organisms do not occur directly through the elevated  $p\text{CO}_2(\text{aq})$  itself, nor even directly through the lowered pH, but rather, experiments suggest (Langdon *et al.*, 2000; Leclercq *et al.*, 2000; Schneider and Erez, 2006), through lowered calcium carbonate saturation state ( $\Omega$ ). This is consistent with experimental results examining *inorganic* precipitation and dissolution of calcium carbonate. Experiments in artificial seawater solutions found that inorganic precipitation of  $\text{CaCO}_3$  is increasingly likely and/or rapid as  $\Omega$  increases further above 1.0, and dissolution is increasingly likely and/or rapid as  $\Omega$  decreases further below 1.0.

I now briefly review the evidence with regards to each major group.

#### *Corals and coralline algae*

Experimental studies on coralline algae (Agegian, 1985), reef-building corals (for example Gattuso *et al.*, 1998; Marubini *et al.*, 2001; Schneider and Erez, 2006) and coral communities (for example Langdon *et al.*, 2000; Leclercq *et al.*, 2000) have found that calcification rate (rate of accretion of calcium carbonate) declines with declining  $\Omega$ . The rate at which crustose coralline algae colonise empty surfaces is found to be lower at high  $\text{CO}_2$  (Kuffner *et al.*, 2007). The pre-industrial geographical distribution of scleractinian (stony) corals was largely restricted to tropical and sub-tropical waters with high values of  $\Omega$  (Kleypas *et al.*, 1999b; Guinotte *et al.*, 2003). There is now a large body of evidence strongly suggesting that coral calcification will be severely, and detrimentally, affected by projected ocean acidification (see the aforementioned references and also the review by Kleypas *et al.*, 2006). It has variously been estimated that the global sum of coral  $\text{CaCO}_3$  production may decrease by 14–30% by 2050 (Kleypas *et al.*, 1999a) or 9–30% by 2100 (Gattuso *et al.*, 1999).

Only a small number of studies have come to a different conclusion. For instance, Pelejero *et al.* (Pelejero *et al.*, 2005) disputed the link between pH and coral calcification rate, based on an observed lack of correlation between (i) thickness of coral annual bands (calcification rate) and (ii) seawater pH estimated from boron isotopic composition, both measured from the same ~300-year-old massive *Porites* coral in the

Flinders Reef (Coral Sea). The significance of their results is called into question, however, by (a) difficulty in reconciling their pH reconstruction with constraints on other carbonate system parameters (see follow-ups to original article: Matear and McNeil, 2006; Pelejero *et al.*, 2006), and (b) their inability to reliably reconstruct  $\Omega$  (Pelejero *et al.*, 2006). Whereas  $\Omega$  and pH will fall together in the surface ocean in the future, they are not guaranteed to have co-varied over the last 300 years in a coral lagoon in which calcification and photosynthesis rather than  $\text{CO}_2$  invasion will have dominated carbonate chemistry. Reynaud *et al.* (Reynaud *et al.*, 2003) found no effect of elevated  $p\text{CO}_2$  (lower pH and  $\Omega$ ) on coral calcification, except when the high  $p\text{CO}_2$  was accompanied by an increase in water temperature.

#### *Coccolithophores*

Concern over acidification impacts on coccolithophores stem from results of laboratory experiments by Riebesell *et al.* (Riebesell *et al.*, 2000) on *Emiliania huxleyi* and *Gephyrocapsa oceanica*, which showed less rapid calcification per cell at high  $\text{CO}_2$  levels. This concern has been reinforced by results of further laboratory studies (Zondervan *et al.*, 2001, 2002) and also by results of mesocosm studies, which found slower rates of calcification and smaller coccoliths in high  $\text{CO}_2$  bags (Delille *et al.*, 2005; Engel *et al.*, 2005). Separate studies looking at impacts of variable calcium ion concentrations also found that lower levels of calcium (lower  $\Omega$ ) led to malformed coccoliths and a diminished rate of calcification (Herfort *et al.*, 2004; Trimborn *et al.*, 2007). The timing of temperate latitude coccolithophore blooms during the year has been found to coincide with a large seasonal increase in saturation state (Merico *et al.*, 2006).

Not all results are in agreement, however. Some earlier studies came to different conclusions about the link between  $\Omega$  and coccolithophore calcification (Nimer and Merrett, 1993; Buitenhuis *et al.*, 1999) and in the last few years other studies have also found contradictory results (Sciandra *et al.*, 2003; Langer *et al.*, 2006; M. D. Iglesias-Rodriguez *et al.*, submitted), on one occasion with the previously untested species *Calcidiscus leptoporus* and *Coccolithus pelagicus* (Langer *et al.*, 2006). Biodiversity of coccolithophores has been found to be largely unaffected during a palaeo acidification episode; there was no great extinction of coccolithophores during the Paleocene–Eocene thermal maximum (Gibbs *et al.*, 2006), although a recent study questions the severity of the surface acidification at this time (Zeebe and Zachos, 2007). At the time of writing, the likely consequences of acidification for coccolithophores are, therefore, somewhat unclear.



### *Foraminifera*

Less is known about the degree of susceptibility of these organisms because of the difficulty in maintaining them alive in culture. The limited number of laboratory experiments that have been carried out suggest a less rapid rate of calcification as a consequence of lowered saturation state (Figs 1–4b of Kleypas *et al.*, 2006 and references therein), and foram shell thickness has been used a palaeo proxy for carbonate ion concentration (Barker and Elderfield, 2002; although see also de Villiers, 2004 for an opposing view). Unlike coccolithophores, which are absent from polar waters (where saturation states are lowest), two species of foraminifera are found there (Schiebel and Hemleben, 2005). This diversity is, however, much lower than in tropical waters (ca. 50 species; Schiebel and Hemleben, 2005). Foraminifera become on average smaller from the tropics to the poles (Schmidt *et al.*, 2006).

## GLOBAL WARMING

### Direct effect of warmer temperatures on calcification rate

All chemical rates increase exponentially with temperature. Reactions proceed more rapidly in warmer conditions. For ectotherms (organisms not regulating their internal temperature, which includes all of the quantitatively most significant calcifiers on Earth: corals, coral-line algae, coccolithophores and foraminifera), their internal temperatures rise and fall in concert with the ambient temperature of the environment. The rates at which they carry out various biochemical reactions should also, therefore, in principle, be controlled by seawater temperatures.

A caveat to this general rule, however, is that it does not hold when the reactions are resource limited. It would seem that this caveat does not apply to biocalcification at sea, because the resources (dissolved calcium and DIC) are among the most abundant in seawater (present at concentrations of  $\sim 10.6$  and  $\sim 2.1$  mmol L<sup>-1</sup>, respectively). A second caveat is that the general rule only holds if the chemical conditions are in any case suitable for the reaction to take place. The rate of spontaneous crystallization from a solution, for instance, will always be zero if the solution is undersaturated, regardless of temperature. In the case of biocalcification, although seawater is theoretically supersaturated with respect to CaCO<sub>3</sub>, in actual fact spontaneous abiotic precipitation (in the form of events called “whittings”, Robbins *et al.*, 1997) is rare and

restricted to a few atypical locations such as the Persian Gulf and the Bahamas Banks. Therefore, biocalcification requires intervention on the part of the organisms (for instance in order to manipulate the chemistry of the solution) and allocation of energetic resources in order to make it take place.

The picture from first principles is therefore inconclusive as to whether or not biocalcification rates should be stimulated by increased sea-surface temperature (SST). The picture from experimental and *in situ* observational studies is also rather unclear, especially as regards coccolithophores for which little evidence currently exists (Paasche, 2001). At the end of blooms of the coccolithophore *Emiliana huxleyi* “overcalcification” occurs, whereby many more coccoliths are produced than are needed simply to cover the cell with a single layer, leading to mass shedding of detached coccoliths into the water (Holligan *et al.*, 1993). Experiments (summarized by Paasche, 2001) suggest that this phenomenon occurs because nutrients have run out, and so incoming energy cannot be allocated to growth. In these circumstances, when energy, C and Ca are all readily available, calcification can take place at little cost. In such circumstances, we might expect global warming to lead to greater rates of calcification in the future.

Lough and Barnes (Lough and Barnes, 2000) surveyed coral accretion rates of *Porites* corals across many degrees of latitude and found a positive correlation between calcification and SST. For coral reefs, it has been proposed that elevated SSTs will enhance coral calcification (McNeil *et al.*, 2004 and references therein). This conclusion has been criticized, however, by Kleypas *et al.* (Kleypas *et al.*, 2005), who contend that the conclusion is derived from data at the low end of ambient temperatures experienced naturally by living corals, and is therefore inappropriate for extrapolating to temperatures higher than today.

### Coral bleaching and SST

A second effect of SST on calcification comes through bleaching events. The corals making up surface-dwelling coral reefs are symbiotic associations between the coral polyps themselves (which are animals) and photosynthetic algae called zooxanthellae, which they host within their tissues. Corals become pale or white (“bleached”) in appearance when possessing no zooxanthellae, as opposed to their various colours when hosting algae. When stressed, corals can lose their zooxanthellae, leading to bleaching. Bleaching events are often fatal to the reef corals but are not always so: new algal symbionts can sometimes be acquired over time. Nevertheless, the loss of symbionts is at the very least

a sign of stress; bleaching events can be triggered by various factors including episodes of warmer SST. Overall, the impacts are considerable, with “almost 30% of corals having disappeared since the beginning of the 1980s” (Hoegh-Guldberg, 2005).

A problem that besets all attempts to estimate the future frequency of bleaching events and the probable consequences for coral extent and effects on calcification is that the ability of coral reef communities to change in response to rising temperatures is largely unknown. As temperatures rise above the upper limits of the existing dominant corals, will those corals be able to acclimatize or adapt through evolution? And if not, then will die-offs of dominant corals just lead to replacement by other species better able to tolerate the higher temperatures? The speed of any evolutionary or community composition changes would need to be quick enough to keep pace with the rate of global warming (McNeil *et al.*, 2005). In assessing this possibility, it should be kept in mind that the recent frequency of bleaching events is highly unnatural; before 1979, coral bleaching was largely unknown (Hoegh-Guldberg, 1999).

In the meantime, it is suggested that predictions of future calcification rates should consider the effects of both declining saturation states and of increasing temperatures, as well as other factors (Reynaud *et al.*, 2003; de Villiers, 2004; Delille *et al.*, 2005; Silverman *et al.*, 2007; Zondervan, 2007).

### Stratification

As pointed out by Holligan and Robertson (Holligan and Robertson, 1996), open-ocean calcifying organisms are observed to be on the whole more successful (in terms of percentage of the phytoplankton community) in warmer climates closer to the equator. This agrees with the distribution of coccolithophores (McIntyre and B  , 1967), which occur in all oceans with the exception of polar oceans (Winter, 1994). Although large, satellite-visible blooms of coccolithophores mostly occur at temperate and sub-polar latitudes (Iglesias-Rodr  guez *et al.*, 2002), in terms of annual average percentage of the phytoplankton community, coccolithophores are at least equally successful at low latitudes, where vertical  $\text{CaCO}_3$  fluxes measured by sediment traps are high (Ragueneau *et al.*, 2000), as are  $\text{CaCO}_3$  to organic carbon export ratios (Sarmiento *et al.*, 2002). The other two quantitatively significant open-ocean calcifiers, foraminifera and pteropods, seem to have an even more widespread distribution, with both organisms being successful at high latitudes near to the poles (Orr *et al.*, 2005). Coral reefs (excluding the non-symbiotic coldwater corals to be discussed below in the section on years 2000–2100) are largely restricted

to low latitude waters ( $<30^\circ$ ) with high  $\Omega$  values (Kleypas *et al.*, 1999b). The reasons for greater success of coccolithophores and corals away from the poles probably differ between the two groups, but are probably, in the case of coccolithophores, related to stratification.

Blooms of the most numerous coccolithophore species, *Emiliania huxleyi*, are found to occur only in highly stratified waters (Nanninga and Tyrrell, 1996; Tyrrell and Merico, 2004). The reason for this association is not completely understood, but may be tied to higher average light levels in shallow mixed layers (Nanninga and Tyrrell, 1996), to silicate exhaustion leading to diatom non-competitiveness (Egge and Aksnes, 1992), or to elevated  $\Omega$  levels following blooms (pH,  $[\text{CO}_3^{2-}]$  and  $\Omega$  are all driven to higher values when DIC is taken up by phytoplankton) (Merico *et al.*, 2006). The analysis of a large dataset of measurements of bulk calcification and silicification rates at sea shows that calcification is relatively more restricted to surface waters than is silicification, and that calcification rate seems to be light dependent (Poulton *et al.*, 2006).

Whatever the underlying reason, there are reasons to believe that increased warming of sub-polar and polar oceans, leading to decreased ice cover, earlier and stronger stratification and longer phytoplankton “growing seasons”, is likely to open up new habitats for potential colonisation by coccolithophores. An increasing frequency of coccolithophore blooms has already been documented in the Barents Sea, part of the Arctic Ocean (Smyth *et al.*, 2004).

A further, and even less direct, potential consequence of stratification on global calcification rates, is through the tendency of stratification to inhibit vertical nutrient fluxes. Because surface waters are nutrient poor and deeper waters nutrient rich, and stratification impedes their exchange, increased stratification in the future could negatively impact on the vertical upwards supply of nutrients to surface waters. This supply is the controlling factor for global phytoplankton growth, and the overall ocean fertility would therefore seem likely to decline as a result of this process, although increased storminess in a warmer climate could potentially counterbalance this effect. If overall global primary productivity declines, calcifying organisms are likely to decline in number.

Corals, conversely, thrive in nutrient poor locations and may therefore be favoured by a decrease in oceanic nutrients, if this is not outweighed by increased nutrient fluxes to the coastal zone associated with the application of fertilisers to agricultural land. The latter effect may, in some locations, tip the competitive balance away from corals towards seaweeds, which prosper at higher nutrients.

## SEA LEVEL RISE

The process by which coral atolls are built up on subsiding volcanic islands depends on the ability of coral reefs to rapidly grow upwards and generate large amounts of coral debris as they start to become submerged. To maintain an atoll against subsidence, the reefs need to grow upwards more rapidly than the rate at which the atoll platform is sinking. If the reefs sink too far, the lack of light will kill their photosynthetic symbionts and therefore the reefs as a whole. Similarly, if sea levels are rising, then the rate of accumulation of coral rubble on the atoll platform has to occur at a sufficient rate to allow the atoll level to keep pace with the rising sea level. Coral reefs around the world today, as seen on numerous atolls dotting the low-latitude oceans, coped with  $\sim 120$  m of sea level rise following the end of the last ice age. Reef-forming corals are found in the top 30 m or so of the water column. “Drowned reefs” are occasionally observed at greater water depths, perhaps with a scanty covering of corals insufficient for reef building.

Sea level rise could have a 2-fold beneficial effect on coral reefs, providing that acidification and bleaching events do not prevent them from exploiting it.

### Increased room in the vertical dimension

First, the rise in water level over the top of existing coral reefs is likely to stimulate them to extra growth and extra calcium carbonate accumulation (Holligan and Robertson, 1996). Under stable sea level, their growth rate must be inhibited once they grow so high as to start sticking out above the low-water mark (sea level at low tide). In the future, as formerly “topped-out” reefs now find themselves under greater amounts of water, their growth rate is likely to be reinvigorated.

### Increased room in the horizontal dimension

Secondly, flooding of large areas of what is currently low-lying land, because of sea level rise, will increase the area of shallow ocean and thereby increase the potential accommodation space for coral reefs (Holligan and Robertson, 1996). The flooding of continental shelves following the 120 m rise in sea level at the end of the last ice age is thought to have opened up new habitats for corals (Opdyke and Walker, 1992); future sea level rise should do likewise, if corals are still around to take advantage.

Sedimentary evidence of the past sea levels indicates that sea level was  $\sim 120$  m lower than today at the depth of the last ice age ( $\sim 20\,000$  years ago), and

reached a maximum of  $\sim 5$  m higher than today at the height of the last (particularly warm) interglacial (about 125 000 years ago). It is estimated from tide gauge and satellite data that sea level rose by  $\sim 0.2$  m during the twentieth century (IPCC, 2007).

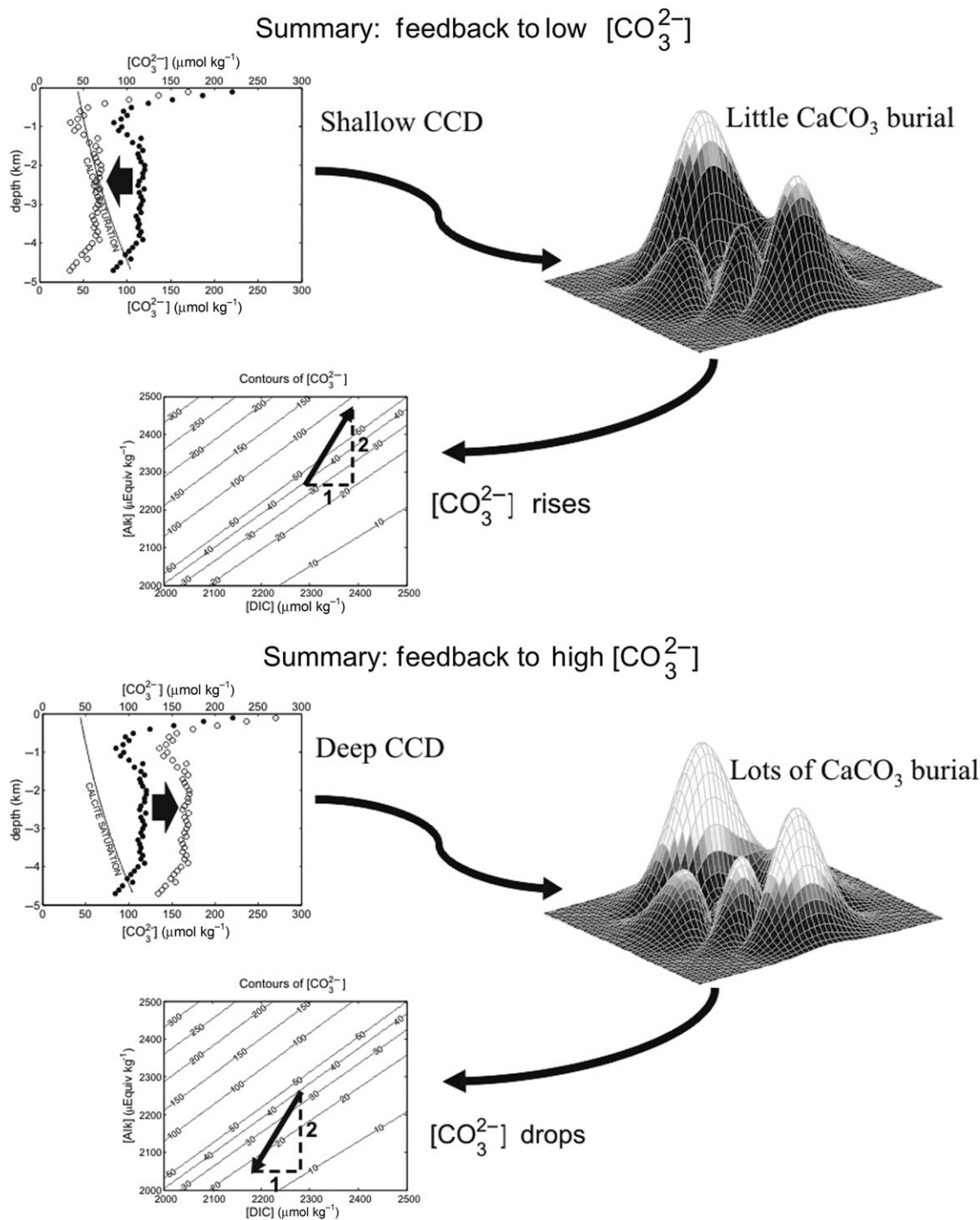
Sea level is predicted to rise by somewhere between 0.2 and 0.8 m over the course of this century (IPCC, 2007). This range of predictions assumes that ice will melt gradually without any sudden changes; collapse of the West Antarctic Ice Sheet, for instance, if it were to occur, would raise sea level by  $\sim 5$  m. The large majority of ice in the ice sheets of Greenland and Antarctica lies at such altitude (and therefore such cold) that rapid melting seems unlikely. Hundreds or thousands of years into the future, however, these ice sheets could also thaw; complete melting of the Greenland ice sheet would engender  $\sim 7$  m of sea level rise, and complete melting of the Antarctic ice sheet  $\sim 60$  m of sea level rise.

Even after global temperatures stabilize, sea levels will continue to rise for many centuries. This is in part because of the long time that it takes for the amount of ice on Earth to come into equilibrium with a change in temperature, and in part because of the slow rate of overturning of the deep ocean (it takes in the order of 1000 years for the whole of the deep ocean to cycle through the surface). Because seawater expands as it warms, thermal expansion of parts of the deep ocean that have not been exposed to global warming will bring about an additional 0.3–0.8 m of sea level rise by year 2300 (IPCC, 2007), even if there were to be no further melting.

## CARBONATE COMPENSATION

We move now from direct anthropogenic effects to induced feedbacks. The ocean has an inbuilt negative feedback process for stabilising ocean  $\Omega$ , albeit one that takes many millennia to counteract perturbations. This process is called carbonate compensation (Broecker and Peng, 1987; Sundquist, 1990; Zeebe and Westbroeck, 2003), which involves automatic adjustment of *lysoclines* in response to chemistry of the ocean interior. A *lysocline* defines the depth at which a form of calcium carbonate starts to dissolve on the seabed. Above the calcite *lysocline*, nearly all of the calcite that falls to the seafloor accumulates in the sediments. Below the calcite *lysocline*, the waters are corrosive to it, leading to the dissolution of some or all of the calcite out of the sediments.

As illustrated in Fig. 2, carbonate compensation involves the adjustment of the calcite and aragonite



**Fig. 2.** The carbonate compensation feedback. The top panel shows the feedback to lower  $[\text{CO}_3^{2-}]$ : when carbonate ion falls below equilibrium levels, the vertical profile of carbonate ion will intersect with the saturating carbonate ion at a shallower depth (upper left), the area of the seafloor over which  $\text{CaCO}_3$  is buried shrinks (right), and the resultant shortfall of burial compared with river inputs causes  $[\text{CO}_3^{2-}]$  to rise. The bottom panel shows the feedback to elevated  $[\text{CO}_3^{2-}]$ : when carbonate ion rises above equilibrium levels, the vertical profile of carbonate ion will intersect with the saturating carbonate ion deeper in the water column (upper left),  $\text{CaCO}_3$  starts to become buried over even larger areas of the seafloor (right), and the resultant excess of burial over river inputs causes  $[\text{CO}_3^{2-}]$  to fall.

lysoclines in the ocean so as to regulate  $\Omega$  (via  $[\text{CO}_3^{2-}]$ ). (Orr *et al.*, 2005). Because the vertical profile of the saturating value of  $[\text{CO}_3^{2-}]$  for each of aragonite and calcite does not change, the intersection point of the



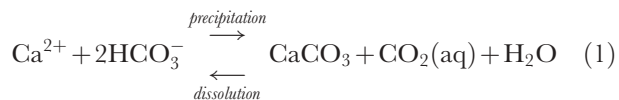
saturation and the actual  $[\text{CO}_3^{2-}]$  will move to shallower depths. This will cause a shallowing of the calcite and aragonite saturation horizons (depths at which  $\Omega = 1$ ). Jansen *et al.* (Jansen *et al.*, 2002) give the following equations for calculating the saturating carbonate ion concentration ( $[\text{CO}_3^{2-}]_c(z)$ ,  $\mu\text{mol kg}^{-1}$ ) as a function of depth ( $z$ , km):

$$[\text{CO}_3^{2-}]_c(z) = 88.7 \exp(0.189[z - 3.82]) \quad (\text{calcite})$$

$$[\text{CO}_3^{2-}]_c(z) = 117.5 \exp(0.176[z - 3.06]) \quad (\text{aragonite}).$$

The depth of the saturation horizon is obtained by finding the value of  $z$  (the depth) at which  $[\text{CO}_3^{2-}]_c(z)$  is the same as the actual deep ocean  $[\text{CO}_3^{2-}]$ . Although the lysocline does not lie exactly at the saturation horizon, the two are interlinked. These equations emphasize the sensitivity of saturation horizons to deep water  $[\text{CO}_3^{2-}]$ . For instance, even only a 25% drop in average deep water  $[\text{CO}_3^{2-}]$ , taking it down from  $\sim 90 \mu\text{mol kg}^{-1}$  today (Broecker, 2003) to  $67.5 \mu\text{mol kg}^{-1}$  in the future would, according to the equations, cause the global calcite saturation horizon to shallow from an average depth of 4 km to 2.2 km. Much larger decreases in deep  $[\text{CO}_3^{2-}]$  are in fact forecast (see the previous section on ocean acidification). A model of ocean acidification predicts, under almost all emissions scenarios, that the average calcite lysocline depth will be shallower than 0.5 km by the year 2300 (Caldeira and Wickett, 2005).

Shallowing of the lysoclines will increase global dissolution and decrease burial. This will tend to oppose the low  $[\text{CO}_3^{2-}]$  values of an acid ocean, by driving an imbalance between the riverine input of dissolved calcium and carbon and their removal in buried calcium carbonate. The chemical equation for calcification and/or dissolution is given by



Dissolution of 1 mole of  $\text{CaCO}_3$  (or an equivalent reduction in  $\text{CaCO}_3$  burial) therefore leads to addition of 1 mole of DIC to seawater, together with a simultaneous addition of 2 moles (charge equivalents) of alkalinity. When the carbonate chemistry is calculated out, these changes to DIC and alkalinity induce an increase in the carbonate ion concentration, completing the negative feedback. This increase in ocean carbonate ion concentration will continue until the original, steady-state, carbonate ion concentration is re-attained. The e-folding

response time (the time for the deviation of a variable from its equilibrium value to decrease by a factor of  $e$ ) for carbonate compensation has variously been estimated at between 6 and 14 ky (Sundquist, 1986; Archer *et al.*, 1997, 1998; Zeebe and Westbroek, 2003).

Carbonate compensation as described here is brought about purely by changes in lysocline depths in response to changes in  $\Omega$ . There are likely to be several other changes to oceanic  $\text{CaCO}_3$  cycling that will also contribute to restoration of  $\Omega$  to its equilibrium value:

- (1) production of  $\text{CaCO}_3$  may well decline in a more acidic surface ocean, as discussed above, leading to a lighter rain of particles out of the surface ocean and hence to a lighter rain to the sea floor;
- (2)  $\text{CaCO}_3$  that fell to the seafloor in pre-industrial times, before any ocean acidification, may also be affected. As this  $\text{CaCO}_3$ , lying at or near to the surface of the sediments, comes into contact with increasingly acidic deep bottom waters, it is likely that some of it, finding itself now lying beneath a suddenly shallower lysocline, will be chemically eroded via dissolution.
- (3) the combination of warming, higher  $\text{CO}_2$  and increased rainfall in a warmer world may also hasten the rate of weathering of limestone, dolomite and chalk rocks on land, leading to an increased supply rate of calcium and carbon to the oceans.

## FUTURE CaCO<sub>3</sub> CYCLING THROUGH TIME, AND CONSEQUENCES FOR CLIMATE

### Years 2000–2100: acidification and warming

This interval will be characterized by increasing severity of ocean acidification and global warming. Warming is not predicted to greatly affect sea level in this interval. Lysocline depths will shallow noticeably in some locations, but carbonate compensation will not be significant within this short timescale. Even dramatic changes to  $\text{CaCO}_3$  cycling will have only modest consequences for climate in this timeframe.

Within the next 100 years, acidification will be mostly confined to the top few hundred metres of the ocean. Average global surface ocean pH is projected to decline by between 0.14 and 0.35 units between year 2000 and year 2100, based on IPCC emissions scenarios (IPCC, 2007). Although some anthropogenic  $\text{CO}_2$  has already entered the deep ocean (Sabine *et al.*, 2004), this is

mostly in the North Atlantic and the amount involved is small relative to surface ocean uptake. For instance, ~50% of anthropogenic CO<sub>2</sub> is held in the top 400 m (Sabine *et al.*, 2004), despite this making up only about 10% of the ocean volume. Most of the deep waters, especially those >1 km deep, have yet to receive any anthropogenic CO<sub>2</sub> (Sabine *et al.*, 2004). Changes to CaCO<sub>3</sub> cycling during the next century will therefore be largely concentrated in surface waters.

Coral reefs will most likely be strongly hit by the declining surface pH, through the associated depression of  $\Omega_{\text{arag}}$  and hence calcification rate. Whereas the large majority of coral reefs inhabited, in pre-industrial times, waters in which  $\Omega_{\text{arag}} > 4$  (Guinotte *et al.*, 2003), by the time atmospheric CO<sub>2</sub> has doubled with respect to the pre-industrial value (i.e. when it has reached 560 ppm, which could be by year 2050 or even earlier), models predict that almost all of these locations will be experiencing  $\Omega_{\text{arag}} < 4$  (Kleypas *et al.*, 2001; Guinotte *et al.*, 2003). By the end of this century, nearly all corals, if they persist that long, will be inhabiting waters where  $\Omega_{\text{arag}} < 3$  (Guinotte *et al.*, 2003; Kleypas *et al.*, 1999a).

Deepwater corals may also be affected. Deepwater scleractinian coral communities lying at a few hundred metres water depth will be exposed to increasing acidity over the coming decades. Most deepwater coral communities discovered so far are in the North Atlantic, where the aragonite saturation horizon is much deeper (>2000 m) than in the North Pacific (50–600 m) (Guinotte *et al.*, 2006). This is unfortunate because, as just discussed, the North Atlantic is also the place where anthropogenic CO<sub>2</sub> is most rapidly invading the deep ocean. Calculations suggest that ~70% of deepwater coral locations will cross the boundary from supersaturation to undersaturation (with respect to aragonite) by the end of the twentieth century (Guinotte *et al.*, 2006).

Global warming will lead to an increase in the global average temperature of surface air of between 1 and 6°C by the year 2100, depending on which of the IPCC SRES scenarios turns out to be closest to reality (IPCC, 2007). Although there is some delay to global warming because of the large heat capacity of the ocean (meaning that it takes time before increases in atmospheric CO<sub>2</sub> fully impact on global temperatures), nevertheless SST-related impacts such as coral bleaching and ocean stratification are likely to be considerable within the course of the next century.

It is predicted that sea level will rise by between 0.2 and 0.8 m during the next century, depending on future emissions of CO<sub>2</sub> and also on whether elevated temperatures increase the rate of flow of glaciers (IPCC, 2007). Major rises in sea level due to melting of ice sheets are predicted to take much longer. This assumes

that ice will melt gradually without any sudden changes; collapse of the West Antarctic Ice Sheet, for instance, would raise sea level by ~5 m. Although thermal expansion of seawater is instantaneous (as soon as it is heated), only a small fraction of deep waters will come to the surface to be heated by the end of the century.

Although there is some uncertainty as to the impacts on CaCO<sub>3</sub> cycling, even for this shortest-time future prediction, it is nevertheless possible to look at “what if?” scenarios to investigate, using models, the knock on consequences if global calcification and the strength of the inorganic carbon pump were either to strongly plummet (more likely) or to be dramatically accelerated (less likely). Four studies have addressed this issue so far. Heinze *et al.* (Heinze *et al.*, 2004) used the HAMOCC biogeochemical ocean general circulation model (GCM) and forced the CaCO<sub>3</sub> export flux out of surface waters to be equal to the pre-industrial value multiplied by  $[1 - 0.012 (\text{CO}_2^{\text{actual}} - \text{CO}_2^{\text{pre-industrial}})]$ , leading to 50% decrease in CaCO<sub>3</sub> export flux by year 2250. Under this lower future rate of CaCO<sub>3</sub> production in surface waters, the difference in the year 2250 atmospheric pCO<sub>2</sub>, compared to the control run with constant CaCO<sub>3</sub> export flux, was a decrease of only ~10 ppm.

Chuck *et al.* (Chuck *et al.*, 2005) used three models (two box models and a GCM) to investigate a range of future scenarios, one of which was +50% calcification rate over the next 100 years, another of which was –50% calcification rate over the next 100 years. In both cases, in all three models, the results suggested minor impacts by the year 2100: between +4 and +10 ppm for increased calcification and –4 to –10 ppm for diminished calcification. Gehlen *et al.* (Gehlen *et al.*, 2007), using the PISCES ocean GCM, forced lower calcification rates in response to acidification over a period of 140 years. This resulted in an extra amount of only 5.9 Gt C being taken up by the ocean, in comparison with total emissions of 3230 Gt C during the run. Klepper and de Haan (Klepper and Dehaan, 1995) made calcification rate proportional to saturation state in a 2D global ocean model and found that the resulting decline in calcification led to a –19 ppm change in atmospheric CO<sub>2</sub> by year 2100. These numbers compare with the projected rises in atmospheric CO<sub>2</sub> over this period of several hundred parts per million (IPCC, 2007) and a sensitivity to processes on land of up to 250 ppm (Cox *et al.*, 2000).

The impact of altered calcification on atmospheric pCO<sub>2</sub> levels and climate is therefore small on a centennial timescale, and similar results have been obtained in model runs when the possible ballast effect (Armstrong *et al.*, 2002; Klaas and Archer, 2002) of

CaCO<sub>3</sub> export on organic carbon export is also included (Barker *et al.*, 2003; Heinze, 2004). No model runs have yet calculated the impact of smaller DMS emissions on climate, if coccolithophores become more scarce in future. The radiative forcing impact of coccolith light scattering on planetary albedo and therefore on the global energy balance is rather small, a radiative forcing of only about 0.22 W m<sup>-2</sup> (Tyrrell *et al.*, 1999).

### Years 2100–2700: greatest severity of surface acidification and warming

If emissions continue increasing such that fossil fuel reserves run out in a few centuries time, as often predicted, then this interval will be characterized by the greatest severity of surface ocean acidification and global warming. As acidification reaches the deep ocean, the CCD will rise sharply, but carbonate compensation is likely to be only a secondary influence within this timescale. Large increases in sea level are likely as sea level slowly catches up with the changes in temperature. Changes in CaCO<sub>3</sub> cycling will be of increasing significance to climate within this time interval, although still most likely of secondary importance compared to other factors.

The interval of minimum surface seawater pH is predicted to occur between about year 2300 and year 2700, after which it will start to increase again, according to the study by Caldeira and Wickett (Caldeira and Wickett, 2003). Although some of the constants of carbonate chemistry are quite sensitive to temperature, the net direct effect of global warming on ocean pH will not be great (Cao *et al.*, 2007). Global warming impacts on saturation states, however, will be more important, buffering fossil fuel-driven decreases by ~15% (McNeil and Matear, 2007). Although largely insensitive to temperature, the exact times and magnitudes of pH decreases will obviously be highly sensitive, however, to the exact pattern of future CO<sub>2</sub> emissions and sequestration as well as to whether, and if so how, global warming affects ocean circulation. The rate of acidification of deep waters could be strongly affected if increased stratification (complete or partial shut-down of the circulation) retards the penetration of anthropogenic CO<sub>2</sub> into the deep ocean. If circulation patterns are not strongly affected and if high atmospheric CO<sub>2</sub> concentrations are realized then it seems inevitable that the calcite and aragonite lysoclines will both shallow to within a few hundred metres of the ocean surface (Caldeira and Wickett, 2005), even under moderate emissions scenarios, thus bringing a temporary end to most CaCO<sub>3</sub> burial in the deep ocean. This will at least

be the case in most basins by year 2700, although the oldest deep waters, for instance in the North Pacific, should still remain unaltered by acidification.

Sea level will rise by at least several metres. Even after global temperatures stabilize, levels will continue to rise for many centuries. This is in part because of the long time that it takes for the amount of ice on Earth to come into equilibrium with a change in temperature, and in part because of the slow rate of overturning of the deep ocean (it takes order 1000 years for the whole of the deep ocean to cycle through the surface). Because seawater expands as it warms, thermal expansion of parts of the deep ocean that have not as yet been exposed to global warming will by itself bring about an additional 0.3–0.8 m of sea level rise by year 2300 (IPCC, 2007). If elevated global temperatures are sustained throughout this period (e.g. 1°C or more than the 1990s) then it is probable that there will be at least partial deglaciation of the Greenland ice sheet and areas of ice on Antarctica, contributing 4–6 m or more to sea level rise (IPCC, 2007). Complete disintegration of the West Antarctic ice sheet would raise sea level by ~5 m, and complete melting of the Greenland ice sheet by ~7 m (IPCC, 2007).

If corals prove somehow able to adapt to and cope with the severe acidification and warming, then the large increase in sea level could favour them. The increase in water level over and above the top of existing reefs should promote extra growth, and more habitats should become available to coral colonization, as large areas of low-lying land are inundated. Likewise, if planktonic calcifiers cope with the acidification, then additional habitats are likely to have opened up to them, in polar waters which will be warmer, more stratified and with longer seasons favourable for phytoplankton growth. Future saturation states will, as today, be lowest towards the poles (Orr *et al.*, 2005), however, which might prohibit future calcifier success there.

If, as anticipated, coral calcification declines rapidly in the future, then this will make a considerable difference to the carbon cycle of the shallow waters of the coastal ocean. Model calculations suggest that a combination of inhibited calcification and stimulated photosynthesis (due to increased nutrients coming down rivers) will change the coastal zone from being a net source of CO<sub>2</sub> as at present, to a net sink by the year 2300 (Andersson *et al.*, 2006). The impact will not be so great at the global scale. Heinze *et al.*'s (Heinze *et al.*, 2005) model calculations, which include a 50% decrease in CaCO<sub>3</sub> export flux by year 2250, suggest a decrease in atmospheric CO<sub>2</sub> compared with constant calcification of only ~10 ppm.

### Beyond year 2700: recovery, of a sort

This interval will be characterized by recovery from the perturbation imposed by the rapid burst of fossil fuel emissions, assuming that they have all, or mostly, been burnt prior to year 2700. The oldest deep waters will at last come to the surface and become exposed to elevated  $\text{CO}_2$ , absorbing some of it and thereby removing excess  $\text{CO}_2$  from the atmosphere and the surface ocean. This will start a recovery from the greatest severities of global warming and surface ocean acidification. The next stage of the recovery, involving carbonate compensation, will be instigated by the acidification of the deep ocean. The recovery process will not, however, return the Earth system to the same state as before. The new state that the system will settle towards will consist of an ocean containing perhaps twice as much carbon as before, an atmosphere with more carbon dioxide, and a warmer climate. A fortunate side-effect is likely to be protection against ice ages, such that the next few ice ages could be avoided.  $\text{CaCO}_3$  cycling will therefore be of crucial importance over this longest timescale.

The large majority of ice in the ice sheets of Greenland and Antarctica lies at such altitude (and therefore such cold) that rapid melting seems unlikely. Hundreds and thousands of years into the future, however, under a persistently warmer climate, the major ice sheets may also thaw. Complete melting of the Greenland ice sheet would cause  $\sim 7$  m of sea level rise, and complete melting of the Antarctic ice sheet would cause  $\sim 60$  m of sea level rise. The resultant flooding of low-lying land would bring about a shift in the disposition of global surface area between ocean and land. The area of shelf seas (defined as seas with water depths  $\leq 200$  m) would increase compared with today, leading to a greater area of habitat potentially suitable for corals, for those species that survive the earlier acidification and warming.

The impact of decreased calcification on atmospheric  $\text{CO}_2$ , less important in previous periods, becomes more important as time progresses; by year 3000, according to model calculations (Ridgwell *et al.*, 2007), a decrease in marine  $\text{CaCO}_3$  production will drive a 4–13% decrease in the atmospheric  $\text{CO}_2$  content compared with runs in which calcification is unaffected. Although the initial effect of decreased calcification and increased dissolution is to lower atmospheric  $\text{CO}_2$ , its eventual effect is to prevent atmospheric  $\text{CO}_2$  from returning back down to pre-industrial levels.

The time taken for one cycle of the overturning circulation of the deep ocean to be completed is of order 1000 years. Acidification of the whole of the deep sea should therefore be more or less complete by about

year 3000, as long as warming does not shut down the circulation. This ties in with model calculations of large decreases in deep-sea pH ( $-0.4$  units) past year 2800 (Caldeira and Wickett, 2003).

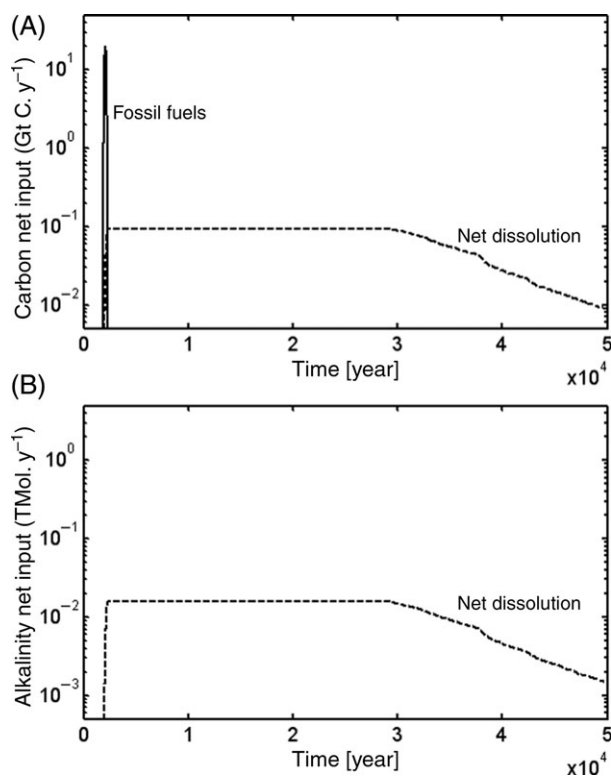
This deep-sea acidification will set in train the carbonate compensation negative feedback described earlier in the section of the same name. For all emissions scenarios with total emissions of between 1250 and 20 000 Gt C, and for all scenarios leading to stabilization of atmospheric  $\text{CO}_2$  at  $\geq 550$  ppm, the average depth of the calcite lysocline in the oceans will shallow to within a few hundred metres of the surface (Caldeira and Wickett, 2005), compared with today where it lies at several kilometres depth in all ocean basins. It is calculated that this shift will be largely completed by year 2300 (Caldeira and Wickett, 2005).

The  $e$ -folding time of carbonate compensation, when calculated as the time taken for the imbalance between river inputs and  $\text{CaCO}_3$  burial to restore  $\Omega$ , is of order 10 000 years. Compensation could occur much more quickly. It may be that pre-existing  $\text{CaCO}_3$ , created before the industrial revolution, may also be dissolved away by anthropogenic  $\text{CO}_2$ . Dissolution need not be constrained to act solely on  $\text{CaCO}_3$  created after the ocean has become more acid. Broecker (Broecker, 2003) argues that bioturbation (the stirring of the top layer of marine sediments by burrowing organisms) will bring enough old  $\text{CaCO}_3$  into contact with acidified deep water to “neutralize” all fossil fuel  $\text{CO}_2$ . Therefore, it is not inconceivable that, instead of taking tens of thousands of years, carbonate compensation could be accomplished more rapidly (see also Archer *et al.*, 1998 for another calculation of the impact of  $\text{CaCO}_3$  “burn-down”). Two other feedbacks could also accelerate carbonate compensation: (i) increased weathering of limestones in a warmer climate and (ii) decreased  $\text{CaCO}_3$  flux out of the surface layer, due to acidification.

Although the timescale of restoration of  $\Omega$  is difficult to be sure of, the end-point of the process is better understood.

Carbonate compensation will restore the ocean towards balanced  $\text{CaCO}_3$  cycling (inputs to the ocean as a whole equal to outputs), which will most likely be accomplished once the ocean has returned to a value of  $\Omega$  close to the pre-industrial value. But in so doing, it will amplify other aspects of the fossil fuel perturbation. The excess carbon added via fossil fuels will, for instance, be supplemented (rather than counteracted) by the feedback, as shown in Fig. 3A. Even more carbon will be introduced, primarily by (i) additional dissolution of old seafloor  $\text{CaCO}_3$ , and (ii) large-scale prevention of  $\text{CaCO}_3$  burial (shallow CCD) while river inputs continue unimpeded. At the same time as exacerbating the





**Fig. 3.** Excess DIC and alkalinity fluxes, over and above those making up the normal, equilibrium balance of fluxes: **(A)** additional DIC fluxes. Solid line shows the addition of dissolved inorganic carbon (DIC) due to invasion of fossil fuel CO<sub>2</sub> into the ocean. Dashed line shows the net addition of DIC due to the carbonate compensation feedback, as the rising of the CCD towards the surface brings about an increase in dissolution and a decrease in burial. As long as river inputs of dissolved carbon do not decrease, the decline in burial leads to a net input of DIC. **(B)** Additional alkalinity fluxes. Invasion of uncharged CO<sub>2</sub> molecules (fossil fuel CO<sub>2</sub>) has no direct impact on alkalinity. The carbonate compensation feedback, on the other hand, will strongly perturb alkalinity because river input of charged calcium and bicarbonate ions will continue, whereas burial output of solid CaCO<sub>3</sub> will strongly decline. All fluxes in units of Gt C year<sup>-1</sup>. Note the log-scale on the y-axis.

excess carbon, the changes in CaCO<sub>3</sub> cycling will add alkalinity (Fig. 3B), which was not initially perturbed by diffusion of CO<sub>2</sub> across the sea surface.

Such predictions could be confounded, however, if human intervention through geo-engineering projects leads to mitigation of CO<sub>2</sub> rise through means other than those involving CaCO<sub>3</sub>. If large amounts of CO<sub>2</sub> are eventually pumped back underground, for instance, then ocean acidification and consequent carbonate compensation will be diminished.

In terms of climate, the most interesting carbonate system variable is atmospheric CO<sub>2</sub>. Many different models (Archer *et al.*, 1998; Sundquist, 1986, 1990; Caldeira and Wickett, 2003; Lenton and Britton, 2006; Tyrrell *et al.*, 2007) concur in predicting extremely long-lasting perturbations to atmospheric CO<sub>2</sub>, in the absence

of large-scale CO<sub>2</sub> sequestration underground. CO<sub>2</sub> in the models does not fall back to pre-industrial levels in the millennia following fossil fuels. These models all show a long-term residual of excess CO<sub>2</sub> in the atmosphere, amounting to something like 8–10% of total cumulative emissions. The reasons for the post-fossil fuel recovery settling back towards higher CO<sub>2</sub> have been examined by Tyrrell *et al.* (Tyrrell *et al.*, 2007).

The climate implications of the excess CO<sub>2</sub> are considerable. Archer and Ganopolski (Archer and Ganopolski, 2005) have calculated that the long-term global warming is likely to lead to skipping of the next glacial cycle (no next ice age), and, if most of the recoverable fossil fuels are eventually burnt, to a possible omission of the next five ice ages.

## CONCLUSIONS

This paper has taken an earlier paper (Holligan and Robertson, 1996) as inspiration, and attempted to update their discussion of anthropogenic impacts on CaCO<sub>3</sub> cycling in the light of more recent work, in particular that on biological consequences of ocean acidification and on long-term climatic impacts of ocean acidification.

At least some of the many CaCO<sub>3</sub>-using marine organisms are likely to be strongly affected by ocean acidification, with potential for weakening of the ocean CaCO<sub>3</sub> pump. The exact outcome will depend on future emissions, the exact effects of acidification in conjunction with simultaneous global warming and other changes, and whether a reduction in shell/skeleton integrity will lead to populations being severely predated upon. The importance of all of this for climate is not likely to be significant over the next few centuries, but changes in CaCO<sub>3</sub> cycling will eventually come to play a dominant role in the recovery from peak CO<sub>2</sub> and global warming. Intricacies of the carbonate compensation recovery process mean that it may impart protection against future ice ages.

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