

DECREASING ATMOSPHERE CO₂ BY INCREASING OCEAN ALKALINITY

THE OCEAN DIMENSION: WOULD THE CONCEPT WORK AND WHAT WOULD BE THE ENVIRONMENTAL CONSEQUENCES?

A report based on literature sources and simple calculations

Prof. Gideon Henderson
Dr. Ros Rickaby
Dr. Heather Bouman

University of Oxford, Department of Earth Sciences
and
The James Martin 21st Century Ocean Institute

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Executive Summary

This report considers the implications to ocean chemistry and biology of adding $\text{Ca}(\text{OH})_2$ to surface seawater to reduce atmospheric CO_2 (the “*Cquestrate*” scheme).

Addition of 1 mole of $\text{Ca}(\text{OH})_2$ causes uptake from the atmosphere of between 1.6 (warm water) and 1.8 (cold water) moles of CO_2 . This addition also increases pH, total dissolved inorganic carbon (DIC), and the calcium-carbonate saturation of seawater.

In the extreme case, where 50% of fossil fuel CO_2 emissions are sequestered with this scheme, 41 Gtonnes per year of calcite must be calcined and added to seawater. This is equivalent to ≈ 40 times the annual mining of calcite in the US, and to ≈ 43 times the riverine input of Ca^{2+} . If spread uniformly in the surface ocean this leads to small increases of ocean Ca^{2+} (0.2% per year), and alkalinity (2% per year).

Application of the scheme would be limited by the level of saturation of seawater at which inorganic CaCO_3 precipitation occurs, because such precipitation would reverse the initial effect of alkalinity addition. The saturation state is increased by adding Ca^{2+} and by the resulting increase in CO_3^{2-} . The safe level of saturation to avoid CaCO_3 precipitation is not well known. If $\text{Ca}(\text{OH})_2$ is spread uniformly in the surface ocean this limit will not be reached, but addition at selected locations will lead to significant increases in saturation. The rate at which $\text{Ca}(\text{OH})_2$ can be added at such locations without CaCO_3 precipitation would need to be assessed using laboratory saturation experiments, and with 3D ocean models that mimic ocean mixing and circulation. It is likely that a significant fraction of the surface ocean will need to be receive alkalinity through mixing to avoid excessive changes in saturation.

An increase in biological production of CaCO_3 is expected due to higher saturation, even at saturation levels below that required for inorganic CaCO_3 precipitation. This represents a negative feedback on the initial addition of alkalinity but, because the biogenic formation of CaCO_3 is small compared to the fluxes of alkalinity required to make a significant change to the carbon cycle, this feedback is expected to be relatively minor.

On long timescales (>100 years) increased alkalinity will be advected to the deep ocean and will increase the rate at which CaCO_3 is removed from seawater. This is a partial negative feedback on the initial addition of alkalinity but, because it is driven by ocean mixing which also exposes low- CO_2 deep waters to the atmosphere, it occurs on the same timescale that fossil-fuel CO_2 is adsorbed by simple solubility in seawater.

Marine species may respond to increases in four parameters as a result of the scheme: saturation, pCO_2 , DIC, and pH. There is presently insufficient research to fully assess the impact of these changes. If alkalinity addition is done at a level to only reverse ocean acidification, the net result is expected to be advantageous to marine ecosystems. Greater changes, such as those at the point of $\text{Ca}(\text{OH})_2$ release, will have a mixed effect dependent on which of the four environmental parameters are most important for the metabolism of each species. A safe level of pH change of <0.2 has been suggested by previous reports assessing biological responses to changing pH. Such a level of change places similar constraints on the required dispersal of alkalinity as does the likely saturation constraint.

Previously suggested schemes involving changing ocean alkalinity generally have the same seawater saturation constraint encountered by the *Cquestrate* scheme.

Addition of alkalinity would be best pursued in regions of high winds, fast circulation, and thick mixed-layer depth to maximize dispersal of alkalinity. Cold water is also favoured. The Southern Ocean fits these criteria well.

Overall, there appears to be no serious flaw in the oceanic aspects of the *Cquestrate* scheme, but further work is required to assess the maximum allowable saturation state of the oceans, the delivery mechanism and ocean dispersal of the alkalinity, and the biological response to this alkalinity addition.

1. Scope and limits of this report

The report describes the oceanic implications of adding slaked lime – Ca(OH)_2 – to the oceans to cause a reduction in atmospheric CO_2 and thereby mitigate global warming. This process is referred to here as the *Cquestrate* scheme, as detailed at <http://www.cquestrate.com/>.

In particular, this report addresses

- the immediate and long-term whole-ocean inorganic response to addition of sufficient Ca(OH)_2 to counteract anthropogenic CO_2 release
- a preliminary assessment of the local inorganic response to focused Ca(OH)_2 release at various rates
- an assessment of the likely biological implications of Ca(OH)_2 addition
- some preliminary comments on particularly good or bad regions for the release of Ca(OH)_2 from an ocean chemistry and biology point of view
- an indication of further work that would be required to more completely assess the workability and environmental impacts of ocean Ca(OH)_2 addition

The report is informed by a literature survey, by simple calculations, by limited ocean modelling, and by the expert opinion of the three authors.

The report focuses on the ocean component of the concept only, and does not address the land-based environmental impacts. It also does not address any of the engineering issues related to the concept such as mining, calcining, or distributing to the ocean of the calcium products.

The report does not deal with legal or regulatory issues relating to Ca(OH)_2 addition to the oceans, nor with the economic or overall carbon budget implications of the complete *Cquestrate* scheme.

This report also does not deal with the general desirability of pursuing this or any other large scale geoengineering procedure to mitigate global warming. With today's level of environmental understanding, such schemes do not remove the present imperative to reduce emissions of CO_2 , and require significant further research and investigation before their feasibility can be appropriately assessed.

2. Simple ocean chemistry of alkalinity addition

Unlike many atmospheric gases (e.g. N_2 , O_2), CO_2 doesn't simply dissolve in seawater, but reacts with it to form the weak acid, carbonic acid (e.g. ZEEBE and WOLF-GLADROW, 2001):



This dissociates to the bicarbonate and carbonate ions:



These reactions enable water to adsorb significantly more CO_2 than other gases such that the oceans contain 60 times more carbon than the (pre-anthropogenic) atmosphere.

Only the dissolved gas species CO_2^g exchanges with the atmosphere, so the concentration of this species sets the exchange of carbon between the atmosphere and the surface ocean.

$$\alpha = \text{CO}_2^{\text{g}} / \text{pCO}_2$$

Eq. 4

(where α is a constant at a given temperature, CO_2^{g} is the dissolved CO_2 concentration, and pCO_2 the atmospheric partial pressure)

If CO_2^{g} is high, carbon moves from the ocean to the atmosphere, if low, from the atmosphere to the ocean. CO_2^{g} is, in turn, controlled by the pH of seawater. As pH increases, CO_2^{g} decreases (Fig 1) so that the oceans tend to adsorb more carbon to re-establish equilibrium.

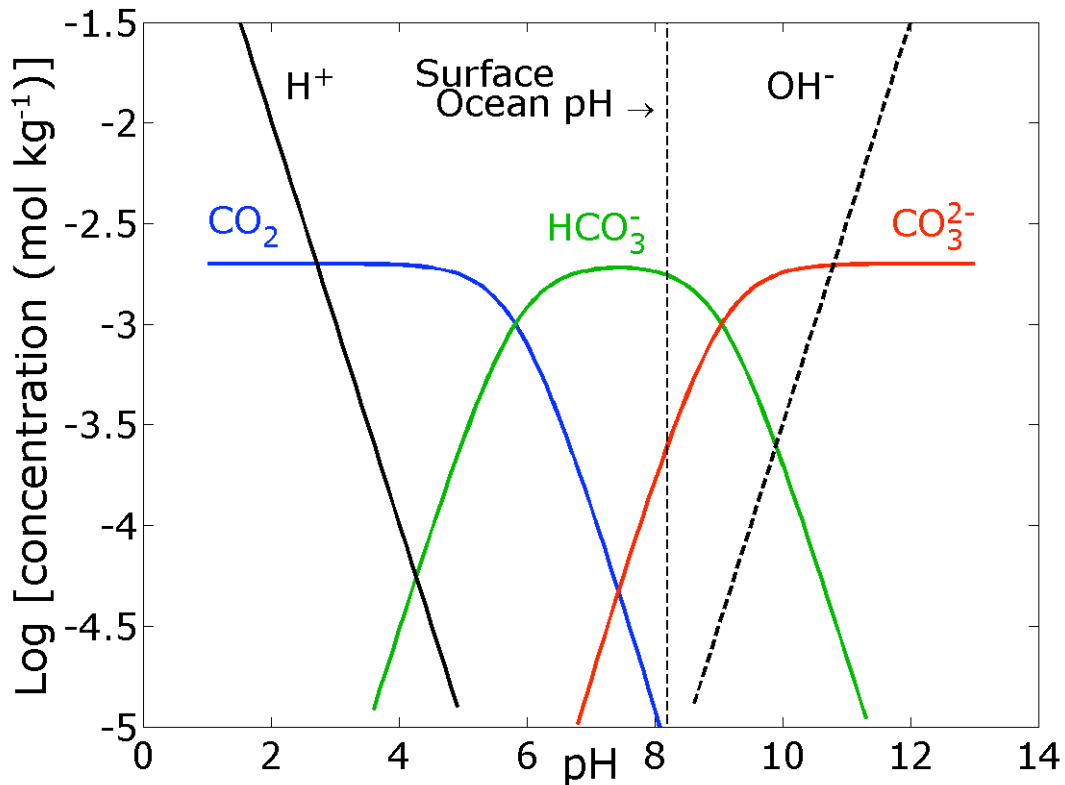


Fig 1: Concentrations of the various carbon species found in seawater with varying pH. Typical seawater pH is shown by the vertical dashed line. Increasing pH leads to a decrease in CO_2 , and an increase in CO_3^{2-} .

In the proposed *Cquestrate* scheme, alkalinity is added to seawater as $\text{Ca}(\text{OH})_2$ (slacked lime) to increase the pH of seawater and cause uptake of atmospheric CO_2 . One mole of added $\text{Ca}(\text{OH})_2$ adds 2 moles of alkalinity, which can be thought of as neutralizing 2 moles of carbonic acid and therefore causing uptake of 2 moles of new atmospheric carbon to re-establish ocean-atmosphere equilibrium.

In more detail, however, some of this alkalinity neutralizes bicarbonate so somewhat less than 2 moles of carbonic acid are neutralized (and less than 2 moles of carbon taken from the atmosphere). The sensitivity of carbon uptake for addition of one mole of $\text{Ca}(\text{OH})_2$ is dependent on the pH (Fig 2)

In turn, pH is dependent on temperature, with increased solubility of CO_2 at lower temperatures leading to lower pH. With today's range of ocean temperatures, sensitivity ranges from 1.57 to 1.81 (Fig 3). The average surface temperature of 17°C equates to a sensitivity of 1.7.

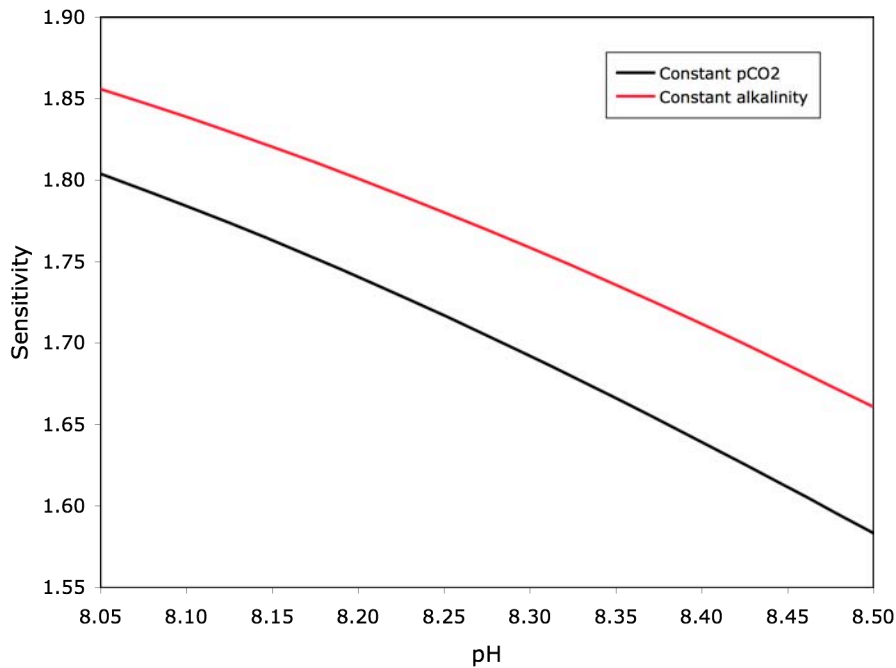


Fig 2: Sensitivity (= mole of atmospheric carbon uptake per mole of added $\text{Ca}(\text{OH})_2$). The red curve shows the sensitivity at a constant alkalinity of 2308 and is calculated by allowing pCO_2 to vary from 100 to 440 ppmV. The black curve shows sensitivity at a constant pCO_2 of 390 ppmV and is calculated by allowing temperature to vary between 0 and 30 °C. The black curve is the more realistic for consideration of the modern ocean. Values calculated using the equilibrium coefficients of DICKSON and MILLERO 1987 and the CO_2Sys programme of LEWIS and WALLACE (1998).

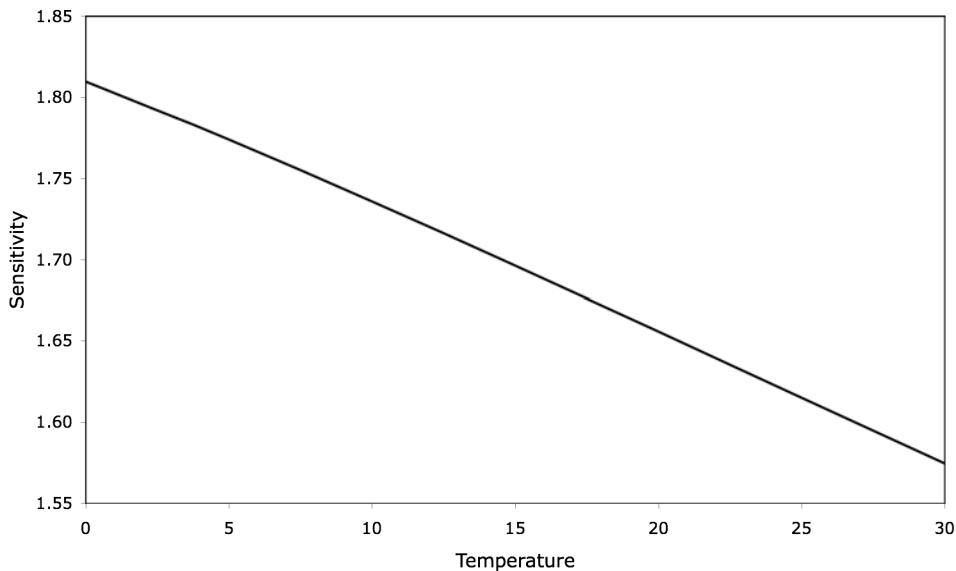


Fig 3: Sensitivity (= mole of atmospheric carbon uptake per mole of added $\text{Ca}(\text{OH})_2$) versus temperature at an atmospheric pCO_2 of 390 ppmV. Calculated using the equilibrium coefficients of DICKSON and MILLERO 1987 and the CO_2Sys programme of LEWIS and WALLACE (1998).

3. The scale of alkalinity addition required to adsorb anthropogenic CO_2 emissions

Fossil fuel burning is presently releasing ≈ 7 Gtonnes of carbon per year (IPCC, 2007), equivalent to $\approx 6 \times 10^{14}$ moles of carbon per year. For illustrative purposes we assume that the *Cquestrate* scheme is pursued so that 50% of fossil fuel CO_2 is adsorbed to seawater, along with all the CO_2 released

during the required calcining of calcite. This is an extreme case and represents the maximum likely demand for the scheme. At an average sensitivity of 1.7, this scenario requires $\approx 4 \times 10^{14}$ moles of $\text{Ca}(\text{OH})_2$ addition to seawater, or 41 Gtonnes of calcite per year to be mined, calcined, slacked, and added to the oceans (for comparison, present US mining of calcite is ≈ 1 Gtonne per year; RAU et al., 2007). This rate of Ca^{2+} addition is some 43 times the natural riverine Ca^{2+} flux to the oceans but, because of the large amount of Ca^{2+} in seawater, would raise surface seawater Ca^{2+} concentrations by only 0.2% per year. It would raise surface ocean alkalinity by 2% per year. An increase in surface ocean alkalinity of 10% is therefore sufficient to adsorb 50% of fossil fuel CO_2 emissions for ≈ 5 years (including the additional CO_2 released during calcining). Such a 10% increase in alkalinity is used as an example case elsewhere in this report.

	Units	Amount	Source
<i>Values used in calculations:</i>			
Annual CO_2 emissions from fossil fuel burning	Gtonnes C yr ⁻¹	7	(IPCC, 2007)
Total anthropogenic CO_2 emissions 1751-2004	Gtonnes C	315	
Depth of mixed layer	m	50	
Volume of surface ocean	m ³	1.81×10^{16}	(SARMIENTO and GRUBER, 2006)
Flux of river water	m ³ yr ⁻¹	3.70×10^{13}	(SARMIENTO and GRUBER, 2006)
Ca^{2+} concentration of ocean water	micromol m ⁻³	10,600,000	(SARMIENTO and GRUBER, 2006)
Ca^{2+} concentration of river water	micromol m ⁻³	364,000	(SARMIENTO and GRUBER, 2006)
Total Ca^{2+} in surface oceans	micromol	1.92×10^{23}	
Riverine Ca^{2+} flux	micromol yr ⁻¹	1.35×10^{19}	
Biogenic CaCO_3 production in ocean	moles Ca yr ⁻¹	3.20×10^{13}	(MACKENZIE et al., 2004)
Average alkalinity of surface oceans	micromol kg ⁻¹	2308	(SARMIENTO and GRUBER, 2006)
Total US mining of limestone	Gtonnes yr ⁻¹	1.0	(RAU et al., 2007)
Solubility of $\text{Ca}(\text{OH})_2$	g l ⁻¹	1.85	
Solubility product, K_{sp} , for $\text{Ca}(\text{OH})_2$		1.2×10^{-14}	
<i>To sequester 50% of fossil fuel CO_2 emissions</i>			
<i>(assuming an effectiveness of 1.7 and that CO_2 from calcining must also be sequestered)</i>			
Mass limestone required	Gtonnes yr ⁻¹	40.8	
number of times US mining		40.80	
fraction of Ca^{2+} added relative to surface ocean		0.0021	
fraction of Ca^{2+} relative to river flux		43.27	
moles of Ca^{2+}		4.08×10^{14}	
moles of alkalinity per kg of surface ocean		4.51×10^{05}	
percent change in surface ocean alkalinity		1.95	

Table 1: Values used in this report, with literature sources where appropriate.

4. Seawater carbonate saturation as a limitation

Surface seawater is super-saturated with respect to the two common forms of CaCO_3 – calcite and aragonite (Fig 4). Spontaneous precipitation of these minerals does not occur due to inhibition by other chemical components in seawater (particularly Mg^{2+} and SO_4^{2-} for calcite and organic acids for

aragonite). At some level of supersaturation, however, this inhibition would be overcome and precipitation of carbonate would occur. Although not certain, calcite is more likely to be precipitated in waters below about 6°C, and aragonite at warmer temperatures (MORSE et al., 1997). Addition of Ca(OH)₂ to seawater increases the saturation state due both to the small increase in Ca²⁺, and the related and somewhat larger increase in CO₃²⁻. To any extent that this leads to precipitation of CaCO₃, it reverses the *Cquestrate* process and returns CO₂ to the atmosphere.

The level of saturation at which spontaneous carbonate precipitation will occur is not particularly well constrained by observations. For calcite, one study (MORSE and HE, 1993) suggests a saturation ratio of ≈19 to generate homogenous (e.g. un-nucleated) precipitation at 20°C (compared to seawater saturation of ≈5 today). Similar saturation values (18) are reported in a more recent study of spontaneous precipitation (RAU et al., 2007) although details of that study are sparse. Studies of spontaneous aragonite precipitation have not to our knowledge been reported. This is an area where additional research is required to fully assess the potential of the *Cquestrate* scheme.

Saturation is strongly influenced by temperature, increasing as temperature rises (Fig 4). In the modern ocean, neither calcite nor aragonite is spontaneously precipitated even in warm tropical seas, providing a minimum value for the saturation state at which such precipitation occurs. Addition of alkalinity to colder waters should therefore not lead to precipitation until at least the saturation state of present warm waters is reached. As an example, for waters at 5°C, alkalinity could be increased to a value as high as 3450 before the saturation state observed in today's warm ocean is reached (Fig 5). This argument places some minimum on the level of alkalinity increase possible without causing inorganic carbonate precipitation. Addition to higher values might also be possible, but would require laboratory and/or field study to assess the saturation ratio at which inorganic precipitation of carbonate occurs.

The discussion in this section considers only the direct inorganic precipitation of carbonate. A change in biological production rates of carbonate is considered in Section 7 below.

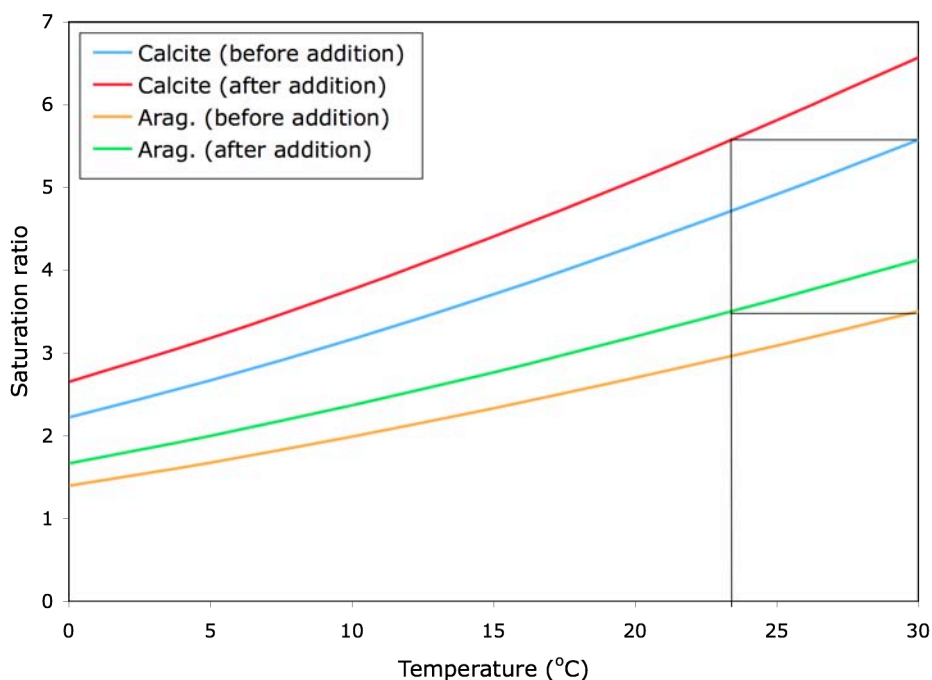


Fig 4: Saturation ratio (where 1 = exactly saturated) for calcite and aragonite in today's ocean (blue and orange respectively). Because no spontaneous precipitation of these minerals is observed in modern seawater, a lower bound can be placed on the saturation ratio required for such precipitation of 5.6 (calcite) and 3.5 (aragonite). These values suggest that a 10% increase in alkalinity (the effects of which are shown by red and green curves), will not cause precipitation of carbonate in waters cooler than 23°C.

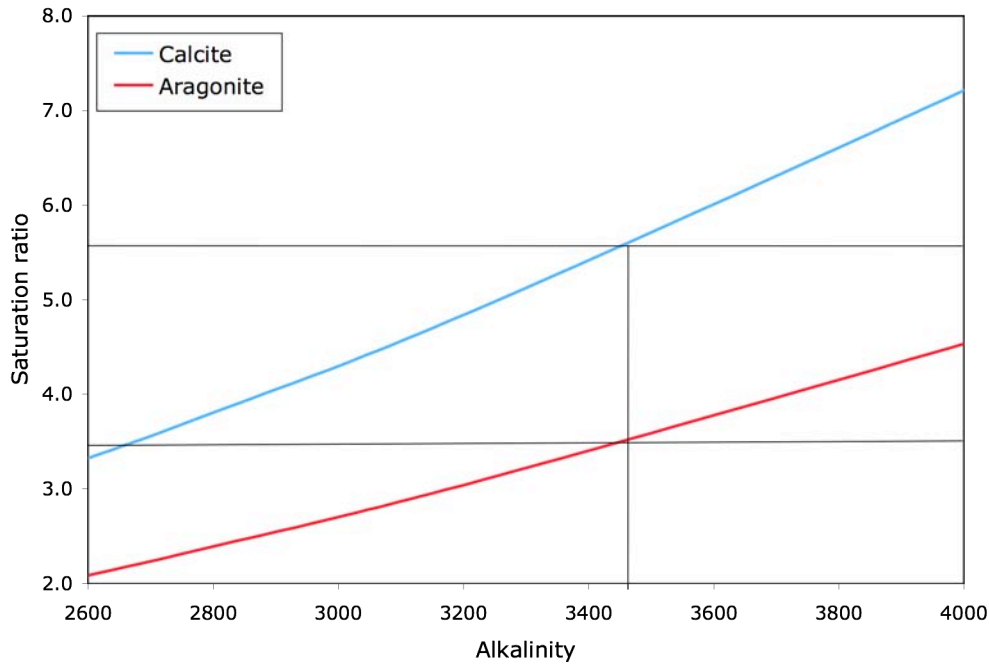


Fig 5: Saturation ratios for calcite and aragonite in water at 5°C in equilibrium with an atmosphere of 390 ppmV CO₂. Black lines indicate the saturation state observed in today's warm ocean and provide a minimum value of alkalinity that can be reached without precipitation of aragonite.

5. The long-term ocean response to alkalinity addition

If the alkalinity is added for long periods, ocean saturation will continue to rise (Fig 6) and any threshold value of saturation for carbonate precipitation is more likely to be crossed (see previous section).

Increasing surface ocean alkalinity and saturation levels will also eventually have an impact on conditions in the deep ocean. Slow circulation of waters to depth in the oceans means that this process will occur on the timescale of centuries (Fig 6). Increasing saturation levels in the deep ocean will deepen the lysocline (the depth in the oceans at which calcite becomes undersaturated and, below which, is dissolved from ocean sediments). A deeper lysocline will lead to an increase in net removal of CaCO₃ from the ocean (because less is dissolved on the seafloor). This represents a loss of alkalinity, and therefore partially undoes the effect of adding alkalinity to the surface ocean. This effect is therefore a long-term negative feedback, but it is unlikely to completely reverse the effectiveness of alkalinity input because the fluxes of carbonate in the natural cycle are smaller than those that those required by the *Cquestrate* scheme. The slow timescale on which lysocline deepening occurs also means that this process is not a serious pitfall for the *Cquestrate* process because, on that timescale, ocean mixing will have led to natural sequestration of CO₂ in the deep ocean by simple solubility.

No additional long-term effects are anticipated when stopping addition of alkalinity.

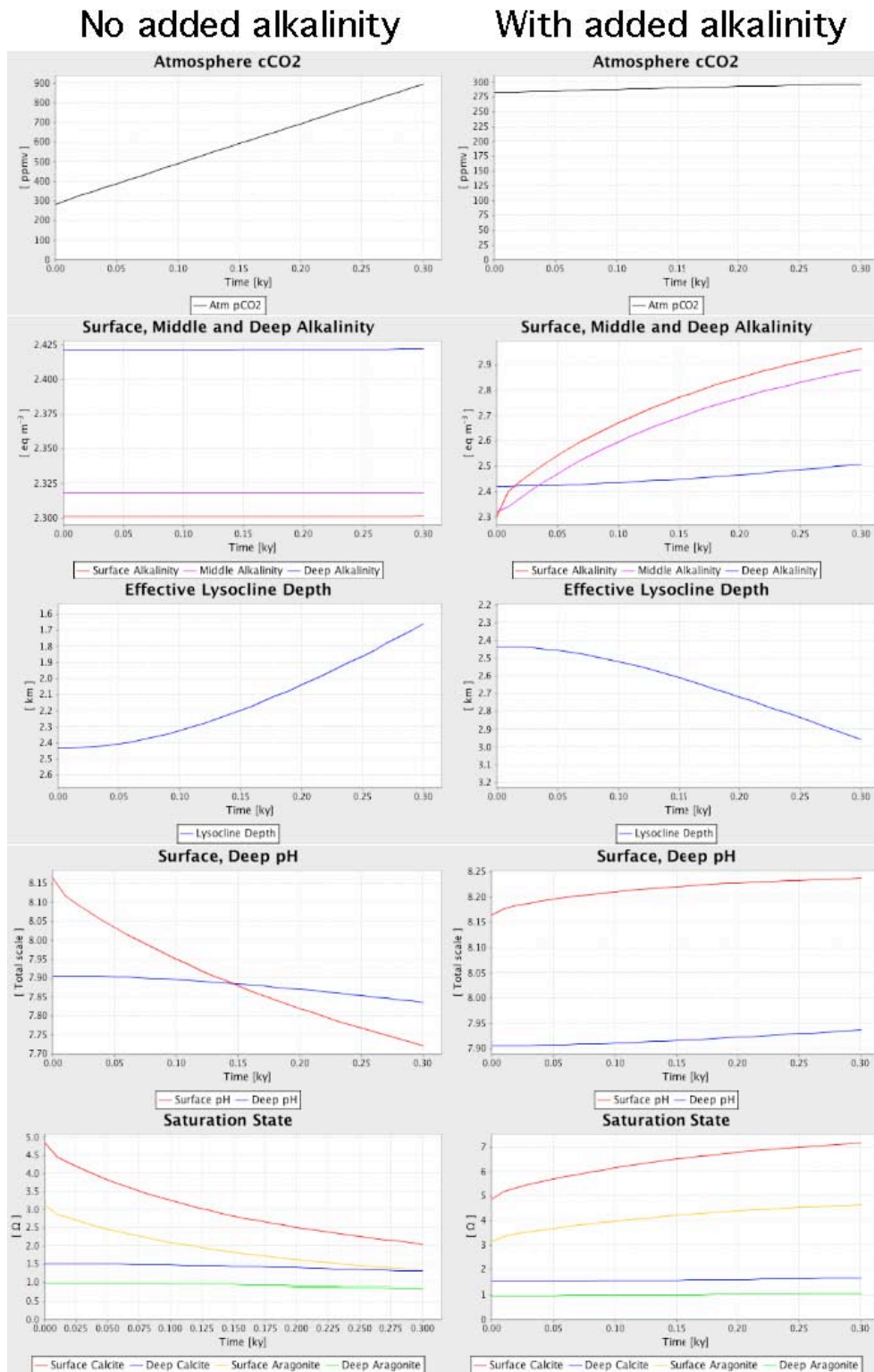


Fig 6: Output from a box model mimicking all significant features of the ocean carbon system and run for 300 years (model available from <http://www.noc.soton.ac.uk/jmodels/>). Left hand panels take an initially equilibrium carbon cycle and perturbs it with a sufficient C flux to cause a 2 ppmV increase in atmospheric CO₂ per year, approximately equivalent to today's rate of CO₂ rise (note that this is a simplified case designed to illustrate today's conditions, rather than using a variable future emission scenario for fossil fuel CO₂). Right hand panels impose the same C flux, but also increase the riverine alkalinity flux by a factor of 20 to mimic the *Cquestate* process of adding alkalinity to the oceans. Note that scales are not identical in left and right panels. The increased alkalinity flux in the right hand panels prevents the significant changes in atmosphere CO₂ and ocean pH seen in the left-hand figures. The right hand panels also illustrate the long-term effects on ocean saturation due to continued addition of alkalinity.

6. Local inorganic effects of intense alkalinity addition

Previous sections have assumed that $\text{Ca}(\text{OH})_2$ is added uniformly throughout the surface ocean. In practise, of course, $\text{Ca}(\text{OH})_2$ will be added at specific locations and will therefore cause a more extreme increase in carbonate saturation and pH at those locations.

If sufficient alkalinity is added to seawater to sequester 50% of fossil fuel emissions for 5 years (see Section 3), this represents a 10% increase in alkalinity for the whole surface ocean, but an increasingly large percentage increase if added to only a fraction of the surface ocean. The effects on saturation state and pH of reducing the volume of surface ocean involved in the process are illustrated in Figs 7 and 8. Using warm tropical waters to provide a minimum allowable saturation level suggests that 20% of the surface ocean would need to be involved in such addition in order to avoid carbonate precipitation. This calculation is for the extreme case and the required volume of ocean involved obviously decreases as the amount of CO_2 sequestered decreases.

The distribution of $\text{Ca}(\text{OH})_2$ into seawater represents probably the most significant oceanic challenge for the *Cquestrate* scheme. To stay inside the cautious alkalinity bound set in Fig 5 would require ≈ 2000 litres (i.e., 2 m^3) for every mole of Ca^{2+} added. If calcite saturation levels as high as 18 are possible without calcite formation this volume is significantly reduced. But the need for widespread distribution of the alkalinity into the surface ocean remains. Making use of the natural circulation and mixing of the oceans will be essential to this distribution.

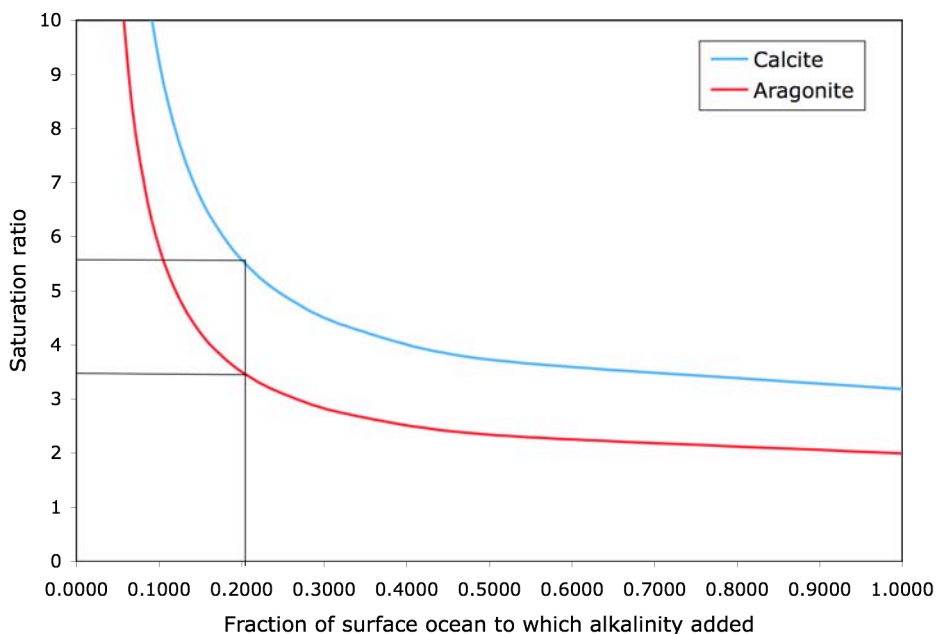


Fig 7: Effect on saturation ratio of adding alkalinity to various fractions of the surface ocean. This example calculation is equivalent to those conducted in Fig 5 (10% increase in average whole surface-ocean alkalinity; 5°C water, 390 ppmV CO_2) but with the fraction of surface ocean involved altered. Thin black lines represent the saturation levels of today's tropical seawater, providing a minimum saturation ratio to avoid precipitation of carbonate.

Calculating the maximum desirable flux of $\text{Ca}(\text{OH})_2$ for a point source or sources is not straightforward. It would rely on assessing a maximum saturation and/or pH that is acceptable to avoid carbonate precipitation or ecosystem damage (presently poorly known – see Section 4). It would then require assessment of advection and diffusion of alkalinity from that point due to ocean

circulation. This calculation would be highly dependent on the location(s) selected. Appropriate 3D ocean models exist which could address this issue with further work.

The chemical limit of $\text{Ca}(\text{OH})_2$ addition might also be set by its own solubility. This is 1.85 grams per litre, corresponding to a Ca^{2+} concentration of ≈ 25 mMol per litre. At saturation for $\text{Ca}(\text{OH})_2$, and equilibrated with an atmosphere of 390 ppmV CO_2 , the pH of seawater could be ≈ 9 , and the saturation of calcite and aragonite ≈ 170 and ≈ 110 respectively. These values are doubtless sufficient to cause spontaneous precipitation of calcite and aragonite, indicating that it is the solubility of CaCO_3 (as in Section 4), rather than that of $\text{Ca}(\text{OH})_2$, that limits the maximum rate of $\text{Ca}(\text{OH})_2$ addition.

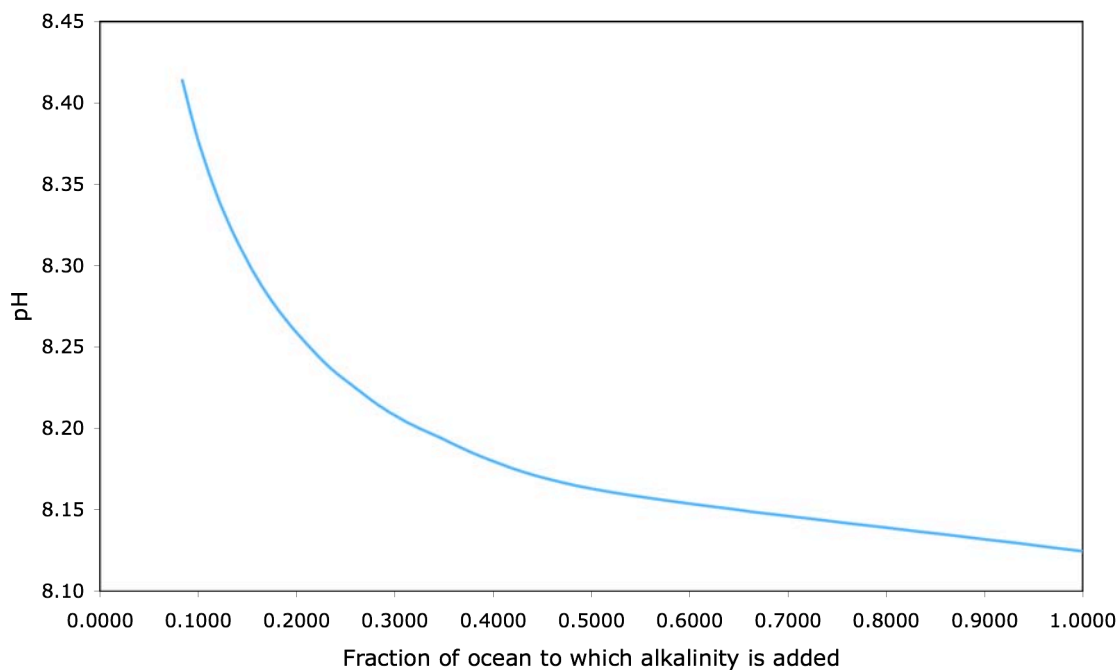


Fig 8: Effect on pH of adding alkalinity to various fractions of the surface ocean. Conditions as in Fig 7.

7. Possible biological feedbacks to alkalinity addition

Increasing ocean alkalinity may cause feedbacks in the carbon cycle due to changes in the biological production of either particulate organic carbon (POC), or of biogenic CaCO_3 . This section addresses these feedbacks purely for their chemical impact on the effectiveness of the scheme. The wider implications of alkalinity addition for ocean biology are considered in Section 9.

Increasing alkalinity leads to higher total dissolved inorganic carbon (DIC) in seawater and, because this DIC is a building block of POC, this might lead to more formation of POC (RIEBESELL et al., 2007). Any settling of this additional POC from the surface layer of the ocean would remove additional carbon from the surface ocean and therefore reduce atmospheric CO_2 . The extent of such additional POC production is likely to be small, however, because POC production is normally thought to be limited by the nutrients phosphate and nitrate rather than by availability of DIC. Only if oceans ecosystem can alter their ratio of carbon to phosphate and nitrate away from normally observed Redfield ratios would this effect be appreciable (modern marine POC has a uniform C:N:P ratio – the Redfield ratio – apparently set by biological processes).

Increasing alkalinity leads to higher carbonate saturation, and therefore makes it easier for calcifying organisms to build carbonate shells. There is evidence to suggest that such calcification increases at high pH (e.g. LANGER et al., 2006), causing an increase in the CaCO_3/POC ratio in biogenic material settling from surface layer. This increase in CaCO_3 precipitation will partially reverse the *Cquestrate* process. The scale of this feedback is not likely to be large, however. The flux of CaCO_3 from the surface ocean today is 3.2×10^{13} moles per year (MACKENZIE et al., 2004), less than 10% of the Ca^{2+} addition flux required to sequester 50% of anthropogenic carbon emissions (see Section 3). Surface ocean organisms would need to adjust their rate of calcification dramatically in response to relatively small changes in saturation state to play any noticeable role in reversing the *Cquestrate* process.

If both POC and carbonate production were to be increased by addition of alkalinity, the net effect would be consumption of additional atmospheric CO_2 .

8. Impurities in carbonate

Limestone is not pure CaCO_3 and contains impurities. The impact of these impurities on the marine system should be considered before adding calcined limestone products to seawater. Mg is the most concentrated impurity, but Mg concentrations are high in seawater ($\text{Mg}/\text{Ca} \approx 5$ mol/mol) and addition of Mg in limestone will therefore have significantly less impact on the ocean Mg budget than on that of Ca.

Additions of nutrient elements (particularly P and Fe) from limestone could serve to increase production of POC in seawater (which consumes CO_2). P/Ca ratios in limestone are typically in the ppm range, about two orders of magnitude lower than in surface seawater, so increased productivity due to additional P are expected to be small. Fe contents of limestone can be higher, with Fe contents in the 0.1% to 1% range not uncommon (e.g., KABANOV, 2006). If added to areas of the ocean where biological productivity is presently limited by Fe supply, this could enhance production of POC, and therefore consume carbon and serve to reduce atmospheric CO_2 . This mechanism has been proposed as an alternative approach to carbon sequestration. A small component of such Fe fertilisation might be a secondary effect of adding impure $\text{Ca}(\text{OH})_2$ to seawater if pursued in a region of Fe limitation. Both the effectiveness and the wisdom of Fe fertilization remains controversial, however, as discussed in articles such as BUESSELER et al., (2008).

9. Effect of alkalinity addition on ocean species and ecosystems

Addition of $\text{Ca}(\text{OH})_2$ to the ocean raises pH, alkalinity, saturation state, and DIC. To understand the independent implications for ocean species and ecosystems of these four chemical modifications is difficult because, in most experimental manipulations that mimic changes in the carbon environment, change is achieved by titration resulting in correlated changes in all carbon-system parameters. Understanding the chemical controls on physiology is therefore in the preliminary stage. Significant research in this area is ongoing, however, driven by concern about future ocean acidification. This research has focused on the effects of lowering ocean pH, but it also provides some indication of the effects of increasing pH.

Separating the effects of the four chemical responses to increased ocean alkalinity is important because there are competing influences. For instance, photosynthesisers require CO_2^g and may be better adapted to high CO_2^g , whilst calcifiers require CO_3^{2-} and may be better adapted to low CO_2^g .

The biological response to increased alkalinity fall into four end-member categories - primary response to i) saturation state, ii) CO_2^g , iii) DIC and iv) pH.

i. Saturation state

Marine calcifiers which mediate calcification by providing nucleation sites on a biological template (e.g. corals) are most likely to increase their calcification in response to rising alkalinity and saturation state. If suitable control of alkalinity were possible, it might benefit such species by protecting them against the damaging effect of ocean acidification.

ii. $p\text{CO}_2$

Adding alkalinity to seawater causes a reduction in CO_2^g . This is then corrected by influx of CO_2 from the atmosphere but at least temporarily, and more continuously in locations where alkalinity addition continues, marine species will experience lower seawater CO_2^g . In the modern ocean CO_2^g conditions are undersaturated for Rubisco, the enzyme which catalyses photosynthesis in all phytoplankton. So all photosynthesisers have evolved to employ strategies to acquire and concentrate carbon at the site of photosynthesis. The increased $p\text{CO}_2$ of the recent past is generally thought to be beneficial to this process (ROYAL SOCIETY, 2005). Some phytoplankton species that form an integral part of ocean biogeochemical cycles may also be sensitive to limitation by CO_2^g . The nitrogen-fixing cyanobacterium *Trichodesmium*, for instance, which is responsible for large fraction of primary productivity in the nutrient impoverished regions of the ocean, shows reduced rates of carbon and nitrogen fixation under low $p\text{CO}_2$ conditions (HUTCHINS et al., 2007; RAMOS et al., 2007). There is also evidence that the size structure of marine phytoplankton may be influenced by CO_2 concentrations. A significant increase in the abundance of small nanophytoplankton was observed in low CO_2 enclosures (ENGEL et al., 2008). If the size and taxonomic structure of phytoplankton communities is altered by changes in CO_2^g , this has important implications for the trophic structure and biogeochemical function of marine ecosystems. If alkalinity is added to the extent that it corrects for recent and future ocean acidification the effect is to maintain the direct CO_2 uptake processes close to those in the pre-industrial ocean. At point of addition, however, where continued addition of alkalinity leads to long-term lowering of CO_2^g , species that are unable to (or inefficient at) concentrating carbon within the cell will be disadvantaged.

iii. DIC

Some organisms may be able to manipulate their internal pH to access the carbon from HCO_3^- ions. These species will be advantaged by the impact of increasing alkalinity (RIEBESSELL et al., 2007) which will create a greater carbon resource for their metabolism by permanently raising DIC. The addition of bicarbonate, for instance, doubled the skeletal growth rate of the coral *Porites porites* (MARUBINI and THAKE, 1999) apparently due to DIC limitation. Those authors proposed that increasing DIC of marine ecosystems could aid the regeneration of damaged reefs, although to our knowledge no such experiments have been attempted in the natural environment.

iv. pH

$\text{Ca}(\text{OH})_2$ addition will cause an initial rapid increase in pH followed by a slow return, due to atmospheric CO_2 uptake, to an equilibrium value slightly higher than the initial conditions. The biological impact depends on the size of the initial input, the rate at which it is mixed, and the rate atmospheric CO_2 is taken into the surface ocean. Thus, both short-term (hours to weeks) and long-term (months to years) changes in ocean chemistry and their potential impact on marine ecosystems must be considered. Almost all enzymes have an optimum pH for operation and there is likely to be a metabolic cost for organisms to maintain intracellular pH for cell function (RAVEN et al., 1985). Thus rapid or extreme changes in external pH may cause a reduction in cell growth. Two significant studies have reviewed the pH tolerance of marine phytoplankton, one examining the results obtained from batch culture experiments, the other from a variety of laboratory and enclosure experiments. Both studies show no class-specific tolerance to change in pH (HANSEN,

2002; HINGA, 2002) and even different clones of the same species can exhibit markedly different relationships between pH and growth rate (HINGA, 2002). Of the 35 coastal phytoplankton species examined in the review of HINGA (2002) most attained over 80% of their maximum growth rate in conditions within 0.5 pH units of their optimum pH. When the pH range was extended to ± 1.0 unit, however, a considerable reduction in maximum growth rate across a wide range of species was observed. Although liming has been used to restore freshwater ecosystems from the harmful effects of acid rain with moderate success, extreme changes in pH can result in a rapid decline in biodiversity in that setting (SCHINDLER, 1997). To avoid the risk of pH shock, water quality guidelines of both the U.S. Environmental Protection Agency (1976) and the Canadian Council of Ministers of the Environment (1999) recommend that to protect marine biota with narrow pH tolerances, human activities should not result in a change in environmental pH of more than 0.2 pH units from normally occurring values. In the absence of more complete experimental evidence about the response of marine species to changing pH, this figure is reasonable to apply at local sites of alkalinity input, and more widely. To fall within this pH range and accomplish the intended sequestration of atmospheric CO₂, a significant fraction of the global ocean (>10%) must be involved in the alkalinity addition during the extreme CO₂ sequestration scenario used as an example elsewhere in this report (Fig 8). This places a somewhat similar constraint as CaCO₃ saturation on the level of alkalinity dispersal required for safe operation of the *Cquestrate* scheme.

In summary, the addition of alkalinity to the marine environment will cause changes in ocean chemistry which may effect the growth of marine organisms. Whether the addition of Ca(OH)₂ leads to a major shift in species composition depends on the extent to which the chemical properties of the surface ocean change and the length of time before equilibrium is restored. Any resulting changes in the taxonomic and size structure of marine phytoplankton will impact higher trophic levels that rely on phytoplankton as a food source. Shifts in phytoplankton composition may also affect the cycling of elements other than carbon. Nitrogen fixers play a central role in the global nitrogen cycle by providing new nitrogen to oligotrophic ecosystems and some marine algae produce dimethyl sulphide (DMS), which may play a role in climate regulation through the production of cloud condensation nuclei. To anticipate the climate-related implications of the *Cquestrate* scheme will also require a detailed understanding of the response of the functional groups that drive marine biogeochemical cycles.

10. Summary of existing literature suggesting alkalinity approaches for sequestering CO₂

Similar schemes involving altering ocean alkalinity have been proposed. The IPCC report on CO₂ Capture and Storage (IPCC, 2005) provides a clear summary of early work in this area and of the broader context of such schemes. Four general approaches have been suggested:

i. Calcining limestone and adding CaO to seawater

This is the approach on which the *Cquestrate* scheme is based. It was first suggested by Kheshgi (1995) who particularly considered the energy and carbon requirements of the scheme. This author considered use of soda-ash (Na₂CO₃) which is readily soluble in seawater, but rejected this approach because of the scarcity of soda-ash deposits. His paper goes on to consider the energetics and carbon budget of calcining calcite for addition to seawater. It reaches the same conclusion as that here, that addition of 1 mole of CaO to seawater leads to ≈ 1.8 moles of CO₂ uptake. It does not consider the issues of CaCO₃ saturation, however, nor the implications of this approach for ocean biology.

ii. Accelerated weathering of carbonate minerals

Rau and colleagues have suggested direct reaction of CO₂ with CaCO₃ at point of CO₂ production to produce Ca²⁺ and 2HCO₃⁻ (RAU and CALDEIRA, 1999, RAU et al., 2007). In its net resulting chemistry, this scheme is identical to that above. Resulting products would most easily be expelled

to seawater, in which case the same issues related to saturation of CaCO₃ as those in the *Cquestrate* scheme would operate. This scheme is critically dependent on the rate of reaction between CO₂ and CaCO₃ that can be achieved. This issue falls outside the scope of this report, but experiments reported in the literature suggest that reaction rates might be fast enough to make this approach workable (RAU et al., 2007).

iii. Accelerated weathering of silicate minerals

This scheme, proposed by HOUSE et al. (2007) differs from those above in making use of silicates rather than carbonates, but is similar in that it involves adjusting ocean alkalinity to draw CO₂ from the atmosphere. NaCl in seawater is electrochemically converted to HCl and NaOH. This creates alkalinity (NaOH) and shifts seawater to higher pH to cause drawdown of CO₂ in a similar manner to that in the *Cquestrate* scheme. The HCl is reacted with silicate minerals and the products stored or returned to seawater. The net reaction in this scheme is:



This net reaction is slightly exothermic, but only if the energy released during reaction of NaOH with CO₂ is recovered, which would require this process to be occur in an engineered environment rather than in seawater.

As with schemes involving carbonate, this scheme has implications for seawater CaCO₃ saturation. If minerals are selected to neutralize the HCl that do not include significant Ca, then the Ca²⁺ of seawater is not increased. But the major part of the increase in saturation state with increasing alkalinity is due to changes in the concentration of CO₃²⁻, rather than to addition of Ca²⁺. If the effects of the scheme could be distributed throughout the ocean to compensate pH decrease due to rising CO₂ then it would cause no net change in saturation. But if done at discrete locations, it encounters similar issues of local saturation as the *Cquestrate* scheme.

iv. Direct dissolution of calcite in seawater

Although the surface of the oceans are saturated for CaCO₃, increased solubility with pressure makes CaCO₃ undersaturated at depth. CaCO₃ settling through the water column will start to dissolve when reaching this undersaturated depth (i.e. at the lysocline), thereby increasing ocean alkalinity. When upwelled to the surface, this alkalinity will lead to the uptake of CO₂ in a similar way to that in the *Cquestrate* scheme. Addition of limestone powder to upwelling regions of the ocean has been proposed as a possible mechanism to uptake a limited amount of CO₂ (HARVEY, 2008). This scheme is limited by the kinetics of limestone dissolution and by the rate of global upwelling. Its proponent has suggested a possible uptake of 1 Gtonne per year if CaCO₃ is added in many locations around the world but this is likely to be a maximum uptake and would require additional experiments on the kinetics of the process to assess. Most problematic for this scheme is that the drawdown of CO₂ ramps up slowly over 100 years. This slow response would also make field testing of the scheme difficult.

11. Possible locations for alkalinity addition from an oceanographic perspective

Only the oceanographic considerations for choice of location for Ca(OH)₂ addition are considered here. These considerations would need to be balanced with other considerations such as location of available energy sources and limestones to assess optimal locations for the entire *Cquestrate* scheme.

The rate of dispersal of the Ca(OH)₂ by ocean mixing and circulation is an important consideration. Good locations for addition of Ca(OH)₂ are those with high average wind-speeds to generate local mixing, large mixed-layer depths to provide a large volume of water to mix into, and rapid ocean

currents to move alkalinity away from the point of input. Maps of these three variables are provided in Figs 9 to 11. The Southern Ocean fits these criteria well, with possible targets being the Drake Passage and New Zealand. The North Atlantic region also features high wind speeds and surface currents so might represent a suitable target. The effects of ocean mixing and transport is readily amenable to 3D modelling to better assess the best location(s) from this perspective.

Ocean temperature is also a consideration because colder waters are relatively less saturated for CaCO_3 than warmer waters (e.g. Fig 4) and because the sensitivity of CO_2 uptake is increased in cold water (Fig 3). High latitude regions are therefore likely to be preferred.

It might be prudent to avoid regions close to anoxia because any increase in biological productivity as a response of Ca(OH)_2 addition may move sediments and bottom waters closer to anoxia.

The possible impact on ecosystems of some Fe addition with the Ca(OH)_2 should be considered, particularly if performed in a region where macronutrients are not fully used (e.g. Southern Ocean, North Pacific, Equatorial Pacific).

Addition of Ca(OH)_2 close to calcifying ecosystems struggling with ocean acidification (e.g. coral reefs) might be beneficial to those systems, but very careful control of the addition would be required in order not to cause more harm than good, and such an approach would certainly require prior additional research.

Any regions selected for Ca(OH)_2 addition will have an ecosystem tuned to exploit the local environment which will be at least somewhat perturbed by changes in alkalinity, DIC, and saturation. Thorough assessment of the local biological response would be required in any setting before the scheme was implemented. This assessment would include laboratory and mesocosm experiments, possibly followed by small and medium scale field trials.

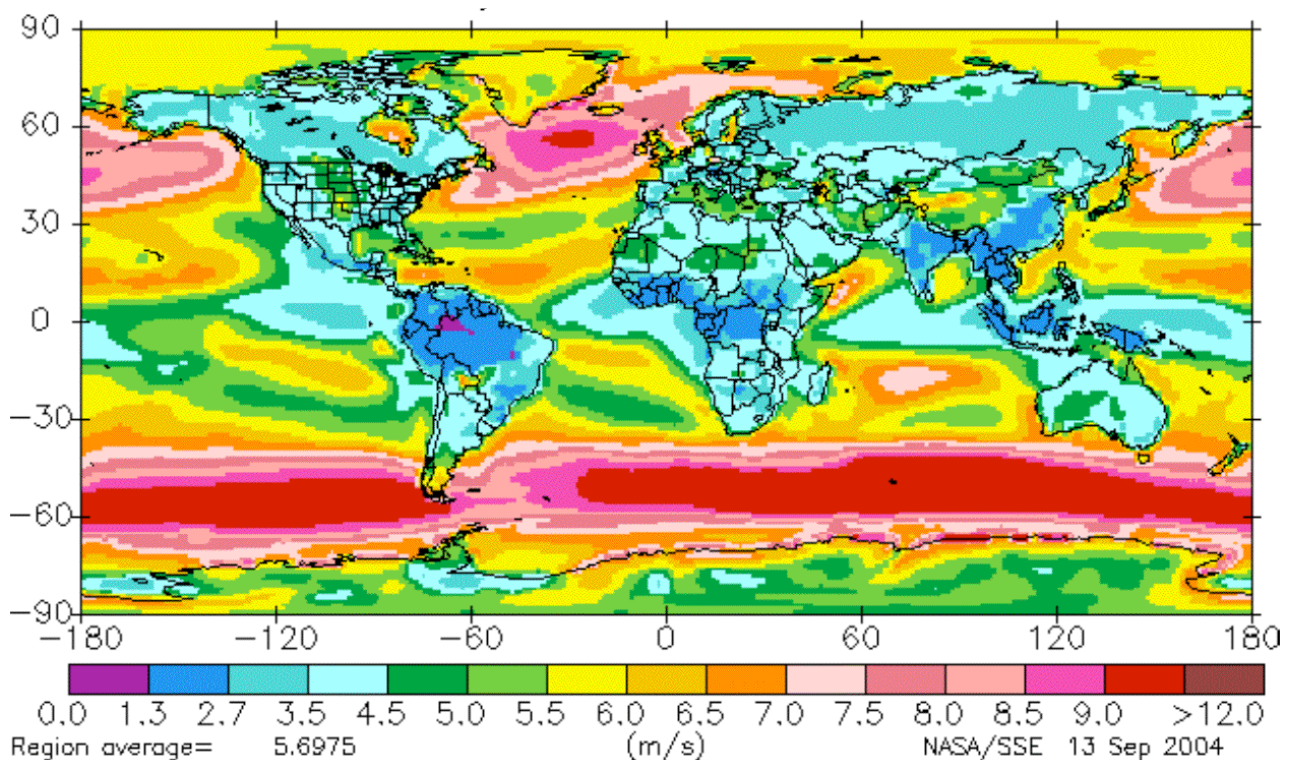


Fig 9: Average wind-speed at 10 m height for the period 1983-1993. Based on NASA calculations (available at <http://www.climate-charts.com/World-Climate-Maps.html>)

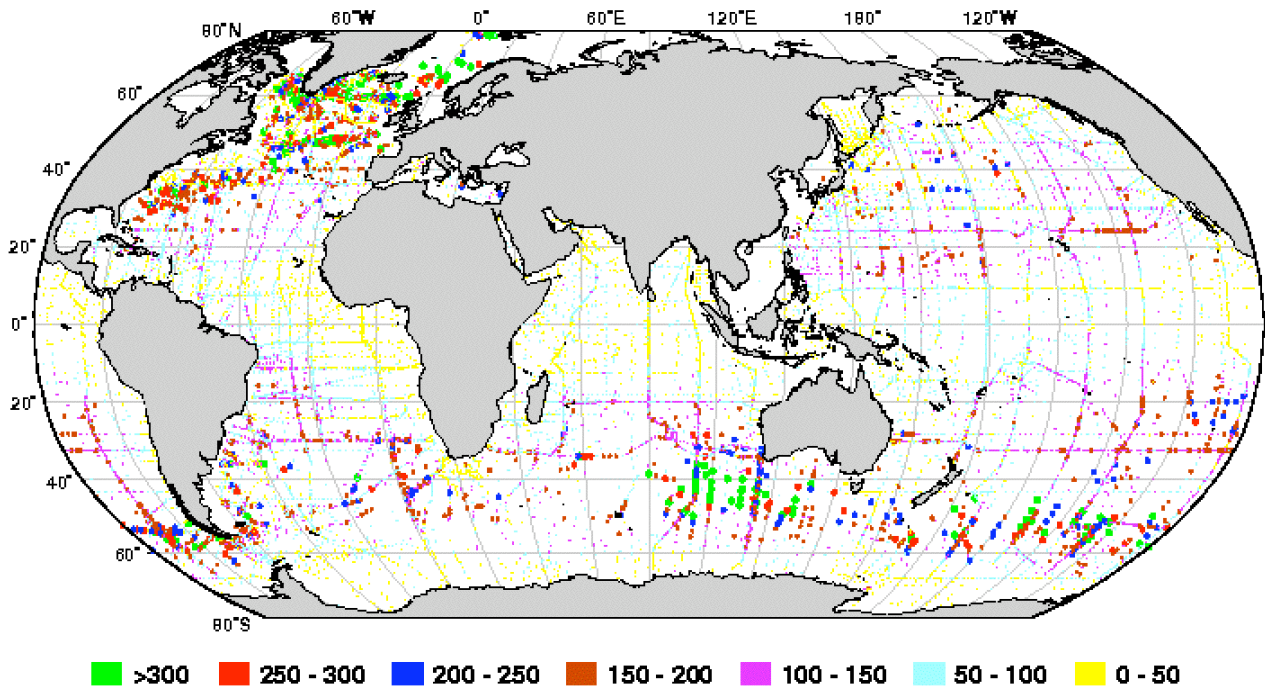


Fig 10: Mixed layer depth in meters assessed by the level of 95% oxygen saturation following TALLY (1999).

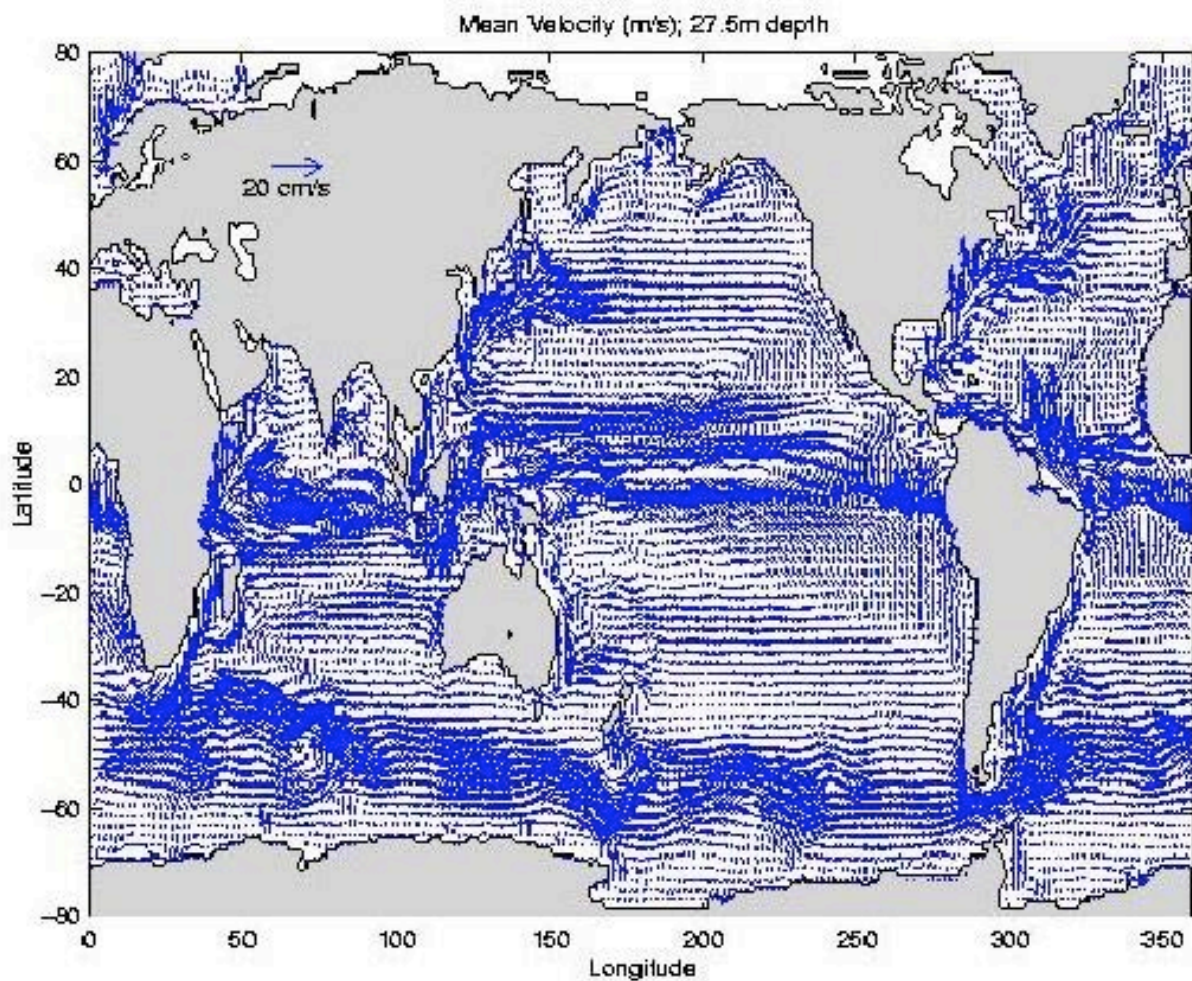


Fig 11: Mean water velocities at 27.5m depth based on the assimilated data-field of the ECCO model. Map and further details available at <http://www.compas.ucsd.edu/vision.html>.

12. Further work required to assess the *Cquestrate* scheme

Three significant uncertainties in the ocean response to addition of $\text{Ca}(\text{OH})_2$ will require additional research before the workability of the scheme can be further assessed:

1. Saturation levels of CaCO_3 for precipitation of calcite and aragonite

This report has generally taken the cautious approach of assuming that saturation should not be taken higher than that in the modern tropical ocean. This is a safe lower bound on permissible saturation from an environmental perspective, but places stringent requirements on the dispersal of alkalinity. If saturation can be significantly higher (perhaps to values of 19 suggested by the limited literature on the subject) this lessens the difficulty of dispersion. Further laboratory assessment of the relationship between saturation state and inorganic CaCO_3 precipitation is required. This should be done both in the presence of carbonate seed crystals and without, and at a range of temperatures. Such work would be reasonably straightforward to perform, and would require careful monitoring of carbonate precipitation in controlled laboratory environments.

2. The dispersal of alkalinity by ocean mixing and circulation

High-resolution 3D modelling should be performed to assess the maximum flux of alkalinity that can be added at a single location without crossing saturation thresholds. This work would identify the realistic size of atmospheric CO_2 reduction that could be achieved with the *Cquestrate* scheme, and the best locations at which to pursue the scheme. The use of inverse modelling techniques would be an efficient approach to these problems. This research can readily be achieved by adding appropriate chemical subroutines to existing 3-D ocean models.

3. What is the biological response to increased alkalinity

The response of ocean species to changing carbon parameters is a research field somewhat in its infancy, and one that has largely focused on the response to a decrease rather than an increase in pH. The effect of increasing alkalinity (and associated changes in pH, DIC and saturation) on marine species will require more research. Initial laboratory experiments should quantify physiological responses, including growth rates, photosynthesis, respiration and other sensitivity indices, for a variety of marine organisms that may be affected by $\text{Ca}(\text{OH})_2$ addition. Species should include representatives of important functional groups (ie. calcifiers, nitrogen-fixers, DMS producers). This should be followed by mesocosm experiments to investigate community responses (ie. shifts in species composition, food web structure, biogeochemical cycling) and by an integrated modelling approach to determine the likely consequences of ocean liming on marine ecosystems (including higher trophic-levels) and biogeochemical cycles. This represents a larger research effort than required for 1 and 2 above. It is realisable with existing techniques, but would require significant time and human resources to achieve. Limited laboratory work could be performed without such significant investment, however, to make an initial assessment of the response of some critical species to $\text{Ca}(\text{OH})_2$ addition.

Although it falls outside the remit of this report, an additional issue for further research will be design and assessment of appropriate mechanisms for the dispersal of $\text{Ca}(\text{OH})_2$ to surface seawater.

All such further research would lead, if serious problems were not encountered, to a small-scale field trial and should consider the design of such a trial during their progress.

References

- Buesseler, K. O., Doney, S. C., Karl, D. M., Boyd, P. W., Caldeira, K., Chai, F., Coale, K. H., de Baar, H. J. W., Falkowski, P. G., Johnson, K. S., Lampitt, R. S., Michaels, A. F., Naqvi, S. W. A., Smetacek, V., Takeda, S., and Watson, A. J., 2008. ENVIRONMENT: Ocean Iron Fertilization--Moving Forward in a Sea of Uncertainty. *Science* **319**, 162-.
- Canadian council of ministers of the environment, 1999. Canadian water quality guidelines for the protection of aquatic life: pH (marine). In: Canadian environmental quality guidelines, 1999. Winnipeg.
- Engel, A., Schulz, K. G., Riebesell, U., Bellerby, R., Delille, B., and Schartau, M., 2008. Effects of CO₂ on particle size distribution and phytoplankton abundance during a mesocosm bloom experiment (PeECE II). *Biogeosciences* **5**, 509-521.
- Hansen, P. J., 2002. Effect of high pH on the growth and survival of marine phytoplankton: implications for species succession. *Aquatic Microbial Ecology* **28**, 279-288.
- Harvey, L. D. D., 2008. Mitigating the atmospheric CO₂ increase and ocean acidification by adding limestone powder to upwelling regions. *Journal of Geophysical Research-Oceans* **113**.
- Hinga, K. R., 2002. Effects of pH on coastal marine phytoplankton. *Marine Ecology-Progress Series* **238**, 281-300.
- House, K. Z., House, C. H., Schrag, D. P., and Aziz, M. J., 2007. Electrochemical acceleration of chemical weathering as an energetically feasible approach to mitigating anthropogenic climate change. *Environmental Science & Technology* **41**, 8464-8470.
- Hutchins, D. A., Fu, F. X., Zhang, Y., Warner, M. E., Feng, Y., Portune, K., Bernhardt, P. W., and Mulholland, M. R., 2007. CO₂ control of Trichodesmium N₂ fixation, photosynthesis, growth rates, and elemental ratios: Implications for past, present, and future ocean biogeochemistry. *Limnol. Oceanogr.* **52**, 1293-1304.
- IPCC, 2005. *Carbon dioxide capture and storage*. CUP, Cambridge.
- IPCC, 2007. Fourth Assessment Report Summary for Policy Makers.
- Kabanov, A. A., 2006. Thermal stability of limestone with a medium content of iron. *Russian Journal of Applied Chemistry* **79**, 157-159.
- Kheshgi, H. S., 1995. Sequestering atmospheric carbon dioxide by increasing ocean alkalinity. *Energy* **20**, 915-922.
- Langer, G., Gussone, N., Nehrke, G., Riebesell, U., Eisenhauer, A., Kuhnert, H., Rost, B., Trimborn, S., and Thoms, S., 2006. Coccolith strontium to calcium ratios in *Emiliania huxleyi*: The dependence on seawater strontium and calcium concentrations. *Limnol. Oceanogr.* **51**, 310-320.
- Lewis, E. and Wallace, D. W. R., 1998. Program developed for CO₂ system calculations. <http://cdiac.ornl.gov/oceans/co2rprrt.html>.
- Mackenzie, F. T., Lerman, A., and Andersson, A. J., 2004. Past and present of sediment and carbon biogeochemical cycling models. *Biogeosciences* **1**, 11-32.
- Marubini, F. and Thake, B., 1999. Bicarbonate addition promotes coral growth. *Limnol. Oceanogr.* **44**, 716-720.
- Morse, J. W. and He, S. L., 1993. Influences of T, S and p(CO₂) on the pseudo-homogeneous precipitation of CaCO₃ from seawater - implications for whiting formation. *Mar. Chem.* **41**, 291-297.
- Morse, J. W., Wang, Q., and Tsio, M. Y., 1997. Influence of temperature and Mg:Ca ratio on CaCO₃ precipitates from seawater. *Geology* **25**, 85-87.
- Ramos, J. B. E., Biswas, H., Schulz, K. G., LaRoche, J., and Riebesell, U., 2007. Effect of rising atmospheric carbon dioxide on the marine nitrogen fixer Trichodesmium. *Glob. Biogeochem. Cycles* **21**.
- Rau, G. H. and Caldeira, K., 1999. Enhanced carbonate dissolution: a means of sequestering waste CO₂ as ocean bicarbonate. *Energy Conversion and Management* **40**, 1803-1813.
- Rau, G. H., Knauss, K. G., Langer, W. H., and Caldeira, K., 2007. Reducing energy-related CO₂ emissions using accelerated weathering of limestone. *Energy* **32**, 1471-1477.
- Raven, J. A., Osborne, B. A., and Johnston, A. M., 1985. Uptake of CO₂ by aquatic vegetation. *Plant Cell and Environment* **8**, 417-425.
- Riebesell, U., Schulz, K. G., Bellerby, R. G. J., Botros, M., Fritsche, P., Meyerhofer, M., Neill, C., Nondal, G., Oeschies, A., Wohlers, J., and Zollner, E., 2007. Enhanced biological carbon consumption in a high CO₂ ocean. *Nature* **450**, 545-548.
- Royal Society, 2005. Ocean acidification due to increasing atmospheric carbon dioxide. The Royal Society, London.
- Sarmiento, J. L. and Gruber, N., 2006. *Ocean biogeochemical dynamics*. 526pp.
- Schindler, D. W., 1997. Liming to restore acidified lakes and streams: A typical approach to restoring damaged ecosystems? *Restoration Ecology* **5**, 1-6.
- Tally, L. D., 1999. Some aspects of ocean heat transport by the shallow, intermediate, and deep overturning circulations, *Mechanisms of global climate change at millennial time scales*.
- United States Environmental Protection Agency, U. S. E. P., 1976. Quality Criteria for Water. U.S. Environmental Protection Agency, Washington, DC.
- Zeebe, R. E. and Wolf-Gladrow, D., 2001. *CO₂ in seawater: Equilibrium, kinetics, isotopes*. Elsevier, Amsterdam.