Assessing ocean alkalinity for carbon sequestration

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Key Points

The ocean naturally stores a very large quantity of carbon as dissolved carbonate and bicarbonate ions

It may be possible to store additional carbon in this sink to mitigate climate change at costs that are comparable to conventional mitigation

Research is needed to understand the impacts and the feasibility of this approach

Abstract

Over the coming century humanity may need to find reservoirs to store several trillions of tons of carbon dioxide (CO_2) emitted from fossil fuel combustion, which would otherwise cause dangerous climate change if it were left in the atmosphere. Carbon storage in the ocean as bicarbonate ions (by increasing ocean alkalinity) has received very little attention. Yet, recent work suggests sufficient capacity to sequester copious quantities of CO_2. It may be possible to sequester hundreds of billions to trillions of tonnes of C without surpassing post-industrial average carbonate saturation states in the surface ocean. When globally distributed, the impact of elevated alkalinity is potentially small, and may help ameliorate the effects of ocean acidification. However, the local impact around addition sites may be more acute but is specific to the mineral and technology.

The alkalinity of the ocean increases naturally because of rock weathering in which > 1.5 moles of carbon are removed from the atmosphere for every mole of magnesium or calcium dissolved from silicate minerals (e.g., wollastonite, olivine, anorthite), and 0.5 moles for carbonate minerals (e.g., calcite, dolomite). These processes are responsible for naturally sequestering 0.5 billion of CO_2 tons per year. Alkalinity is reduced in the ocean through carbonate mineral precipitation, which is almost exclusively formed from biological activity. Most of the previous work on the biological response to changes in carbonate chemistry have focused on acidifying conditions. More research is required to understand carbonate precipitation at elevated alkalinity to constrain the longevity of carbon storage.

A range of technologies have been proposed to increase ocean alkalinity (accelerated weathering of limestone, enhanced weathering, electrochemical promoted weathering, ocean liming), the cost of which may be comparable to alternative carbon sequestration proposals (e.g., \$20 - 100 tCO_2^{-1}). There are still many unanswered technical, environmental, social, and ethical questions, but the scale of the carbon sequestration challenge warrants research to address these.

Index Terms/Keywords

A_T	Total Alkalinity, see section 2
AWL	Accelerated weathering of limestone
BECCS	Biomass energy carbon capture and storage
CO_2	Carbon dioxide
C	Carbon. Descriptions of global distribution and fluxes are described in billions of tons (Gt) of C to account for the various compounds in which C exists. The equivalent amount of CO_2 can be calculated by multiplying by 3.67.
$CaCO_3$	Calcium carbonate (typically as calcite or aragonite polymorphs)
CaO	Lime
$Ca(OH)_2$	Portlandite
CCD	Carbonate compensation depth (in the ocean)
CCS	Carbon capture and storage
C_T	Dissolved inorganic carbon (also 'DIC')
Gt	Gigatons (or Pg)
kJ	Kilojoules
Ksp	Solubility product constant
μatm	Microatmospheres (units of pressure)
NaOH	Sodium hydroxide
pCO_2	Partial pressure of CO_2
PIC	Particulate inorganic carbon
POC	Particulate organic carbon
ppmv	Parts per million by volume
RCP	Representative concentration pathway (of greenhouse gases in the atmosphere to produce between 2.6 and 8.5 W m^{-2} of radiative forcing on the global climate system)
$\Omega_{calcite}$	The saturation state of calcite in solution ($\Omega_{aragonite} \approx 0.66 \; \Omega_{calcite}$)
[X]	Square brackets denote concentrations of aqueous element or compound X

1.   Introduction

1.1   *Context and Scope*

Stabilizing and reducing atmospheric carbon dioxide (CO_2) concentrations to avoid 'dangerous' climate change is one the greatest challenges facing humanity in the 21st Century. Long-term sustainable solutions include the reduction of CO_2 emissions by decarbonizing energy generation, demand reduction through efficiency improvements, and responsible land use management [*Edenhofer et al.,* 2014]. However, these require a tremendous change in our technological and socio-economic systems that may take decades or even centuries to implement. The Paris Agreement [*UNFCCC* 2015], which entered into force in November 2016, aims to hold global temperature changes below 2°C through nationally declared contributions to greenhouse gas emission reductions. While 136 countries have ratified the agreement, the pledged contributions are insufficient to prevent a 2°C temperature rise [*Rogelj et al.* 2016].

Many future scenarios that keep climate change below 2°C do so not only by limiting the use of carbon, but by using technology to limit the impact of carbon use on the atmospheric concentration. These technologies allow the use of fossil fuels but either prevent CO_2 emission into the atmosphere (e.g., carbon capture and storage,[*Metz et al.,* 2005]) or remove CO_2 from the atmosphere once there ('negative emissions', [*Fuss et al.,* 2014; *McLaren* 2012]).

The representative concentration pathway (RCP) that results in a likely temperature rise by 2100 below 2°C is RCP2.6 (Figure 1, see [*van Vuuren et al.,* 2011]), which suggests a cumulative emission of 880 Gt C (we use Gt C in this study, but these values can be converted to Gt CO_2 by multiplying by 3.66) This RCP explicitly includes 40 - 220 Gt C of negative emissions [*Edenhofer*, 2014]. Scenarios where more carbon is burned either result in warming in excess of 2°C, or require even more significant removal of CO_2 at source or from the atmosphere. With current conventional fossil fuel reserves ~3,000 Gt C [*McGlade and Ekins* 2015], carbon storage requirements could extend to thousands of Gt. There are few sinks with the capacity to store hundreds of Gt C, with that most often considered being CO_2 injection underground in depleted hydrocarbon reservoirs or saline aquifers. Estimates of carbon storage in this reservoir are on the order of 100-1,000 Gt C [*Bradshaw et al.,* 2007] Other options include biomass growth (~100 Gt C) [*Nilsson and Schopfhauser*, 1995], mineralization of natural (10^5 Gt C) [*Sanna et al.,* 2014] and waste (~50-100 Gt C) [*Renforth et al.,* 2011] materials, enhanced ocean productivity (26-180 Gt C) [*Denman* 2008], and the subject of this review: inorganic storage in the ocean.

The oceans contain ≈38,000 Gt C, some 45 times more than the present atmosphere, and oceanic uptake has already consumed close to 40% of anthropogenic C emissions [*Sabine and Tanhua*, 2010]. On long-timescales (~100-200 ka) the ocean and weathering will reduce atmospheric CO_2 to values close to pre-industrial [*Lord et al.,* 2016]. So the issue is not capacity, but rather a question of how to accelerate oceanic uptake and storage in a safe and cost effective way. Given the increasing reliance of future climate scenarios on negative emission, and the size of C sequestration that may be required, it is important to explore and understand the feasibility of all possible C sinks, including acceleration of the natural oceanic sink.

Sequestration of inorganic C in the ocean is the least represented climate mitigation strategies in the literature [*Bellamy et al.,* 2012]. This has led to considerable uncertainty about the potential storage capacity, environmental impact, and cost of this approach [*NAS* 2015]. The aim of this paper is to review all aspects of the inorganic C sink in the ocean, including the function of alkalinity in the natural oceanic C cycle (section 2), the changes in ocean chemistry imposed by artificial alkalinity changes (section 3), the stability of increased alkalinity in the ocean (section 4), technologies for increasing ocean alkalinity (section 5 and 6), and the potential environmental impact (section 6 and 7). This builds on existing general discussions of geochemical C sequestration, which ocean carbon storage is introduced in the context of other removal schemes [*Lackner* 2002; *Stephens and Keith* 2008]. Alkalinity storage in the ocean raises issues around environmental impact, quantification, monitoring, governance, and longevity, all of which will be explored in detail in this review.

Storage of C by increasing ocean alkalinity requires the extraction, processing, and dissolution of minerals. This results in chemical transformation of CO_2 and sequestration as bicarbonate and carbonate ions (HCO_3^-, CO_3^{2-}) in the ocean. Dissolution of a mole of Ca^{2+} or Mg^{2+} sequesters close to 2 moles of C (see section 2). So even dissolution of carbonate minerals (e.g., $CaCO_3$) which contain a mole of C leads to some drawdown of CO_2. Table 1 presents some reaction pathways for naturally occurring and anthropogenically produced minerals. A list of acronyms is included in the appendix.

1.2   History of research investigating ocean alkalinity as an engineered carbon sink

The use of enhanced ocean alkalinity for C storage was first proposed by *Kheshgi* [1995]. Realizing the slow rate of natural mineral dissolution, *Kheshgi* [1995] proposed the creation of highly reactive lime (CaO) or portlandite (Ca(OH)$_2$) from the calcination of limestone. Notionally, CaO or Ca(OH)$_2$ would readily dissolve in the surface ocean and sequester CO$_2$ through the reactions in Table 1. The high energy costs of creating lime, and research focus on other forms of climate change mitigation, has meant that the proposal was largely disregarded in the 1990's and early 2000's. Interest in ocean liming (and more generally ocean alkalinity for carbon storage) was reinvigorated around debates about geoengineering [e.g., *The Royal Society*, 2009]. In this context, the techno-economic feasibility of Ocean Liming was re-examined by *Renforth et al.,* [2013], who suggest similar energy and financial requirements to other air capture technologies. However, both *Kheshgi* [1995] and *Renforth et al.,* [2013] recognized that the production of lime from limestone may not be the most efficient process for increasing ocean alkalinity due to the large energy and CO$_2$ burden of calcination. The development of this idea and the proposed integration of mineral carbonation [*Renforth and Kruger* 2013] is expanded upon here in section 5. Consideration of ocean alkalinity carbon storage has largely been driven by technology proposals. An unpublished white paper [*Henderson et al.,* 2008] discussed the broad range of biogeochemical consequences of ocean liming, and highlighted knowledge gaps including poor constraints of the relationship between elevated carbonate mineral saturation and precipitation, uncertainty in the impact of elevated alkalinity on biology, and the rate of dispersion/dilution of added materials.

An alternative proposal was developed independently by *Rau and Caldeira* [1999], who suggested that the dissolution of carbonate minerals (e.g., CaCO$_3$) exposed to waste flue gas CO$_2$ and seawater (Accelerated Weathering of Limestone; AWL) as a means for increasing ocean alkalinity. The ultimate fate of the stored carbon is the same as ocean liming (i.e. HCO$_3^-$ and CO$_3^{2-}$ ions), but the reaction pathway is different. Raising the partial pressure of CO$_2$ to >5,000 μatm (at a total pressure of 1 atm) in contact with seawater, creates the conditions in which carbonate minerals can spontaneously dissolve. Therefore, contacting carbonate minerals, seawater and power station flue gas (10 % CO$_2$ at 1 atm), would result in increased alkalinity in the effluent discharged back to the ocean. The key limitation of this process is the amount of water required, in which thousands of tons of seawater are needed per ton of CO$_2$ sequestered. However, *Rau and Caldeira* [1999] point out that the once-through cooling water consumed within some power stations equates to around 400 tons per ton of CO$_2$ emitted, thus lowering the additional water requirements of AWL. *Caldeira and Rau* [2000] suggested the cost and environmental impact compares favorably to direct injection of CO$_2$ in the deep ocean. The engineering requirements were developed in *Rau et al.,* [2007], and *Langer et al.,* [2009] who explored the processing and handling costs of an up-scaled industry (discussed further in section 5). *Rau* (2011) provided results from the operation of a bench-scale experiment, which demonstrated high levels of CO$_2$ sequestration largely as a function of the solution/gas volume ratio within the reactor. He showed that a solution:gas flow ratio of 8 was sufficient to capture 85 % of the CO$_2$ from a 10 % gas at 1 atm. *Chou et al.,* [2015] investigated the operation of a two stage AWL reactor in which gas-liquid equilibration occurs prior to solid-liquid equilibration, and found lower carbon

sequestration efficiencies of <50 %. Despite this work, AWL research has been largely confined to small-scale experiments.

The dissolution of minerals in a carbonic acid solution is relatively slow compared to stronger acids. Therefore, *House et al.,* [2007] proposed the creation of alkalinity in the ocean through electrolysis (equation 10 in Table 1) and the reaction of the Cl_2 and H_2 gaseous products in a fuel cell to produce electricity and hydrochloric acid (equation 11). The acidity is then neutralized through the dissolution of a silicate mineral (equation 12). While the kinetics of this process would be rapid, the energy requirements are substantial (section 5). An alternative electrochemical approach was proposed in which $CaCO_3$ [*Rau* 2008] or a magnesium silicate [*Rau et al.,* 2013] was dissolved around an acidic anode and a high pH ($Ca(OH)_2$ or $Mg(OH)_2$) solution was created around the cathode. The high pH solution would then be used to remove CO_2 from air directly, with the resulting bicarbonate-rich solution added to the ocean. Alternatively, the hydroxide could be added to the ocean to consume excess CO_2. In either case ocean alkalinity is increased.

A number of studies investigate the potential of adding naturally occurring minerals directly to the land surface [*Hartmann et al.,* 2013; *Hartmann and Kempe* 2008; *Köhler et al.,* 2010; *Manning* 2008; *Manning et al.,* 2013; *Moosdorf et al.,* 2014; *Renforth* 2012; *Schuiling and Krijgsman* 2006; *Taylor et al.,* 2016; *ten Berge et al.,* 2012), coastal environments (*Hangx and Spiers* 2009; *Schuiling and de Boer* 2010; *Montserrat et al.,* 2017; *Meysman and Montserrat* 2017], and the open ocean [*Harvey* 2008; *Köhler et al.,* 2013]. The feasibility of such approaches is still highly contested given the slower dissolution kinetics at ambient temperatures and pressures, and the solubility limits of naturally occurring minerals. However, the direct comparison to elevated temperature/pressure mineral carbonation is problematic, as constraints of reactor size are removed. In chemical engineering, a reaction time on the order of minutes is required to facilitate reasonable reactor sizes for commercial operations. Reactions in the open environment could have a time constraint on the order of years (10^5 -10^6 times longer) because of the much larger volume. On one hand, spreading natural minerals on the land surface [reviewed by *Hartmann et al.,* 2013] potentially allows the naturally corrosive chemistry in soil pore waters [*Manning and Renforth* 2013] to be used to accelerate dissolution kinetics. Notionally, the products of dissolution (including increased alkalinity of rainwater) are transported to the ocean via runoff, rivers and shallow groundwater. Alternatively, *Manning* [2008] and *Manning et al.,* [2013] suggest that solution chemistry in soil pore-waters may promote the precipitation of carbonate minerals, which has been demonstrated widely in anthropogenic soils [*Renforth et al.,* 2009; *Washbourne et al.,* 2015, 2012]. If so, the precipitated carbonate becomes the sink for CO_2 rather than ocean alkalinity. If ocean HCO_3^- and CO_3^{2-} were the sole repository of the carbon, then others argue that such an approach may be limited by the saturation state or environmental pH limits of the rain/river water [*Köhler et al.,* 2011]. It may be possible to use the constantly refreshed water of coastal environments, in which wave action could increase the attrition of mineral particles [*Schuiling and de Boer* 2010; *Montserrat et al.,* 2017; *Meysman and Montserrat* 2017]. However, the slightly alkaline pH of ocean water is likely to retard dissolution kinetics so that very small particles are needed [*Hangx and Spiers* 2009]. For instance, *Köhler et al.,* [2013] investigated the direct addition of olivine particles to the surface ocean. As it is imperative that the added particles dissolve within the mixed layer, they suggest that crushing and grinding to a diameter of 1 μm is necessary.

It is highly unlikely that any of the above proposals (e.g., Figure 2) will form humanity's sole response to climate change. However, at this stage, there is nothing that warrants their exclusion from research and policy development, particularly considering that mineral weathering and ocean alkalinity production is the primary mechanism whereby nature will eventually consume and store anthropogenic CO_2.

2. Ocean Carbon Cycle

Several inter-related processes are responsible for inorganic removal of CO_2 from the atmosphere: weathering of silicate and carbonate rocks, reaction with carbonate sediments, and the alkalinity, or buffering capacity, of the ocean. This section provides a brief overview of these processes and their operation in the natural Earth system. It is important to note that these processes are distinct from "the biological pump" in which organic material is produced and settles to the deep ocean (equating to a carbon flux of ~10 Gt C a^{-1}). That process also plays a critical role in the C cycle and is the focus of C-sequestration schemes involving ocean fertilization [e.g., *Wallace et al.,* 2010; *Williamson et al.,* 2012]. Overview of the full carbon cycle has also been provided elsewhere, including recently by the IPCC [*Ciais et al.,* 2014], and is not repeated here.

2.1 Weathering of silicate minerals

Many silicate minerals were formed at high temperature and are unstable in the presence of water at the temperature and pressure conditions of the surface Earth. These minerals break down slowly at the surface in a variety of reactions together referred to as chemical weathering. At its simplest, these reactions can be characterized by the weathering of wollastonite ($CaSiO_3$, equation 13).

$$CaSiO_3 + CO_2 \leftrightarrow CaCO_3 + SiO_2 \qquad \text{equation 13}$$
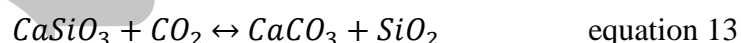
Other silicate minerals involve a full array of elements and produce a range of other end-products, frequently including clay minerals, but, as above, are often characterized by the consumption of CO_2 (see Table 1 for examples).

These weathering reactions are exothermic, but do proceed slowly due to the significant kinetic limitation created by the strong bonding found in silicate minerals. Because of their importance in global geochemical cycles, controls on the rates at which these reactions proceed have been extensively studied for individual minerals and in natural soils and catchments [*White and Brantley* 1995]. The principle factors controlling weathering rate are the temperature, run-off (to provide water to remove reaction products), and the available surface area (i.e. the grainsize of the rock or mineral [*West et al.,* 2005]). Biological activity also accelerates weathering [e.g., *Cockell* 2011]

The total removal of CO_2 from the atmosphere by natural weathering of silicate minerals may be as high as ≈0.25 Gt C a^{-1} [*Suchet and Probst* 1995; *Gaillardet et al.,* 1999; *Hartmann et al.,* 2009] but is poorly constrained due to difficulty in separating fluxes from weathering silicates and carbonates, and may be significantly smaller [*Liu et al.,* 2011]. On geological timescales, this removal flux is balanced by volcanic sources of CO_2 from the Earth interior.

These weathering and volcanic fluxes are very small compared to a total mass of carbon in the ocean-atmosphere-biosphere system of ≈42,000 Gt C [*Ciais et al.,* 2014], so that imbalances between weathering and volcanism must be sustained over long periods (i.e. 100-1,000 ka) to cause significant direct change to the surface-Earth carbon system and climate. Nevertheless, such changes in the weathering/volcanism balance are fundamental in controlling the climate system, and the temperature dependence of weathering rate provides a long-term negative feedback on climate change to keep Earth's long-term climate in a relatively narrow range [*Berner et al.,* 1983].

2.2 *Alkalinity control of ocean C content*

Carbon dioxide reacts with water to form the weak acid, carbonic acid (equation 14).

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \qquad \text{equation 14}$$
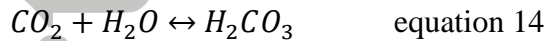
This acid dissociates to form bicarbonate ion (HCO_3^-) and carbonate ion (CO_3^{2-}), with the extent of dissociation controlled by the excess base in the water. Alkalinity is, by definition, a measure of this excess base (i.e. the capacity of a solution to neutralize acid). As alkalinity increases, more dissociation of carbonic acid occurs, and greater amounts of C are held in solution as HCO_3^- and CO_3^{2-} (see Box 1 for details). Seawater has a high alkalinity (2.5 mEq kg^{-1}) which, coupled to the large volume of the ocean, make oceanic inorganic C by far the largest C reservoir in the ocean-atmosphere-biosphere system (≈42,000 Gt C; [*Ciais et al.,* 2014]).

The functional value of alkalinity as a chemical property is that it remains unchanged with pressure or temperature, its change describes the cumulative effect of numerous chemical equilibria, and it is a measurable parameter that is useful in reconstructing those systems. There are many definitions of alkalinity, with an entire chapter in the definitive text book, *Zeebe and Wolf-Gladrow* [2001] devoted to this subject. In the context of this review, however, we use the definition provided by *Dickson* [1981] in which 'total alkalinity' (A_T) is the proton deficiency of a solution relative to an arbitrarily defined zero point (with additional useful definitions provided in text of the supporting information [*Drever*, 1988]). The zero point being the pK value of 4.5 at 25°C and zero ionic strength, such that acids with $K < 10^{-4.5}$ (e.g., carbonic acid, boric acid) are proton acceptors and acids with $K > 10^{-4.5}$ (e.g., hydrofluoric acid, hydrochloric acid) are proton donors. (equation 15).
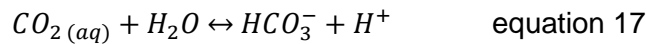
$$A_T = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^-] + 2[PO_4^{2-}] + [H_3SiO_4^-] + [HS^-] + 2[S^{2-}] + [NH_3^-] - [H^+] - [HSO_4^-] - [HF] - [H_3PO_4] \qquad \text{(equation 15)}$$

Box 1: The carbonate system

A partial pressure difference of CO_2 over water will promote transfer across the liquid-gas interface and the dissolution of CO_2 into the liquid. Some of that CO_2 will hydrate to form carbonic acid (H_2CO_3). As aqueous CO_2 is far more concentrated, it is convenient to express $[H_2CO_3]$ and $CO_{2(aq)}$ collectively as $CO_{2(aq)}$. The equilibrium concentration of CO_2 in the water is governed by Henry's law (equation 16):

$$[CO_{2\,(aq)}] = K_{CO_2} \cdot fCO_2 \qquad \text{equation 16}$$

Where fCO_2 is the fugacity of CO_2 (fCO_2 = pCO_2 for practical purposes), and K_{CO2} is the Henry's constant. The hydrated aqueous CO_2 will deprotonate into bicarbonate (HCO_3^-) and carbonate ions (CO_3^{2-}) (equations 17 and 18). The relative quantities of which are given by the equilibrium constants K_1 and K_2 (equations 19 and 20).

$$CO_{2\,(aq)} + H_2O \leftrightarrow HCO_3^- + H^+ \qquad \text{equation 17}$$

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \qquad \text{equation 18}$$

$$K_1 = \frac{[HCO_3^-][H^+]}{[CO_{2\,(aq)}]} \quad \text{Equation 19} \qquad K_2 = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} \qquad \text{equation 20}$$

H^+ is removed from solution during weathering (equation 1), which results in the forward reactions in equations 17 and 18. Aqueous CO_2 is reduced, and HCO_3^- and H^+ produced, to compensate. Simultaneously, some HCO_3^- will be converted to CO_3^{2-} (equation 18). CO_2 will be transferred from the gas phase into the solution to maintain equilibrium in equation 14).

It is possible to constrain and calculate (at known temperature and salinity) the concentrations of $[CO_{2(aq)}]$ $[HCO_3^-]$, $[CO_3^{2-}]$, pH, DIC, Alkalinity, by only knowing two of the parameters. Details for these calculations are provided in *Zeebe and Wolf-Gladrow* [2001].

The saturation state of a solution with respect to a mineral is defined in equation 21 (for calcium carbonate). Ω = 1 suggests a solution in thermodynamic equilibrium with the mineral phase, whereas, Ω <1 or >1 suggests undersaturation and oversaturation respectively.

$$\Omega = \frac{\gamma_{Ca}\gamma_{CO_3}[Ca^{2+}][CO_3^{2-}]}{K_{sp}} \qquad \text{equation 21}$$

Where γ_{Ca} and γ_{CO3} represent the activity coefficients of calcium and carbonate ions

2.3 *The combined impact of weathering and ocean alkalinity*

Weathering of silicates on land can remove CO_2 from the atmosphere without involving the ocean if the cations releases are all re-precipitated as secondary minerals (e.g., $CaCO_3$) on land For example, the reaction between olivine and CO_2 to produce magnesium carbonate, equation 22).

$$Mg_2SiO_4 + 2CO_2 + 2H_2O \rightarrow 2MgCO_3 + H_4SiO_4 \qquad \text{equation 22}$$
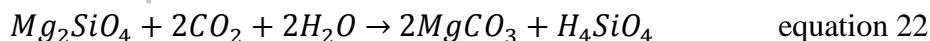
If, on the other hand, the cations are transported to the ocean they increase the alkalinity, and lead to transfer of CO_2 to HCO_3^- and CO_3^{2-}. The resulting decrease of dissolved CO_2 causes uptake of atmospheric CO_2 by air-sea gas exchange.

At the pH of seawater, most of C ($\approx$80-90%) is in the singly-charged HCO_3^- form (see Box 1). Addition of ions with a divalent charge, such as Ca^{2+}, is therefore compensated by formation of two singly-charged ions containing C, and consequently to uptake of two CO_2 molecules from the atmosphere. In practice the uptake is 1.4 to 1.7 molecules because of the presence of some CO_3^{2-}, (i.e. a reduction of uptake efficiency, η, by 15% - 30%), depending on temperature, salinity and pCO_2 (equation 23; see supporting information for derivation [*Dickson*, 1990]). The products of silicate weathering (e.g., equation 2) therefore have potential to make a larger impact on CO_2 removal if they reach the ocean than if they re-precipitate as secondary minerals.

$$\frac{\Delta C_T}{\Delta A_T} = \eta = (S \cdot 10^{-3.009} + 10^{-1.519})ln(pCO_2) - (S \cdot 10^{-2.100}) - (T \cdot pCO_2)(S \cdot 10^{-7.501} - 10-5.598-T\cdot10-2.337+10-0.102 \qquad \text{equation 23.}$$

Where pCO_2 is the partial pressure of CO_2 in equilibrium with the solution (in µatm), and T is the temperature (in °C), and S is the salinity (in %). This relationship was derived from CO2sys [*Lewis et al.,* 1998] using seawater scale pH and equilibrium constants from *Roy et al.,* [1993]. For pCO_2 = 400 ppmv, S = 35 %, and T = 17°C, η = 0.831. This implies that 0.83 moles of carbon are stored per mole of H^+ consumed, or 1.66 per mole of Ca^{2+} or Mg^{2+} added to the ocean.

The divalent cations present in carbonate minerals (e.g., $CaCO_3$) mean that even weathering of carbonates can lead to removal of CO_2 from the atmosphere. If carbonate minerals (e.g., in limestone) dissolve on land and subsequently re-precipitate, there is no net effect on CO_2, but if the Ca^{2+} reaches the ocean, the resulting increase in alkalinity leads to uptake of CO_2. Because the dissolution of $CaCO_3$ releases a C atom, the net impact of such dissolution on CO_2 uptake is smaller (0.4 to 0.7) than Ca^{2+} ions released from silicate weathering, but it is important to note the rather counter-intuitive fact that dissolving $CaCO_3$ in seawater leads to uptake of CO_2 from the atmosphere.

2.4   The oceanic alkalinity cycle

To a first approximation, the active oceanic cycle of alkalinity is that of Ca^{2+}, and particularly the processes of formation and dissolution of $CaCO_3$ (Figure 3 A). Seawater in the surface ocean is supersaturated with respect to calcite by a factor of about 4 times (and aragonite by about 2.5 times), but the presence of other elements in seawater prevent inorganic precipitation of calcite in almost all oceanic settings [*Berner* 1975]. Many species of plant and animal have, however, developed chemical approaches to overcome this limitation and precipitate $CaCO_3$ as calcite or aragonite, leading to removal of Ca^{2+} (and alkalinity) from the surface ocean. This removal occurs in the shallow water, neritic zone, particularly in large tropical reefs and carbonate platforms (e.g., corals, halimeda) and in the open ocean in planktonic ecosystems (e.g., coccolithophores, foraminifera). By removing alkalinity,

biological production of $CaCO_3$ from surface seawater leads to a flux of CO_2 from the ocean to the atmosphere [*Frankignoulle et al.,* 1994]. This is in contrast to the biological production of organic C (i.e. soft tissue), which causes subsequent ocean uptake of CO_2.

The deep ocean is characterized by dissolution of $CaCO_3$ and an increase in alkalinity (Figure 3 B; and *Andersson* [2014]). Remineralization of settling organic C at depth releases CO_2 and decreases the pH of seawater. This, coupled to a decrease in calcite solubility with increasing pressure, means that at some depth in the ocean, termed the calcite saturation horizon, water become undersaturated for calcite (Figure 4; [see *Zeebe* 2012]). At slightly greater depth – the lysocline – dissolution rates are sufficiently fast that sediment start to lose an appreciable fraction of the calcite settling from above. The depth at which dissolution of calcite removes virtually all calcite is termed the calcite compensation depth. This deep-ocean dissolution of $CaCO_3$ leads to an increases in alkalinity of up to 10% relative to surface waters. It serves to partially neutralize the acidity generated by remineralization of organic matter; a process termed carbonate compensation [*Ridgwell and Zeebe*, 2005]. On timescales longer than the circulation of the ocean (i.e. >1 ka), carbonate compensation alters the alkalinity of the whole ocean and acts as a natural buffer to offset changes in atmospheric CO_2 created by imbalances elsewhere in the C cycle.

Upwelling of deep elevated alkalinity waters to the surface, which typically happens at high latitudes in the ocean, leads to surface variation in alkalinity of about 5% (Figure 5). Seasonal variation of up to 80-110 µeq kg^{-1} are also seen, resulting from changes in vertical mixing [*Lee et al.,* 2006], riverine inputs [*Cai et al.,* 2010], and especially primary production [*Wolf-Gladrow et al.,* 2007].

2.5 The oceanic alkalinity cycle

Imbalances between the input and removal fluxes of alkalinity can result in changes in global oceanic alkalinity and therefore the capacity of the ocean to store C. Such alkalinity-induced changes in partitioning of C between atmosphere and ocean are thought to play an important role in controlling climate change on timescales of 1 ka and longer [e.g., *Zeebe* 2012]. Through studying these natural changes in ocean alkalinity, it may be possible to constrain future changes in ocean chemistry from artificial changes in ocean alkalinity.

The oceanic residence time of Ca^{2+} with respect to riverine input is greater than 1000 ka (Figure 3A), on which timescale the balance between volcanic degassing and sedimentary removal of C becomes a dominant control. So the major way in which alkalinity changes become important is changes in precipitation and particularly dissolution of $CaCO_3$ (i.e. through carbonate compensation). Two time periods, (the Pleistocene and the Paleocene-Eocene) provide an indication of such processes.

Several processes may have led to higher ocean alkalinity during the glacial periods of the Pleistocene (e.g., the last glacial, 20 ka ago). Such higher alkalinity would increase storage of CO_2 in the ocean, and contribute to the decrease of atmospheric pCO_2 known to be a significant cause of glacial cooling. One such process, operating in the surface ocean, is that lower glacial sea level would leave less continental shelf area for formation of carbonate

reefs. The resulting decrease in $CaCO_3$ precipitation, and probable erosion and dissolution of old reefs, would increase global ocean alkalinity [*Opdyke and Walker* 1992]. Another process, but operating in the deep ocean, stems from changes in ocean circulation in the Atlantic leading to sluggish deep waters containing substantially more re-mineralized CO_2. This would lower deep-water pH to raise the lysocline, and thereby add alkalinity by dissolution of $CaCO_3$ [*Boyle* 1988; *Sigman et al.,* 2010].

Geochemical proxies have been developed to reconstruct past aspects of the ocean carbonate system, with two, measured in marine carbonates, seeing the greatest use: carbonate B isotope composition systematically reflects changing concentrations of B species with pH, and an empirical relationship is observed between carbonate B/Ca and the concentration of CO_3^{2-}. Application of such proxies has been used to reconstruct past ocean carbonate chemistry. One such study indicates higher alkalinity in the glacial ocean [*Rickaby et al.,* 2010], though this is not observed in all ocean regions [*Zeebe and Marchitto* 2010]. No single model is yet accepted to explain glacial-interglacial atmospheric pCO_2 cycles, but it is clear that the CO_2 removed from the atmosphere during glacials was stored in the ocean. Alkalinity changes may have played a role in this storage (see *Sigman and Boyle* [2000] for a summary of glacial-interglacial pCO_2 mechanisms).

A second example of the role of ocean alkalinity in the global carbon cycle is provided by an abrupt warm period 56 Ma ago; the Paleocene-Eocene Thermal Maximum (PETM). This event is thought to have been triggered by a massive release of C to the ocean-atmosphere system (>2,000 Gt C) probably from catastrophic breakdown of methane clathrates [*Archer et al.,* 2009]. Although the source of the C differs, this rapid C release is widely seen as a useful analogue for the likely response of the Earth system to present-day anthropogenic C release [*McInerney and Wing* 2011]. At the PETM, the large increase in CO_2 in the ocean resulting from C release led to significant decreases in ocean pH and shoaling of the lysocline to increase ocean alkalinity [*Zachos et al.,* 2005]. This carbonate compensation buffered a significant fraction of the change in CO_2 and occurred on a timescale of <10,000, short geologically, but still a slow response relative to human timescales. The controls of atmospheric CO_2 on glacial/interglacial time periods are reviewed by *PAGES* [2016] and *Archer et al.,* [2000].

3.   Modeling elevated alkalinity

The importance of the carbon cycle for climate ensures that a wide range of models have been developed to understand and predict its operation. These range from simple box models to highly sophisticated carbon components to general circulation models. These models can be used to provide information about the likely impact of intentional addition of alkalinity to the oceans.

3.1 Box models

At its very simplest, the ocean can be modeled as a single box to consider the scale of change on the natural system required to uptake significant amounts of anthropogenic CO_2. Assuming addition of Ca^{2+}: adding one mole of Ca^{2+} to a single-box ocean causes an increase in HCO_3^- and CO_3^{2-} and the uptake of ≈1.7 moles of CO_2 (see section 2.3). Addition of sufficient Ca^{2+} to fully compensate for present anthropogenic emission of 10 Gt C a^{-1} therefore requires addition of 20 Gt Ca^{2+} a^{-1}. This is ≈20 times the annual riverine input of

Ca^{2+}, a very significant perturbation, and obviously a very substantial undertaking in engineering terms. The large volume of the ocean and its high Ca^{2+} concentration, however, mean that the oceanic perturbation is very much smaller and only a 0.9 mmoles kg^{-1} increase in Ca^{2+} is required. Even if considering the surface ocean alone this annual addition is less than a 0.3% increase in total Ca^{2+}. This simple one-box approach demonstrates the possibility of substantial uptake of C to the ocean with relatively small changes in the ocean, but also the scale of the effort required to effect significant alkalinity addition.

At the next level of sophistication, models which divide the ocean into a small number of boxes can be used to assess changes caused by continued addition of ocean alkalinity. An example is shown in Figure 6, which imposes the 20-fold increase to riverine alkalinity fluxes, as required to compensate for 10 Gt C a^{-1} anthropogenic emissions, for 300 years. Such a model demonstrates the expectation that long-term alkalinity addition could compensate for anthropogenic C addition, and could prevent the associated decrease in ocean pH. They also show the scale of change in alkalinity in the surface and deep ocean that results from this intervention, and the significant changes in lysocline depth that arise both from anthropogenic C emission, and from alkalinity addition. *Paquay and Zeebe* [2013] used a slightly more complex model with 10 boxes (for the surface, intermediate and deep ocean for the 3 largest ocean basins and the high latitudes) to investigate the impact of adding alkalinity across the entire surface ocean to totally compensate for various carbon emission scenarios. In that study, sufficient alkalinity was added to exactly compensate for pH changes imposed by fossil fuel addition, which was possible even in their largest emission scenario (compensating for 5,000 Gt C over 500 years) by adding up to 15 Gt Ca^{2+} a^{-1}).

3.2 Spatially resolved models

To more completely mimic the ocean response to addition of alkalinity, ocean models with high spatial resolution which capture both ocean circulation and the operation of the carbon cycle can be used. *Ilyina et al.,* [2013], for instance, used the Hamburg Ocean Carbon Cycle Model to simulate the response to the addition of sufficient alkalinity to counteract all anthropogenic emissions from the 'business as usual' A1B baseline scenario ($\approx$1,400 Gt C by 2100). This model assumed addition in particular patches of the surface ocean, equivalent to one seventh of the ocean surface, and was able to assess the distribution of alkalinity and its effects into the global ocean (Figure 7). Alkalinity increased, as expected, to between 2.3 and 3.0 mEq kg^{-1} for most of the ocean, but rising up to 5.5 mEq kg^{-1} in the north Atlantic and North Pacific where alkalinity addition was imposed. Similarly, pH was generally returned to values similar to pre-industrial in much of the ocean, but was elevated around application regions, and calcite saturation similarly increased ($\Omega_{calcite} \approx 20$). As for the simple box models, this spatially-resolved modeling, indicates the general success of alkalinity addition in generating ocean uptake of CO_2, but highlights clearly the challenges imposed by extreme ocean changes (e.g., elevated pH and carbonate saturation) in regions of alkalinity addition.

Subsequent studies have also used full ocean models to assess the impact of alkalinity addition. *Ferrer-Gonzalez and Ilyina* [2016] used a fully integrated Earth System Model and added sufficient alkalinity to compensate emissions from RCP8.5 to a level congruent with

RCP4.5. Despite imposing a uniform distribution of alkalinity addition, the ocean response was more marked in some regions, notably the Arctic, where pH climbed to 8.6 and $\Omega_{calcite} \approx 10$, and the tropics where $\Omega_{calcite}$ was also high. *Keller et al.,* [2014] (using the UVic model) also imposed a uniform alkalinity addition, but limited the amount of addition to that which could be delivered by modern ship fleets (≈ 6 Gt Ca^{2+} a^{-1} as $Ca(OH)_2$ added by uniformly increasing total alkalinity). This level of addition created only modest uptake of CO_2 from the atmosphere (166 Gt C by 2100; ~8% of the A1B/RCP8.5 emissions scenario). While the ocean system was relatively unperturbed in this model, it powerfully illustrates the engineering difficulty inherent in delivering the very large amounts of alkalinity required to compensate for any significant fraction of emitted CO_2. It is likely that alkalinity addition could not be the sole mechanism used for any substantial negative emissions approach, but would be part of a portfolio of measures.

Most models of alkalinity addition do not specify the chemical added to generate change, or assume pure $Ca(OH)_2$, which is effectively "pure" alkalinity. Real world application of alkalinity might, however, be pursued by addition of a particular mineral. *Köhler et al.,* [2013] investigated one such scenario by using a biogeochemical model to assess the impact of direct addition of olivine to the ocean surface. Olivine (forsterite rich, Mg_2SiO_4) dissolution increases total alkalinity with a molar 1:4 olivine/alkalinity ratio) but also releases silicon. The authors force their model with a range of olivine addition scenarios (from 1 to 10 Gt a^{-1}) for localized (ship) and global distribution scenarios. Surprisingly, while there is elevated alkalinity, the model predicts a decrease in $CaCO_3$ export and an increase in organic carbon export due to the fertilization effect of dissolved silica on diatoms. Natural silica flux into the ocean is approximately 170 Mt of Si a^{-1} (e.g., from riverine input) [*Tréguer et al.,* 1995]. There would be approximately 200 Mt of Si released for every Gt of olivine added to the ocean, so it is not surprising that a significant fertilization effect is observed. Olivine also contains iron (as fayilite, Fe_2SiO_4), which may also fertilize biological activity. *Hauck et al.,* [2016] suggests that theoretically around 0.6 Gt C a^{-1} could be sequestered for every Gt a^{-1} of olivine added to the surface ocean, with 57%, 37%, and 6% of the effect coming from alkalinity, iron, and silicon respectively. A complication in this relates to the rate of olivine dissolution required, which are assumed to be instant and complete in the modeling. If CO_2 is removed from the atmosphere, terrestrial carbon sinks would release CO_2 [e.g., *Vichi et al.,* 2013]. This 'rebound' together with emissions from material extraction, processing and transport would also diminish the net sequestration potential of this and other alkalinity addition approaches

The handful of modeling studies investigating an intentional increase of ocean alkalinity have been useful in broadly defining the relationship between carbon sequestration extent and the impact on the ocean carbonate system. Figure 8 shows the range of pathways from these models in Ω-pCO$_2$ space. This figure shows the decrease in $\Omega_{calcite}$ that has already occurred due to anthropogenic CO_2 emissions, and the further decrease expected as CO_2 emissions continue. Alkalinity levels are depicted by the contours (the shaded region representing levels in the modern ocean), and the impact of various model scenarios on this alkalinity.

The models shown on this figure demonstrate the potential advantages to ocean saturation state of alkalinity addition. For instance, some studies suggest increased risk to coral ecosystems when $\Omega_{aragonite}$ falls below 3 ($\Omega_{calcite} \approx 4.5$) in the open ocean surrounding reefs [*Ricke et al.,* 2013]. These ecosystems generally occupy waters with elevated carbonate

saturation, so their fate may be visualized in Figure 8 by the future trajectory of the upper part of the shaded box. By increasing saturation state, alkalinity addition could keep the ocean at a saturation state conducive to continued coral reef health.

4.   Longevity of carbon storage

4.1 The saturation state of carbonate minerals in the ocean

The residence time of dissolved inorganic carbon in the whole ocean is around 100 ka, which would effectively form a permanent storage reservoir on human timescales. However, this may decrease if alkalinity is reduced by increased formation and export of carbonate minerals from the surface ocean. Given that seawater is already supersaturated with respect to some magnesium and calcium carbonate minerals (see Table S1 in supporting information), it is intuitive to think that any additional alkalinity would precipitate out of solution. However, spontaneous nucleation is strongly inhibited in seawater, and carbonate production is thought to be largely biologically controlled, although there is no estimate of the relative proportions. This section considers what controls carbonate production in the ocean, and how this may change if alkalinity was intentionally increased.

Through transport, mixing, and export, elevated alkalinity at the surface will also eventually have an impact on conditions in the interior ocean. Elevated alkalinity in the water column will increase the carbon compensation depth (CCD; the depth in the oceans at which calcite dissolves quicker than it is supplied; [*Ridgwell* 2007]). A deeper CCD will lead to an increase in the extent of sediment exposed to elevated saturation states, and notionally an increase in calcification and export, and thus increase the net removal of $CaCO_3$ from the ocean. This partially undoes the effect of adding alkalinity. However some of this alkalinity will eventually be returned to the surface through upwelling. This effect is therefore a long-term negative feedback. However, 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 on human timescales. *Barker et al.,* [2006] suggest that elevated organic carbon export associated with carbonate production at the surface, may offset any CO_2 release, either through sequestration of organic carbon into sediments/interior ocean, or through enhanced dissolution of sediments from increased oxidation of organic carbon.

It is critical for the assessment of carbon storage due to ocean alkalinity to understand its overall impact on the carbon cycle, particularly on carbon production and export. The following sections present an overview of biological and abiotic controls of carbonate formation in the ocean.

4.2 Biological carbonate precipitation and dissolution

Carbonate precipitation is a key feature in the physiology of a large number of ocean dwelling organisms [*Addadi et al.,* 2006; *Müller* 2011]. Distinction is often made between pelagic (e.g., coccolithophores, foraminifera, pteropods/heteropods) and benthic (e.g., corals, molluscs, and crustaceans) calcifiers. Figure 9 shows the typical morphology of a coccolithophore and foraminifera. There is considerable variation in the mechanisms of calcification [*Müller*, 2011] which result in species/genus variability to environmental stimuli. As such, research investigating species and ecosystem response to ocean acidification

has produced variable results [*Ries et al.,* 2009]. Generally, species that are more efficient at maintaining pH in the internal environment in which they calcify are less affected by changes in carbonate chemistry of the ambient environment.

Elevated CO_2 in the atmosphere lowers $[CO_3^{2-}]$ in the ocean, which puts stress on shell forming organisms ('ocean acidification'). Extensive research has been conducted over the last 20 years to understand the impact of ocean acidification on marine biota and the global carbon cycle [*Doney et al.,* 2009]. Most of this research omits the investigation of elevated saturation states (e.g., Figure 10, which is not exhaustive, but indicative), and primarily focuses on manipulating $[CO_{2\,(aq)}]$ rather than alkalinity.

Phytoplanktonic calcifiers are responsible for a considerable proportion of particulate inorganic carbonate production in the surface ocean. They produce carbonate minerals in controlled microenvironments within the cell [*Marsh* 2003]. By regulating the concentration of Ca^{2+}, CO_2 and pH they can express a high degree of control on the internal saturation state of carbonate minerals. The response of these organisms to an acidifying ocean has been well studied (references in Figure 10). However fewer studies investigate the impact of elevated alkalinity on calcification rate. *Langer et al.,* [2006] investigated a wide range of aqueous carbon dioxide levels by the addition of hydrochloric acid or sodium hydroxide in a closed single species culture experiment ($\Omega_{calcite}$ from 2 to 13, pH 7.8 to 8.7). They measured the cellular carbon content of *Calcidisus leptoporus* and *Coccolithus pelagicus* (important primary producing coccolithophore species). Both species showed a reduction in calcification at elevated calcite saturation, possibly in response to lower concentrations of aqueous CO_2. As ocean acidification is concerned largely with $[CO_{2\,(aq)}]$ and the resulting decrease in $[CO_3^{2-}]$, it is difficult to interpret ocean acidification results for ocean alkalinity carbon storage, which would promote a different relationship between $[CO_{2\,(aq)}]$ and $[CO_3^{2-}]$. For instance, it is possible to modify dissolved inorganic carbon (DIC) while maintaining constant pH to create conditions in which pCO_2 and $\Omega_{calcite}$ are simultaneously elevated [*Rickaby et al.,* 2010]. In these experiments there was little change in particulate inorganic carbon production (for *Gephyrocapsa oceanica and C. pelagicus* at $pCO_2 = 1,800$ ppmv, and $\Omega_{calcite} = 13$), whereas variations in organic carbon fixation were detected. However, *Hermoso* [2015] demonstrated a parabolic relationship between pH (and Ω) and growth rate for the same species. The results in *Bach et al.,* [2011] for *Emiliania huxleyi* are highly relevant to ocean alkalinity addition. By undertaking two experimental regimes in which pCO_2 is manipulated while allowing pH to vary or maintaining it at a constant value, the results decouple the impact of A_T and $[CO_2]$ on inorganic carbon production, and suggest a plateau at around $A_T = 4.9$ mEq kg^{-1}.

Although coral reefs constitute only a small proportion of the ocean they are responsible for up to 50% of the global $CaCO_3$ production [*Mackenzie and Andersson* 2013; *Smith and Kinsey* 1976]. Species of coral express a wide degree of control on the chemistry of their calcifying fluids. Those that have little control generally follow an abiotic relationship between Ω and calcification rate (Figure 11, see below). Whereas, some coral species have evolved a capacity for buffering against lower Ω [*McCulloch et al.,* 2012]. The response of corals to elevated saturation states is poorly constrained. While corals are responsible for

carbonate production, they are also the site for dissolution (e.g., through raised pCO_2 from respiration). Generally, the rate of dissolution follows an abiotic relationship with Ω, which will likely be impeded by elevated alkalinity. *Schneider et al.,* [2011] investigated the response of *Stichopus herrmanni* and *Holothuria leucospilota* (species of sea cucumber) in chemically isolated incubation experiments. These species dissolve calcium carbonate particles within their digestive tract and secrete solutions with elevated levels of alkalinity. In these experiments, alkalinity levels increased by around 0.1 and 0.05 mEq kg^{-1} for *S. Herrmanni* and *H. leucospilota* respectively (70-85 % due to the accelerated dissolution of carbonate, the remainder due to ammonia secretion). The dissolution of carbonate minerals is an important component of the natural carbon cycle (0.1 – 0.2 Gt C a^{-1}), which may be impacted by elevated alkalinity.

Some paleoclimate research attempts to correlate the shell mass or density of marine organisms to the carbonate chemistry of the oceans. Such a record of past calcification rates are important for understanding the potential effects of ocean acidification, but could also be useful for constraining the stability of elevated alkalinity. For instance, *Barker and Elderfield* [2002] derive a relationship between $[CO_3^{2-}]$ of seawater to the shell mass of *Orbulina universa* (a planktonic foraminifera) picked from sediment. Assuming the growth time for the organism remains relatively constant, the shell mass is directly analogous to calcification rate. *Bijma et al.,* [2002] suggest a linear relationship between shell mass and $[CO_3^{2-}]$ (SW = 29.5 + 0.051$[CO_3^{2-}]$), which can be expressed as a function that relates the change in relative growth rate (ΔR) to the change saturation state (%ΔR = 2.0 $\Delta\Omega_{calcite}$, assuming constant $[Ca^{2+}]$ = 10 mmoles kg^{-1}, current $\Omega_{calcite}$ = 4.8, pK_{sp} = 5.62, current core-top shell mass of 38 µg). This suggests that the calcification rate of *O. universa* would increase around 12% for a future ocean with $\Omega_{calcite}$ = 7. This approach yields various sensitives from experimental studies on a range of organisms (increases from 12 to 79%) [*Aldridge et al.,* 2012; *Beer et al.,* 2010; *Marshall et al.,* 2013]. Due to other environmental factors influencing shell mass during growth, there is weak significance in most of the shell mass-$[CO_3^{2-}]$ experimental relationships. As such, this approach only provides a limited constraint on the impact of elevated alkalinity on calcification rate. However, assuming the proportional change is representative of the proportional change in growth rate, the range of values are substantially less than what would be expected from exclusively abiotic controlled kinetics (~138 % rate change over the same increase in $\Omega_{calcite}$, see below). However, if this change was directly translated into elevated PIC export (with no impact on carbon returned to the surface through upwelling) then a future increase of ocean alkalinity [e.g., *Ferrer-González and Ilyina* 2016] would result in a net flux of ~0.5-4 Gt C out of the surface ocean.

Given the relatively low specific gravity of organic molecules (often <1), their aggregation with inorganic carbon is the mechanism by which they sink out of the surface ocean (often referred to as 'ballasting', [*Alldredge and Silver* 1988; *Klaas and Archer* 2002]). The 'marine snow' product has a defined PIC: particulate organic carbon (POC) ratio (the ratio between particulate inorganic and organic carbon, typically 1:4). As such, increased export of inorganic carbon due to increased biological calcification, may also result in increased organic carbon export. Providing the ratio of POC to PIC is > 1, the organic carbon export would offset the CO_2 emission associated with the counter carbonate pump. However, increased biological carbon export (and subsequent remineralization) could decrease the dissolved oxygen content in the water column (see section 7), or result in increased weathering in underlying sediments [*Barker et al.,* 2006].

Considerably more research is required to investigate the response of organisms and ecosystems to elevated alkalinity. An experimental regime for this has been included below in Table 2, which suggests various parameters in the carbonate system for a range of addition scenarios. Scenario A represents the average conditions in the surface ocean following extensive and long term increases in ocean alkalinity as predicted by *Ilyina et al.,* [2013] and this study (section 3.1). Scenario B represents an increase of ocean alkalinity with minimal mitigation of the most extensive CO_2 emission scenario [*Keller et al.,* 2014]. Scenario C represents Scenario A followed by additional CO_2 removal from the atmosphere. Scenarios D and E represent a continuum between Scenario A and the regional 'hot spots' predicted in *Ilyina et al.,* 2013. Scenario F simulates similar $\Omega_{calcite}$ conditions to E with non-equilibrated pCO_2.

4.3 Abiotic Carbonate Precipitation

A long standing discussion since the 1960's [*Broecker and Takahashi* 1966; *Cloud Jr.,* 1962] is whether calcium carbonate can precipitate abiologically from seawater at typical environmental conditions. Early work attempted to explain the formation of 'whitings' [*Broecker et al.,* 2001; *Morse et al.,* 2003], which are characterized by the rapid flocculation and deposition of calcium carbonate crystals (a common feature at the Great Bahama Bank and in the Persian Gulf). Initially, spontaneous (pseudo-homogenous) nucleation of carbonate in seawater was postulated to be the cause. But initial studies by *Pytkowicz* [1965] suggest that highly elevated saturation states were required to spontaneously precipitate calcium carbonate from seawater, confirmed to be between $\Omega_{calcite} \approx 19$ and 25 by *Morse and He* [1993]. Others suggest that carbonate precipitation on re-suspended sediment to be the cause of the whiting events [*Bustos-Serrano et al.,* 2009; *Morse et al.,* 2003]. If precipitation occurs on re-suspended sediment, the availability of a carbonate surface area for nucleation is an important control for carbonate precipitation from seawater.

There have been extensive laboratory studies investigating carbonate precipitation in seawater for 'seeded' experiments (i.e. there is nuclei mineral surface in contact with the solution, Figure 12), in which the rate is proportional to the saturation state through equation 24 [see *Inskeep and Bloom* 1985].

$$R = k(\Omega - 1)^n \qquad \text{equation 24}$$

Temperature is thought to control the mineralogy of the precipitating phase. In seawater, calcite nucleates at temperatures <8°C, and above this aragonite is the precipitating phase [*Morse et al.,* 1997]. Although, the hydrated calcium carbonate polymorph ikaite ($CaCO_3 \cdot 6H_2O$) has been found to be stable at near zero temperatures [*Lu et al.,* 2012].

The role of magnesium [*Berner* 1975], phosphate [*Burton and Walter* 1990] and sulfate [*Busenberg and Plummer* 1985] ions on the inhibition of carbonate precipitation has received substantial attention. Increasing the concentration of magnesium relative to calcium is thought to increase the stoichiometric solubility constant of calcite resulting in a decrease in the $[Ca^{2+}]$ $[CO_3^{2-}]$ ion activity product (IAP, equation 25; adapted from *Mucci and Morse* [1983])

$$IAP = \frac{K_c^0}{K_c^*} \cdot \left(1 - \frac{S}{1000}\right)^2 \qquad \text{equation 25}$$

Where K_c^0 is the thermodynamic solubility of calcite at 25°C and 1 atm ($pK_c^0 = 8.48$) and S is the salinity. pKc^* is thought to vary between 6.59 and 6.27 for $[Mg^{2+}]/[Ca^{2+}]$ between 0 and 20. Therefore, a magnesium to calcium concentration ratio of 5.1 (typical of the surface ocean) would reduce the ion activity product by 45% compared to a magnesium free solution. Although the mechanisms for Mg^{2+} incorporation onto calcite surfaces and its role in the inhibition of precipitation is the subject of continued debate [*Astilleros et al.,* 2010; *Davis et al.,* 2000; *Lin and Singer* 2009; *Morse et al.,* 2007]. This inhibition is not apparent for aragonite, in which there is an order of magnitude less Mg^{2+} adsorption onto the precipitating surface [*Berner* 1975; *Mucci and Morse* 1983]. However, given the elevated saturation state of aragonite in seawater (Table S1 in the supporting information [B*all and Nordstrom* 1991; *Parkhurst et al.,* 1980; *Parkhurst and Appelo* 1999; *Pilson* 1998; *U.S. Environmental Protection Agency* 1998]), some form of inhibition must be occurring.

The presence of phosphate ions (PO_4^{3-}) in seawater has been shown to inhibit calcite precipitation [*Burton and Walter* 1990; *Mucci* 1986] through adsorption onto the calcite surface (equation 26). Both studies investigated elevated initial phosphate concentrations (up to 100's of μmoles of P kg^{-1}) with respect to typical surface ocean concentrations (<1 μmole kg^{-1}).

$$Log\ R = -15.76 - 1.45\log[PO_4^{3-}] + 3.17\log(\Omega - 1) \qquad \text{equation 26}$$

where $[PO_4^{3-}]$ is the phosphate concentration in solution (moles l^{-1}), and R is the precipitation rate (moles m^{-2} hr^{-1}). This relationship is thought to be valid between phosphate concentrations of 1 and 100 μmoles kg^{-1}. Similar to phosphate, the presence of sulfate ions (SO_4^{2-}) in solution has been shown to inhibit the precipitation of calcite [*Bots et al.,* 2011; *Busenberg and Plummer* 1985; *Fernández-Díaz et al.,* 2010; *Tang et al.,* 2012]. SO_4^{2-} is present at concentrations of approximately 28 mmoles kg^{-1} in seawater, but substantially smaller concentrations are sufficient to impede carbonate formation [*Busenberg and Plummer* 1985].

The availability of carbonate mineral surface area in the ocean is therefore critical in upscaling the laboratory derived precipitation rates. This surface area is notionally provided by re-suspended sediment in whiting events on continental shelves [*Morse et al.,* 2003]. The availability of carbonate mineral surface area in the open ocean less well constrained. Using satellite derived Moderate-Resolution Imaging Spectroradiometer data, *Balch et al.,* [2005] present surface particulate inorganic carbon concentrations for a number of oceanic regions. The concentration is larger in coastal areas (2.5-3.7 μg C l^{-1}) compared to the open ocean (0.7 – 2.8 μg C l^{-1}). Assuming the composition of the PIC is aragonite or Mg-calcite (molecular mass between 97 and 100 g(carbonate) mol^{-1}, and assuming up to 20% MgCO$_3$), the concentration of carbonate minerals in the open surface ocean may be between 5.6 and 23.4 μg l^{-1}. *Walter and Morse* [1985] determined the surface area of shallow seawater sediments to be between 0.1 and 24.0 m^2 g^{-1}, although samples were limited to size fraction >37 μm, which would exclude smaller particles with a larger surface area to mass ratio. However, based on these measurements, the volumetric surface area of carbonate minerals in the mixed layer could be between 10$^{-6.3}$ and 10$^{-3.2}$ m^2 l^{-1}. Furthermore, the majority, if not all of the PIC in the surface ocean is produced biologically, which has been shown to considerably less

reactive than synthetic counterparts (see the supporting information [*Cubillas et al.,* 2005; *Hassenkam et al.,* 2011; *Honjo and Erez* 1978; *Keir* 1980; *Walter and Hanor* 1979]), possibly due to a protective organic layer on the mineral surface [*Godoi et al.,* 2009]. Figure 12 suggests that a precipitation rate of around 10^{-5} moles m^{-2} h^{-1} would be expected for seawater ($\Omega_{calcite}$ = 3-4) seeded with carbonate minerals. This could equate to a carbonate formation rate of between 0.01 and 14.3 Gt C y^{-1} in the surface ocean (~300x10^6 km^2, 60 m deep) for a volumetric surface area between $10^{-6.3}$ and $10^{-3.2}$ m^2 l^{-1}. Clearly, the larger value is inconsistent with measurements of carbonate production in the ocean carbon cycle (2 Gt C y^{-1}). However, it is possible that a lower abiotic precipitation rate is presently masked by a larger biological signal. While biological carbonate precipitation depends on numerous factors, the abiotic precipitation follows a predicable relationship with Ω, and (assuming the lower end member) would increase from 0.01 to 0.4 Gt C y^{-1} for an increase in $\Omega_{calcite}$ from its current value to 10 (a 20% increase of carbonate production). This value is speculative, but highlights the potential significance of abiological carbonate precipitation in the ocean at elevated alkalinity.

Spontaneous ('unseeded') nucleation of carbonate minerals is thought to contribute little to carbonate production and export from the surface ocean [*Pytkowicz* 1965]. *Morse and He* [1993] suggest that a calcite saturation state of >19 is required for nucleation in seawater at 25°C. In extended duration experiments *Pokrovsky* [1998] investigated the induction time required for spontaneous CaCO$_3$ (aragonite) nucleation, which is proportional to the saturation state (equation 27)

$$Log\ \tau = A + n\log\Omega \qquad \text{equation 27}$$

Where A is 7.207 and n is -3.784 for [Mg^{2+}]/[Ca^{2+}] ratio of 5.3 at 20°C (Figure 13). Rather than a threshold saturation state to induce carbonate precipitation, *Pokrovsky* [1998] suggests an induction time of around 2 months for $\Omega_{aragonite} \approx 4$ decreasing to around 1 week for $\Omega_{aragonite} \approx 7$, and 9 hours for $\Omega_{aragonite}$ = 15. Similar to seeded precipitation, it is possible that spontaneous nucleation occurs in the surface ocean, but is masked by a larger biological signal, and an increase in carbonate saturation state may accelerate these processes to have a significant impact on the overall carbon cycle.
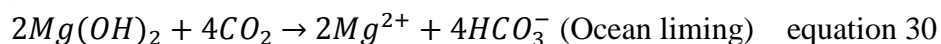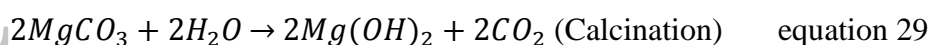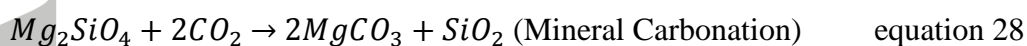
5.   Production processes

5.1 Ocean Liming

Kheshgi [1995] first proposed adding lime (CaO) or portlandite (Ca(OH)$_2$) to the surface ocean. Three schemes were explored including (1) the calcination of limestone, (2) the calcination of limestone with flue gas CO$_2$ capture and sequestration, (3) the calcination of limestone with flue gas CO$_2$ capture and sequestration using oxy-fuel firing (a simplification of the latter is included in Figure 14). Accounting for carbon and energy balances across the whole life cycle, the technoeconomics of this approach was assessed by *Renforth et al.,* [2013], for calcite and dolomite feedstocks. They suggested that lime or dolime production in an oxy-fuel fired kiln with CCS, together with the associated energy costs of raw material preparation and ocean disposal, would require between 6 and 10 GJ per net ton of CO$_2$ sequestered. Note that in engineering calculations it is important to consider the total mass processed, which is why units in this section are in terms of CO$_2$ rather than C. *Renforth et*

al., [2013] also explored the use of steam flash calcination and solar calcination, both of which could potentially reduce the costs of lime production (4 and 2 GJ t CO_2 respectively).

Renforth and Kruger [2013] investigated the possibility of using forsterite rich olivine (Mg_2SiO_4) as a feedstock for a coupled mineral carbonation ocean liming process (Figure 15). Ground olivine could be fed into a (single-stage) mineral carbonation reactor (at elevated pCO_2). This produces magnesite and silica (equation 28). After dewatering, the precipitated magnesite could be fed into a kiln/ slaking system to produce brucite ($Mg(OH)_2$) (equation 29), which could be used for ocean liming (equation 30). The evolved CO_2 is recycled back into the mineral carbonation reactor. The value of this approach is that it avoids the CO_2 burden of decomposing a carbonate raw material, and $MgCO_3$ decarbonates at a lower temperature than $CaCO_3$. However, due to the energy penalty from water evaporation in the kiln, and the additional energy required to grind the olivine, the energy savings over $CaCO_3$ calcination appear to be minimal.

$$Mg_2SiO_4 + 2CO_2 \rightarrow 2MgCO_3 + SiO_2 \text{ (Mineral Carbonation)} \qquad \text{equation 28}$$

$$2MgCO_3 + 2H_2O \rightarrow 2Mg(OH)_2 + 2CO_2 \text{ (Calcination)} \qquad \text{equation 29}$$

$$2Mg(OH)_2 + 4CO_2 \rightarrow 2Mg^{2+} + 4HCO_3^- \text{ (Ocean liming)} \qquad \text{equation 30}$$

A number of multi-step mineral carbonation processes promote the creation of $Mg(OH)_2$ as part of the overall reaction to capture carbon dioxide from point sources as $MgCO_3$ [*Fagerlund et al.,* 2012; *Madeddu et al.,* 2014; *Nduagu et al.,* 2012]. The use of the produced $Mg(OH)_2$ to increase ocean alkalinity has not been explored. However, such a scheme reduces the constraints on plant location (rather than being next to the emission point source it could be located to exploit unused renewable energy), and notionally reduces the overall cost by ~60 – 80 % (from additional CO_2 draw-down per mole of base added). However, it is likely that the $Mg(OH)_2$ will need to be relatively pure for ocean liming to minimize biological impact from Fe and Si that may be present.

5.2 Accelerated Weathering of Limestone

The accelerated weathering of limestone is the process in which flue gasses are scrubbed with a mixture of limestone and seawater [*Rau and Caldeira* 1999; Figure 16]. It is directly analogous to flue gas desulfurization, albeit on a larger scale. Seawater brought into equilibrium with 15% CO_2 and calcite will be able to sequester 0.53 t CO_2 per kt of seawater [*Caldeira and Rau* 2000]. Therefore, a coal fired power station producing 500 MW and 0.5 t CO_2 s^{-1} will require around 900 m^3 s^{-1} of seawater, which is, for example, two orders of magnitude greater than the largest seawater reverse osmosis facilities (1 – 5 m^3 s^{-1} [*Lior* 2012]), and an order of magnitude greater than the largest sewage treatment works (e.g., the Atotonilco el Alto treatment plant, 35 m^3 s^{-1} [*Mendoza* 2012]). However, a once-through seawater cooled, 500 MW plant pumps some 20 m^3 s^{-1} of seawater, meaning that around 6% of the plant's CO_2 could theoretically be converted to seawater alkalinity without new pumping. The volume ratio between liquid and gas in the reactor has a strong influence on capture efficiency, too little water in the reactor and there is insufficient carbonate solubility to remove CO_2 from the gas phase. Increasing the liquid-gas ratio increases the capture efficiency until a maximum is reached, after which the efficiency starts to decrease as CO_2 in the gas is used to suppress the natural buffering of seawater rather than promoting carbonate dissolution. While most of this research has focused on flue gas capture, AWL could be relevant to air capture if applied to mitigation of CO_2 from electricity production via biomass combustion (i.e. an alternative storage mechanism for biomass energy carbon capture and storage).

Langer et al., [2009] suggest that 71% of US power stations are located within 100 km of limestone deposits, and 200 are adjacent to the coast. Given the water requirements, the AWL reactor must be located adjacent to the coast. While there is considerable potential for AWL, (*Rau et al,* [2007] suggests a minimum cost of <$10 per t CO_2 via use of waste limestone and recycled once-through power plant cooling seawater), the engineering requirements require considerable more research.

5.3 Electrochemical splitting

To overcome the CO_2 geological sequestration burden of ocean liming, *House et al.,* [2007] proposed a method to increase aqueous NaOH through direct electrolysis of seawater (Figure 17). This chlor-alkali method has been used industrially for over 100 years to produce NaOH from seawater and brines [*Brinkmann et al.,* 2014]. The electrolysis cell consists of an anode and cathode separated by a sodium permeable membrane. Seawater (or an enriched NaCl

brine) is fed into the section of cell containing the anode, chloride ions are oxidized into chlorine gas. At the cathode, hydrogen ions are reduced from a stream of fresh water to produce hydrogen gas. The result is a movement of Na^+ ions across the membrane and the creation of aqueous NaOH at the cathode. This high pH solution could then be added to the ocean to increase alkalinity. The chlorine and hydrogen gases could be reacted in a fuel cell to produce hydrochloric acid, which must be neutralized through reaction with a silicate mineral. Assuming no efficiency losses, the energy requirements of electrolysis (1.8 GJ per t CO_2) is completely met by the exergy ('available' energy) destruction in the fuel cell and during acid neutralization (1.9 GJ per t CO_2). However applying a range of efficiency scenarios and energy emission intensities, *House et al.,* [2007] suggest that an optimistic scenario (70% efficiency for electrolysis and fuel cell generation, on a 10 moles kg^{-1} NaCl solution) would require between 3 and 18 GJ per t CO_2. More pessimistic efficiencies are unlikely to be carbon negative when exploiting anything but a decarbonized energy sector.

Rau [2008] proposed an alternative method that uses a $CaCO_3$ solution as the electrolyte (Figure 18), in which acid conditions produced around the anode dissolve $CaCO_3$. In such a solution the CO_3^{2-} ions would migrate towards the anode, protonate, and degas as CO_2. The Ca^{2+} cations would migrate towards the cathode to produce a high pH $Ca(OH)_2$ rich solution. Notionally, $Ca(OH)_2$ could precipitate at sufficiently elevated pH and $[Ca^{2+}]$, however *Rau* [2008] suggests the addition of the high pH solution to the ocean as the mechanism for ocean alkalinity increase. The energy requirements for this may be around 5 GJ(electrical) per t CO_2 consumed, which to be CO_2-emissions-negative must be powered by non-fossil-derived electricity. A similar energy expenditure (7.6 GJ_e per t CO_2) was calculated if silicate minerals rather than carbonates were dissolved at the anode in seawater [*Rau et al.,* 2013].

An approach was proposed by *Davies* [2015], in which an $MgCl_2$ rich brine is thermally decomposed into magnesium oxide and hydrochloric acid, which requires around 0.8 GJ of electrical and 13 GJ of thermal energy per t CO_2 sequestered. Like the electrochemical methods discussed above, the hydrochloric acid is disposed/neutralized by reaction with silicate rocks. As *Davies* [2015] suggests, this proposal is probably most suitable for the treatment of desalination reject brines using solar energy, the global potential of which is on the order of 1 Mt CO_2 a^{-1}.

5.4 Comparative Cost Estimate

The limited technoeconomic assessment of these processes largely focus on deriving overall energy and carbon balances, and there has been little optimization. Furthermore, some of the reaction kinetics are poorly constrained (particularly for artificial materials), resulting in considerable uncertainty in the design of the flow sheet. Finally, the energy and cost associated with transporting the material from the extraction site to the processing or application site (see below) can only be estimated at this stage. However, Table 3 brings together the various cost estimates of ocean alkalinity C sequestration technologies. An important consideration is a 'threshold' imposed by the *energy intensity of carbon emissions* derived from fossil fuels (i.e. the inverse of the carbon intensity of fuels; italicized in Table 3). Surpassing 10 GJ t CO_2 of thermal energy or 3 GJ t CO_2 of electrical energy, then it may

be more reasonable to decommission a coal fired power station than to run the negative emission technology. While the predicted financial and energy costs are variable, and at this stage largely speculative, they suggest a level of competitiveness with 'conventional' methods of mitigation.

5.5 Upscaling production

If the proposal is to mitigate humanity's CO_2 emissions then a solution must be able to operate on a scale that is meaningful to the challenge. However, defining what is 'meaningful' is problematic, which has previously been attempted by deconstructing the problem rather than assessing what might be possible. For instance, *Pacala and Socolow* [2004] chose annual emissions 'wedges' of 1 Gt C a^{-1} by 2050 (each wedge mitigating around 14% of their business as usual CO_2 emissions scenario) by upscaling known mitigation strategies. Refining this approach to include projected efficiency improvements and the most up to date emission pathways, *Davis et al.,* [2013] used 19 (9 to stabilize emissions and 10 to reduce to zero), although the wedge size remains the same. A consequence of the wedge approach is that it has conceptually defined the scale at which a mitigation technology should be able to achieve. The problem is the choice of 1 GtC is largely arbitrary. It is possible that the portfolio of climate change mitigation technologies will contain considerably more than 7 or 19 different measures (e.g., the UK Government's pathways calculator contains over 40 proposals [*DECC* 2010], and does not expand upon a range of over 20 geoengineering proposals [*Bellamy et al.,* 2012]). While some measures may be able to operate at a multiple Gt C a^{-1} scale (e.g., renewable energy proposals), many of them could well be more feasible at hundreds of Mt C a^{-1} scale (solving 1 - 5 % of the emission mitigation requirements).

Another important aspect of scale is the cumulative potential of a mitigation strategy. Humanity could emit between 880 (RCP 2.6) and ~thousands of Gt C by the end of the century (section 1). This is particularly important when considering technologies that propose to store CO_2 in another part of the Earth system (or in geological reservoirs), where the capacity of the sink may be limited, and the total requirements of storage could be on the order of trillions of t of C. While the efficacy of a potential technology is an important consideration (i.e. the proportional capacity for dealing with the problem), the decision to invest in a technology must also include the predicted future costs, the required resources to progress development, and the lead time for implementation. There is no widely employed or transparent decision making framework for investment in technology development for a climate change solution portfolio.

For a mineral sequestration technology to capture CO_2 as bicarbonate in the ocean, the theoretical mass ratio between mineral and CO_2 is shown in Table 1. While some of the anthropogenically produced minerals achieve a mass ratio of >1 (CO_2: mineral), their production necessitates the extraction and processing of natural minerals (e.g., the calcination of limestone to produce lime). Therefore, between 1 and 3.5 tons of raw material will need to be extracted for every ton of CO_2 captured. This requirement will increase once inefficiencies are accounted for.

The cement industry is a useful analogue for the scale and rate of deployment of a mineral carbon sequestration technology. The global cement industry extracts around 7 billion tons of raw material (mainly limestone, shale and/or clay), which are ground and processed in a kiln, and the finished product (4.2 billion tons of cement a^{-1}), is distributed locally. In 1960 global cement production was around 0.3 Gt, in 2014 it was 4.2 Gt. The majority of this production capacity was created in China, which had an annual compound production growth of 11.5 % between 2000 and 2012 [*USGS*, 2014]. However, it is unclear how comparable this growth is to a future mineral carbon sequestration industry (i.e. are the constraints comparable?). For instance, infrastructure development during the industrial revolution expanded at about 5%, tractor production in the U.S. during the height of agricultural mechanization grew at a rate of 16%, post-war U.K. road infrastructure grew at a rate of 15%, and recent cement production grew at a rate of 12% ([*DECC* 2015; *Hilbert and López* 2011; *Roth and Divall* 2015; *Renforth et al.,* 2011; *USGS* 2014]), see supporting information Table S3). With appropriate policy/market drivers, an expansion of >20 % may be possible, but 10-15 % may be more realistic, and consistent with historic industrial development.

Figure 19 presents the time required to upscale production to 0.1 (Figure 19A), 1 (Figure 19B) and 10 (Figure 19C) Gt a^{-1} for a range of exponential growth rates (equation 31). A growth rate of 12% would need to be sustained for 45 to 60 years to create 1 Gt worth of production capacity (based on an initial capacity of $1 - 5$ Mt a^{-1}). However, sustaining this growth rate for an additional 20 years would create 10 Gt of capacity. Hypothetically, if 50 Mt a^{-1} of spare capacity was available (and convertible) in existing industries, then the upscaling period would be 26 years for 1 Gt (based on 12% growth)

$$P_t = P_0(1 + r)^t \qquad \text{equation 31}$$

P is the production in year t of the expansion with growth rate r, and P_0 is the initial production.

6   Ocean Transport and Disposal

6.1 Ocean Transport

Moving material from the extraction and production site to the ocean will require a combination of land and ocean transport. The use of these depends on the location of the mineral resource, the processing plant, port facilities, and the application area of the ocean. As such, at this stage, it is possible to make only general statements regarding transport requirements of a mineral carbon sequestration proposal.

Global shipping capacity is around 8 billion tons a^{-1} (the utilization of which broadly follows fluctuations in international trade [*UNCTAD* 2012]). Capacity of material transport over land is likely to be substantially more (10's of billions of tons). For the addition of material to the ocean *Harvey* [2008] suggests a fleet of 3000 ships would be required to add 4 Gt of $CaCO_3$. *Renforth et al.,* [2013] suggest a fleet of 100 ships would be required to add 1 Gt of $Ca(OH)_2$ (the difference between these studies is largely a result of the solubility different of the materials added). Compared to an existing fleet of 50,000, this represents a small expansion. While upscaling transport and infrastructure to cope with additional movement of material could be challenging, upscaling the extraction and processing components would probably be

more limiting. Transport over land incurs substantially more cost (energy and financial) than over the ocean (see supporting information Table S4, [*CEFIC* 2011; *Davis et al.,* 2011]). However, a mineral carbon sequestration technology may have an energy foot print of GJ per ton of material, it may be possible to move material 10s or 100s of km over land and 1000s km over the ocean before significantly impacting the energy or carbon balance of the technology. Given the abundance of mineral resource, it may be possible to optimize a technology to minimize transport requirements. *Moosdorf et al.,* [2014] demonstrated that large distances can be covered with minimal impact on the CO_2 budget of enhanced weathering proposals.

6.2 Ocean addition

Compared to the distributed global impact, the localized impact of increased alkalinity appears to be more substantial. For instance, if alkalinity addition were more rapid than the rate of CO_2 gas to liquid transfer, there would be an increase in $[CO_3^{2-}]$ and $[OH^-]$ and a decrease in $[CO_{2\ (aq)}]$. However, these effects would be highly transient in the open ocean. Figure 20 shows that addition rates would have to be several orders of magnitude larger than suggested in *Renforth et al.,* [2013] before a significant and extended impact on pH was observed (see Box 2 for ocean dispersal discussion). This assumes instantaneous dissolution within the rapidly mixed wake of a ship. It is possible that a particle could sink out of the wake and dissolve in the less turbulent part of the mixed layer, creating areas of elevated alkalinity.

The cumulative effect of regional alkalinity addition over decades may produce conditions with the potential significant ecosystem impact [e.g., *Ilyina et al.,* 2013]. It is conceivable that in some confined environments, or under rapid application rates, the ambient pH may be sufficiently elevated to impact ocean biology. Establishing the relationship between addition rate and local impact could be used to develop application limits to minimize environmental impact. Furthermore, alkalinity addition will likely create secondary environmental impacts specific to the technology and the application site due to the co-dissolution of elements that could stimulate biological activity.

Delvigne 1987;

was adopted by the International Maritime Consultative Organization (now the 'International Maritime Organization') in 1975 based on a paper submitted by the Netherlands and Norway [*IMCO* 1975] and can be formulated as:

7   Environmental impact and regulation

7.1 Global consequences of alkalinity addition

The recent accumulation of anthropogenic CO_2 in the atmosphere has caused a decrease in surface ocean pH by 0.1 units [*Doney et al.,* 2009]. Future CO_2 emissions will decrease the pH further. Increasing the pCO_2 in equilibrium with the ocean increases $[CO_{2(aq)}]$ in solution, and decreases $[CO_3^{2-}]$. Initial experiments [*Riebesell et al.,* 2000] suggested that a reduction in $[CO_3^{2-}]$ and therefore a reduction in the saturation state of carbonate minerals, would lead to a reduction in carbonate formation of calcifying organisms. Substantial research has been undertaken in the last 20 years, which has unearthed a complex relationship between ocean chemistry and ecosystem impact [*Fabry et al.,* 2008; *Rost et al.,* 2008]. The consequences for organisms that precipitate extracellular carbonate (e.g., corals) is somewhat starker [*Hoegh-Guldberg et al.,* 2007]. Broadly, limiting ocean acidification is an important driver for reducing CO_2 emissions. Within this context, some have proposed the intentional addition of alkalinity to the oceans as a means to limit harm [*Rau et al.,* 2012; *Williamson and Turley* 2012].

Almost 50 % of historic anthropogenic CO_2 emissions have been absorbed into the ocean [*Sabine et al.,* 2004]. The ability of the oceans to take up additional CO_2 is described by the Revelle Factor (RF) (i.e. the proportional change of aqueous CO_2 to DIC, equation 33; [*Revelle and Suess* 1957]). The capacity for CO_2 uptake is inversely proportional to RF, and is currently between 9 and 15 [*Sabine et al.,* 2004]. The RF has increased by around 15 % on pre-industrial levels and will increase by 30-50 % for a doubling of CO_2 [*Hauck and Völker* 2015]. Increasing ocean alkalinity will proportionally decrease the RF by around 0.15 to 0.19 (for every % change in alkalinity there will be a 0.15% to 0.19% decrease in RF, Figure 21). If alkalinity increased in the surface ocean from 2.3 to 3.0 mEq kg^{-1}, the Revelle Factor would decrease by around 5% (offsetting 10% of the potential anthropogenic increase).

$$RF = \left[\frac{\frac{\partial[CO_{2(aq)}]}{[CO_{2(aq)}]}}{\frac{\partial C_T}{C_T}} \right]_{A_T=const.}$$ equation 33

As suggested by modeling results in section 5, the globally distributed effects of an increase in ocean alkalinity would be elevated alkalinity, pH or $\Omega_{calcite}$. The consequences of this alkalinity increase on marine ecosystems is poorly understood, but it may provide a competitive advantage for calcifying organisms [*Henderson et al.,* 2008].

The addition of silicate minerals to the ocean could have a substantial fertilization effect from the dissolution of iron and silica in the material [*Köhler et al.,* 2013]. Adding a billion tons of ultrabasic rock to the ocean (for ~0.8 billions of tons of CO_2 removal), will also add ~200 million of tons of silicon and ~70 million tons of iron (see *Renforth* [2012] for a summary of rock chemical constituents). The proportion of Fe or Si dissolved and liberated is likely to be a fraction of the total added in the olivine, although it is difficult to predict [*Hauck et al.,* 2016]. There is considerable literature on the potential environmental impact of ocean fertilization, including increased production of other more potent greenhouse gasses (N_2O and CH_4, [*Fuhrman and Capone* 1991]), lower dissolved oxygen, and nutrient driven ecosystem structural changes [*Lampitt et al.,* 2008]. It may be possible to extract the Mg or Ca from a silicate mineral (thus minimizing Si and Fe added to the ocean) to create pure oxides or hydroxides, however the technology to do this has yet to be developed.

7.2 Localized elevated pH and reduced aqueous CO_2

In marine aquaria, 'calcium reactors' (that cycle the aquarium water through a bed of crushed limestone), or 'Kalkwasser' (a solution of $Ca(OH)_2$), are widely used to prevent problematic decreases in pH caused by respiration and nitrification. As such, alkalinity is typically maintained between 3-6 mEq kg^{-1} [*Tullock and Earle-Bridges* 2002]. Even if sufficient alkalinity were introduced to the ocean mitigate all of anthropogenic CO_2 emissions for the next 100 years, it is not anticipated to greatly exceed 4 mEq kg^{-1}. The first order impact of increasing $[CO_3^{2-}]$ and $[HCO_3^-]$ in seawater is probably minimal. However, addition of alkalinity may induce transient elevated pH and/or lower $[CO_{2\ (aq)}]$ around the point of addition (except AWL, which would likely result in elevated $[CO_{2\ (aq)}]$ around the reactor outlet). *Feng et al.,* [2016] suggest that it may be possible to influence carbonate chemistry at a regional scale (e.g., South China Sea, the Great Barrier Reef). However, the application rate of alkalinity would need to be large to have the desired effect. Ecosystems could also be exposed to the risk of rapid changes in chemistry should the addition be halted.

All autotrophic organisms have evolved strategies to concentrate carbon during photosynthesis. This is to compensate CO_2 undersaturation in the modern atmosphere (and thus ocean) for Rubisco (the enzyme which catalyzes photosynthesis; *Henderson et al.,* 2008). Therefore, transient reductions in aqueous CO_2 caused by alkalinity addition could inhibit photosynthesis, and thus alter the function and structure of phytoplankton communities. *Henderson et al.,* [2008] suggest that changes within the structure of these

primary producers, could have important implications for the function of whole marine ecosystems. For instance, reduced rates of carbon and nitrogen fixation have been demonstrated in *cyanobacterium Trichodesmium* (an important primary producer) at low pCO_2 [*Hutchins et al.,* 2007; *Ramos et al.,* 2007].

Scott et al., [2005] found reduced sodium uptake and ammonia excretion in *Perca fluviatilis* (Perch) exposed to a pH 9.5 (through potassium hydroxide addition). The Na^+ imbalance is thought to allow the fish to retain H^+ and mitigate the effects of alkalosis (elevated blood pH). Higher ammonia retention is a result of a lower concentration gradient across the gills caused by a decrease in the amount of ammonia converted to ammonium at the interface with high pH water [*Saha et al.,* 2002]. In a toxicology study*, Locke et al.,* (2009) suggest that between 100-320 mg l^{-1} (1.3 – 4.4 mmoles l^{-1}, resulting in a pH >10) of $Ca(OH)_2$ is needed to have a detectable impact on the mortality of *Gasterosteus aculeatus* (a common coastal fish) over 96 days. Fish and mammals have developed renal compensation in order to excrete excess alkalinity [*Wood et al.,* 1999], but prolonged exposure may have a chronic impact.

In a single species experiment, *Cripps et al.,* [2013] investigated the impact of $Ca(OH)_2$ addition on *Carcinus maenas* (a globally distributed crab species). The experiments (ranging from pH 8.5 to 8.8, pCO_2 200 to 80 µatm, $\Omega_{calcite}$ = 7 to 13) demonstrated respiratory alkalosis possibly in response to lower levels of aqueous CO_2. However, the authors note that these fluctuations are smaller than the daily changes experienced in intertidal rock pools, and it is not clear how an elevated ambient pH may impact the overall fluctuations in coastal environments. *Locke et al.,* [2009] suggest *Crangon septemspinosa* (a common shrimp species) is sensitive to $Ca(OH)_2$ addition, with 100% mortality for ~100 mg l^{-1} addition after 14 days. Bivalves appear to have less control on the pH within their blood, and are possibly more sensitive to environmental changes [*Byrne and Dietz* 1997], although control may be unnecessary for anything other than shell formation [*Booth et al.,* 1984].

7.3 Localized changes in dissolved oxygen

Dissolved oxygen in the ocean is controlled by a number of mechanisms including the biogenic production at the surface, respiratory removal from remineralization of sinking organic matter, ocean-atmosphere gas exchange, and circulation [*Joos et al.,* 2003]. The deleterious anthropogenic impact on dissolved oxygen is a concern and could increase the extent of oxygen minimum zones [*Stramma et al.,* 2008]. Hypoxia alters benthic ecosystem structure and function, in which smaller taxa are more resilient than larger [*Levin et al.,* 2009]. Although in a modest lime addition scenario (*Keller et al.,* [2014]; equating to cumulative draw down of around 160 Gt C by 2100) no change in dissolved O_2 was demonstrated.

Fertilizing biological activity through the addition of iron and silicon (or increased export through ballasting) may increase dissolved oxygen in the photic zone, but reduce it in the waters below due to remineralization of exported organic carbon [*Fuhrman and Capone* 1991]. Further to biological oxygen removal, fayalite (Fe_2SiO_4), the iron end member of olivine is composed of Fe^{2+} which oxidizes to Fe^{3+} during dissolution in the presence of oxygen ([*Schott and Berner* 1985]; equation 34).

$$Fe_2SiO_4 + \frac{1}{2}O_2 \rightarrow Fe_2O_3 + SiO_2 \quad \text{equation 34}$$
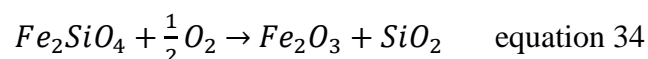
An ophiolite may contain between 0 and 20% FeO [*Miyashiro* 1975]. A rock with a fayalite to forsterite mass ratio of 1:9 (FeO 7%) would consume approximately 12 g O_2 for every kg dissolved. A column of water in the mixed layer (1 m^2 by 60 m deep) could contain on the order of 10 moles of O_2 (~200 moles kg^{-1}, [*Stramma et al.,* 2008]). It would therefore take around 25 kg m^{-2} of rapidly dissolving rock to completely remove O_2 as it sank through the water column. During the European Iron Fertilization Experiment [*Smetak et al.,* 2007], 7 tons of material was rapidly (within 1 day) spread over a 167 km^2 patch ($10^{-4.4}$ kg m^{-2}), which over the following 14 days increased to 740 km^2 (10^{-5} kg m^{-2}). It is therefore possible that oxygen consumption from iron oxidation can be easily mitigated with suitable addition rates, and exploiting rapid dilution in the mixed layer. However, the effects may be more significant in poorly mixed waters, waters with existing hypoxia, and sediments and soils.

7.4 Alkalinity addition in shell fish production and coral reef protection

Lime and hydrated lime have been used for almost a century to control invasive species in shellfish aquaculture (see *Locke et al.,* [2009], and references therein). This involves dipping an entire sock of shellfish into a concentrated solution of lime/quicklime, or spraying a concentrated solution onto a bed [*Piola et al.,* 2009]. For instance, *Switzer et al.,* [2011] report that the addition of $Ca(OH)_2$ was effective at controlling the invasive species of *Didemnum vexillum* (carpet sea squirt) on commercial oysters. However, at one of the treatment sites they report a considerable reduction in the survival rate the stock (although pH remained at ambient levels). This demonstrates the relative sensitivity of species to large transient doses of $Ca(OH)_2$. However, *Locke et al.* [2009] suggests that targeted lime addition to these environments may be able to minimize the impact of ocean acidification or improve water quality in anaerobic estuaries from excess nutrient load.

Given the relative sensitivity of species to lime addition, its use for mitigating the effects of ocean acidification in natural environments requires careful consideration. The addition rate would have to be sufficient to overcome mixing of the local seawater with the ambient environment, but not sufficient to detrimentally impact ecosystems. Work is required to assess locations in which this may be feasible, and how such a scheme may operate.

7.5 Regulation and ethics of adding alkalinity to the ocean

The 1982 United Nations Convention on the Law of the Sea (LOSC [*UN* 1982]) lays down the legal framework for almost all matters relating to the seas and oceans. Carbon storage as alkalinity, as a novel marine activity, is not explicitly addressed in the Convention. Nevertheless, the provisions of the LOSC are generally applicable, setting out the territorial and economic claims of sovereign states, responsibilities for the protection of the marine environment, marine scientific research, and dispute resolution. The LOSC also provides for the development of specific and detailed norms under the Convention for new and emerging marine activities. Within this context, the issue of marine geoengineering was recently addressed under the London Convention and London Protocol [*IMO* 2003] (LC/LP), treaties that regulate marine pollution from the dumping of wastes or other matter at sea. The texts of these instruments excludes the 'placement of matter for a purpose other than the mere disposal thereof, provided that such placement is not contrary to the aims of this Protocol' from the definition of dumping and would therefore apparently exclude the addition of alkalinity to the ocean from falling under these regimes. However, in the case of ocean fertilization the Parties to the London Convention and the London Protocol determined in

2008 that the scope of the London Convention and Protocol includes ocean fertilization activities' due to significant risk that such placement would be contrary to the aims of both the London Convention and the London Protocol. Subsequently, the London Protocol was amended in October 2013 (London Protocol Resolution LP.4(8) – [*IMO* 2008]) to regulate ocean fertilization activities, and also enables the Parties to regulate other marine geoengineering activities in the future, potentially including the addition of alkalinity to the ocean. The amendments need to be ratified by 2/3rds of the Contracting Parties to come into force, which would provide a legally binding mechanism to regulate ocean fertilization, with the possibility of regulating other marine geoengineering activities in the future. On the face of it, carbon storage as alkalinity falls within the definition of 'marine geoengineering' as 'a deliberate intervention in the marine environment to manipulate natural processes, including to to counteract anthropogenic climate change and/or its impacts, and that has the potential to result in deleterious effects, especially where those effects may be widespread, long-lasting or severe.' Hence, though the amendment to the London Protocol is not yet in force, there remains a possibility that the addition of alkalinity to the ocean could be regulated at a later date as a placement of matter into the sea for marine geoengineering purposes. Therefore, the addition of alkalinity to the ocean would likely operate under a complicated regulatory framework. Addition to coastal waters would fall under national (or regional) administration, whereas open ocean addition would require international oversight.

Beyond this, efforts have been undertaken to contribute to the development of an effective governance framework for geoengineering, a term which commonly covers several ocean alkalinity proposals. *Rayner et al.,* [2013] have laid out a set of guiding ('Oxford') principles for geoengineering, including: 1) that it be regulated as a public good; 2) public participation in decision-making; 3) disclosure of research and open publication of results; 4) independent assessment of impacts; and 5) governance before deployment. This wider discussion has highlighted the responsibilities of researchers working on proposals that may eventually lead to widespread or intended impact [*Owen et al.,* 2013]. With this in mind, *Hubert and Reichwein* [2015] suggest a means to codify norms for research within this space, deliberating on the foundational principles (e.g., prevention and precaution), the responsibility of states to prevent activity without prior assessment of harms, and the responsibility of scientists to design and undertake proportional step-by-step activates to further scientific understanding.

7.6 Monitoring

It is possible to achieve precision of less than 0.005 mEq kg^{-1} (0.02%) in routine measurements of seawater alkalinity [*Dickson et al.,* 2007]. This suggests that an addition of 0.005 – 0.015 mEq kg^{-1} a^{-1} could be detected. However, it may be several years before this signal is detectable above the background seasonal variability (0 – 0.08 mEq kg^{-1}). A key limitation will likely be the ability to collect the appropriate amount of samples/data in a short enough time period to accurately quantify alkalinity changes across the whole ocean. Over the last 35 years ocean alkalinity data were collected as part of 42 cruises at 23,000 stations (see CDIAC's ocean carbon data collection http://cdiac.ornl.gov/oceans/). The collection of data from scientific cruises would likely form an important part of an ocean alkalinity monitoring system. However, automated monitoring systems are becoming increasingly common, which currently omit alkalinity or carbonate system measurements, but will likely include these in the near future [*GOOS* 2006].

8   Conclusions and further work

Storage of large volumes of CO_2 may be necessary to prevent dangerous climate change. This paper explores the issues surrounding the chemical transformation of CO_2 through mineral dissolution for storage as ocean alkalinity (HCO_3^- CO_3^{2-} ions). The ocean currently stores around 38,000 Gt C (equivalent to ~140,000 Gt CO_2) in this way, and may be able to store trillions of tons of CO_2 with limited changes in bulk chemistry. If it were used as the sole destination of all anthropogenic CO_2 emissions over the next $100 - 500$ a, then ocean alkalinity would increase from current levels of 2.3 mEq kg^{-1} to ~3 mEq kg^{-1} (resulting in a calcite saturation level of between 5 and 7.5). Considering these changes as an upper end member, it is unlikely that the average saturation state of calcite will surpass its pre-industrial level, although some environments may be more sensitive than others.

Transient localized impact around the point of alkalinity addition could be substantial. On one hand, it may be possible to ameliorate the effects of ocean acidification (i.e. maintaining the saturation state of calcite at an appropriate value) by controlled addition to sensitive environments. However, rapid uncontrolled changes in pH, carbonate saturation state, and dissolved aqueous CO_2 may have detrimental effects on ocean ecosystems. The source of alkalinity may be derived from carbonate or silicate minerals. Direct addition of the latter to the ocean may fertilize biological activity through the co-dissolution of nutrients (e.g., iron and silicon), although it may be possible to extract the magnesium or calcium prior to addition. While the addition of alkalinity is common in several marine environments (e.g., in aquaria and shellfish production), more research is needed to constrain the wider ecosystem response. Table 2 provides a range of carbonate system parameters that could be used as a basis for this experimental work.

Carbonate mineral precipitation is strongly inhibited in seawater, and is almost exclusively produced from biological activity. In the global carbon cycle, up to 2 Gt C a^{-1} is incorporated into carbonate shells in the ocean, of which only <0.3 Gt C a^{-1} makes it into the lithosphere. The remainder is re-mineralized into dissolved aqueous species (into CO_2, HCO_3^- and CO_3^{2-}). As such, the residence time for alkalinity in the ocean is on the order of $100 - 1,000$ ka, and would form, for all practical purposes, a permanent sink for anthropogenic CO_2. However, raised alkalinity in the ocean may change the rate of carbonate mineral production (both biogenic and abiological), but more experimental work is required to constrain this change. Research investigating the change of shell mass with carbonate ion concentration suggest a growth rate change between 10 - 80% for calcite saturation state of 7, which is considerably less than the expected abiological increase of 140 %. Increased alkalinity will also likely reduce the rate at which carbonate is re-mineralized in sediments, and increase the depth of the ocean in which carbonate minerals are thermodynamically unstable ('lysocline'), and thus increase carbonate burial. An increased carbonate production or decrease in remineralization will lower, or reverse, the effectiveness of ocean alkalinity carbon storage. It is possible that increased carbonate production and ballasting will also increase the export of organic carbon. As the particulate organic to inorganic carbon ratio is >1, the effect may result in the additional draw-down of atmospheric CO_2. Considerably more work is required to understand the longevity of carbon storage as elevated alkalinity in the ocean.

A range of techniques have been proposed for increasing ocean alkalinity, which exploit numerous reaction pathways (Table 1). However, all require the extraction, processing, and

reaction of rocks. It may be possible to achieve CO_2:rock mass ratios >1 using ultrabasic minerals (larger than the ~0.6 mass ratio for solid carbonate formation). It may also be possible to use faster dissolving carbonate minerals for alkalinity addition (CO_2: rock mass ratio ~0.5). While some components of these processes already operate at a large scale (e.g., the production of lime), generally the overall technologies have not developed beyond desktop techno-economic assessment or bench scale laboratory work. However, this work suggests some of the proposals to have a range of energy requirements and financial costs comparable to more widely studied alternatives (e.g., 1-10 GJ tCO_2^{-1}, \$50 – 150 tCO_2^{-1}). However, up-scaling these processes to have an impact on anthropogenic CO_2 emissions (i.e. billions of tons CO_2 a^{-1}) is a considerable challenge (as it is for mineral carbonation).

Finally, the modification of the ocean (a global commons) raises issues surrounding regulation, monitoring, and the distribution of impact. The London Convention/Protocol was created to limit dumping of materials in the ocean, and has been amended (yet to be ratified) to include marine geoengineering proposals. More work is required to develop governance for ocean alkalinity carbon storage, but this should be informed by, and tailored to, the potential harms and benefits of specific alkalinity addition approaches.

9   Acknowledgements

10   References

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Table 1. Carbon sequestration reactions for a range of naturally occurring and anthropogenically produced minerals.

Equation Number	Mineral	ΔG_f (kJ/mole)[a]	Reaction	ΔG_r (kJ/mole)[a]	ΔG_r (kJ/mole C)[a]	gCO$_2$/g(mineral)
			Naturally occurring minerals			
1	Magnesite	-1029.5	$MgCO_3 + CO_2 + H_2O \rightarrow Mg^{2+} + 2HCO_3^-$	22.5	22.5	0.52
2	Calcite	-1128.5	$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^-$	22.8	22.8	0.44
3	Dolomite	-2161.7	$CaMg(CO_3)_2 + 2CO_2 + 2H_2O \rightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^-$	48.9	24.5	0.48
4	Forsterite	-2053.6	$Mg_2SiO_4 + 4CO_2 + 4H_2O \rightarrow 2Mg^{2+} + 4HCO_3^- + H_4SiO_4$	-25.3	-6.3	1.25
5	Anorthite	-4007.9	$CaAl_2Si_2O_8 + 2CO_2 + 3H_2O \rightarrow Ca^{2+} + 2HCO_3^- + Al_2Si_2O_5(OH)_4$	-36.8	-18.4	0.32
			Anthropogenically produced minerals			
6	Lime	-603.5	$CaO + 2CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^-$	-117.9	-58.9	1.57
7	Portlandite	-898.4	$Ca(OH)_2 + 2CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^-$	-60.1	-30.0	1.19
8	Periclase	-569.2	$MgO + 2CO_2 + H_2O \rightarrow Mg^{2+} + 2HCO_3^-$	-53.5	-26.7	2.18
9	Brucite	-833.5	$Mg(OH)_2 + 2CO_2 + H_2O \rightarrow Mg^{2+} + 2HCO_3^-$	-26.2	-13.1	1.51
			Electrochemical Weathering			
10			$NaCl(aq) + H_2O(l) \rightarrow NaOH(aq) + 0.5Cl_2(g) + 0.5H_2(g)$			
11			$0.5Cl_2(g) + 0.5H_2 (g) \rightarrow HCl(aq)$			
12		`	$4HCl\ (aq) + Mg_2SiO_4(s) \rightarrow 2MgCl_2(s) + SiO_2(s) + H_2O\ (l)$			

[a]Thermodynamic information was sourced from [*Robie and Hemingway* 1979]

Table 2. Experimental range for testing ocean alkalinity carbon storage.

Scenario	Description	pCO$_2$ (µatm)	A$_T$ (mEq kg^{-1})	Ω_{calcite}[a]	pH[a]
A	Extensive alkalinity addition and a limit to global emissions, global impact	600	3.0	5.3	8.0
B	Extensive alkalinity addition and unabated global emissions, global impact	1000	3.0	3.6	7.8
C	Extensive alkalinity addition and carbon dioxide removal from the atmosphere, global impact	400	3.0	7.0	8.1
D	Rapid alkalinity addition, moderate localized impact	350	4.1	12.7	8.3
E	Rapid alkalinity addition, severe localized impact	350	5.5	20.1	8.4
F	Rapid alkalinity addition, severe localized impact on confined environments	20	2.7	18.2	9.0

[a]Parameters determined using CO2sys [*Lewis et al.,* 1998] using equilibrium constants from *Roy et al.,* [1993] and approximated. Note, pCO$_2$ and A$_T$ are the independent variables.

Table 3. Comparison of electrical and thermal energy requirements and financial costs of ocean alkalinity carbon storage technologies

Technology	GJ tCO_2^{-1}		US\$ tCO_2^{-1}
	Electricity	Thermal	
Ocean Liming (Oxy-fuel flash calciner: limestone)	1.3	4.8	126
Ocean Liming (Endex CFC: limestone)	-0.1	5.5	100
Ocean Liming (Oxy-fuel flash calciner dolomite)	0.7	3.2	95
Ocean Liming (Endex CFC: dolomite)	-0.1	4.2	72
Ocean Liming (Solar calciner: limestone)	0.4	0.6[b]	159
Electrochemical weathering (Mg-Silicate)	5[c]		-
Electrochemical weathering ($CaCO_3$)	5[c]		14-190
Electrochemical weathering (NaOH production)	3-18		-
Direct carbonate addition to upwelling regions	<0.1	3.6	-
Mineral Carbonation/Ocean liming	2.2	5.0	
Accelerated weathering of limestone			10 - 40
Enhanced weathering	0.1–8.4	0.8-4.2	20-600
Direct air capture	7.5 - 10		100-1000
Typical cost of 'conventional' CCS	6.7		30-100
Energy cost of decommissioning coal	*3*	*10*	

[a]Per net ton of carbon dioxide sequestered

[b]Additional thermal requirements from fossil fuels

[c]Per ton of CO_2 extracted rather than net sequestration.

[*Renforth et al.,* 2013; *Renforth and Kruger* 2013 and references therein]
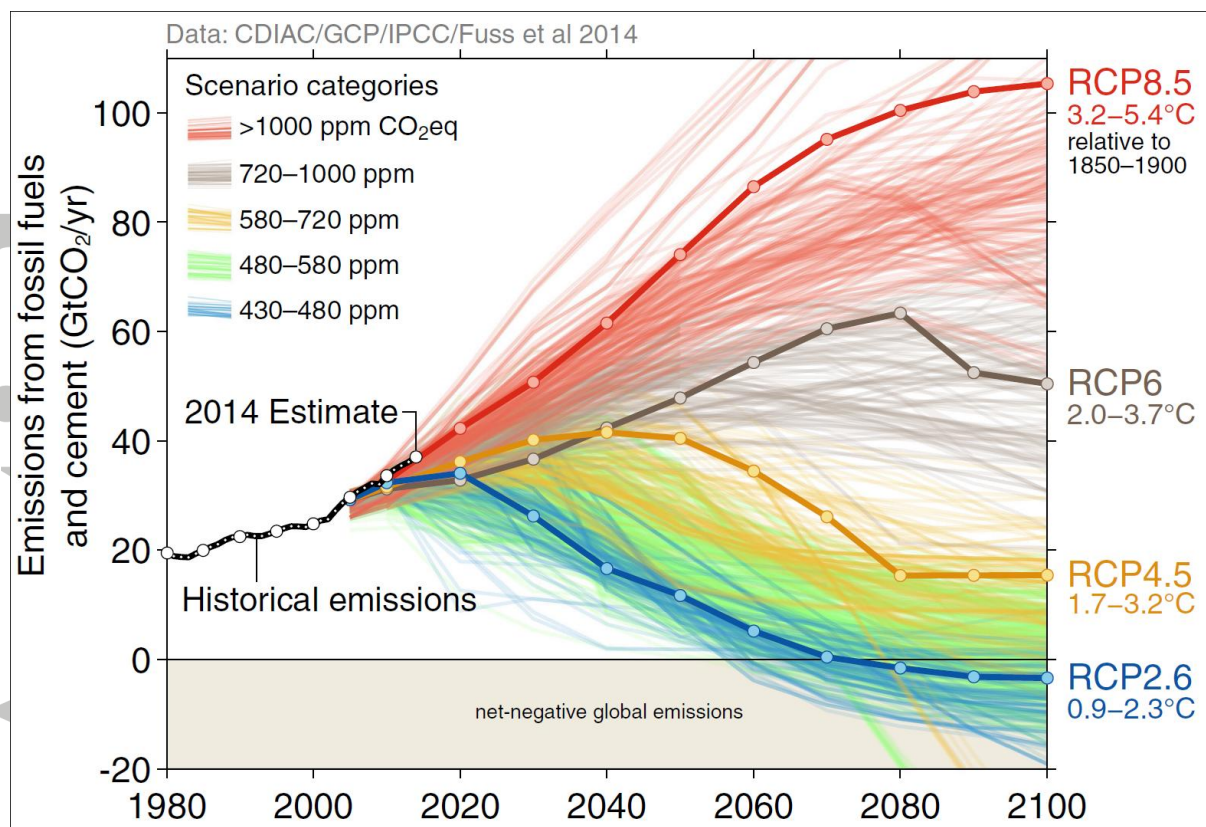
Figure 1: Emission scenarios for representative concentration. Reprinted by permission from Macmillan Publishers Ltd: Nature Climate Change [*Fuss et al.,* 2014], copyright © 2014.
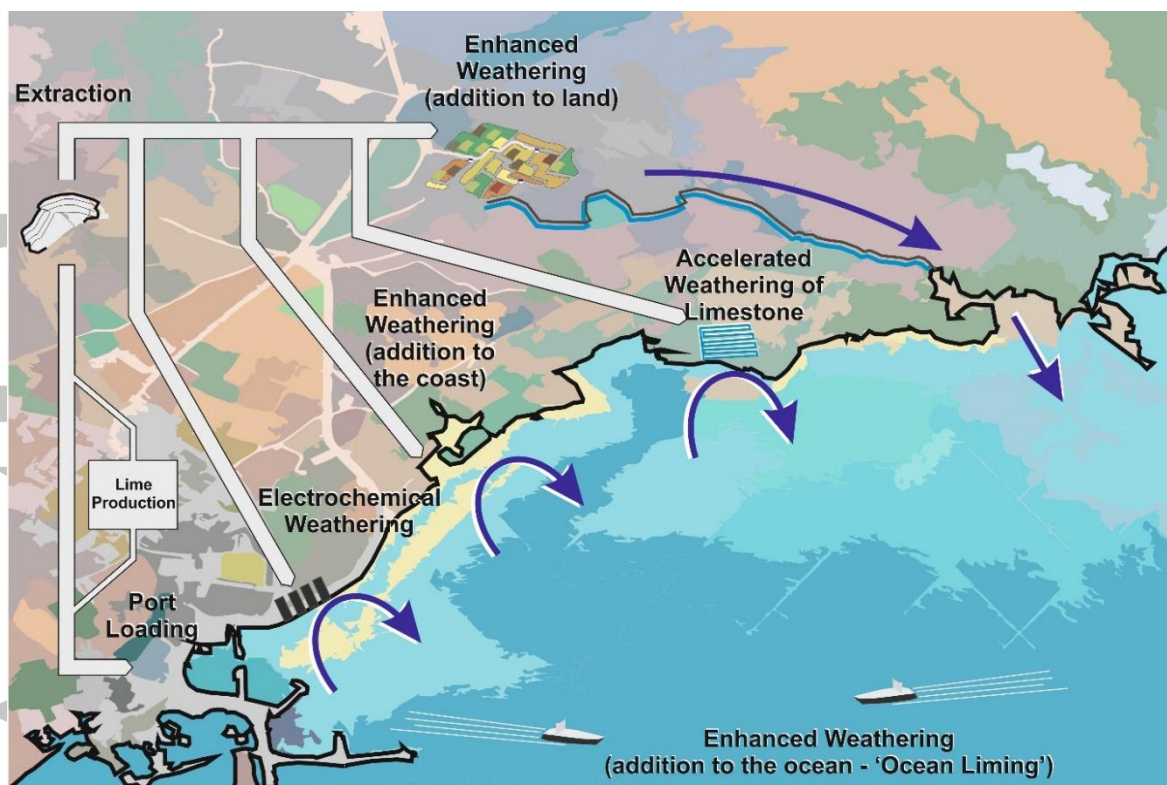
Figure 2: Proposed technologies for carbon storage as ocean alkalinity.
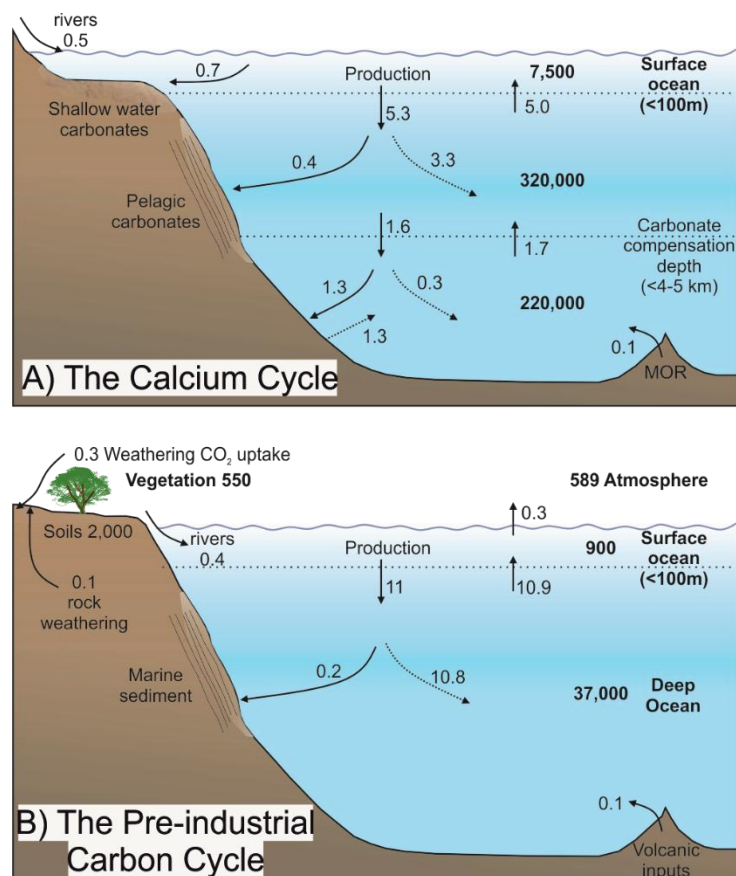
Figure 3: The global ocean A) calcium and B) pre-industrial carbon cycle. Adapted from *Andersson* [2014] and *Sabine and Tanhua* [2009]. Arrows represent fluxes in Gt Ca or Gt C per year (a⁻¹).
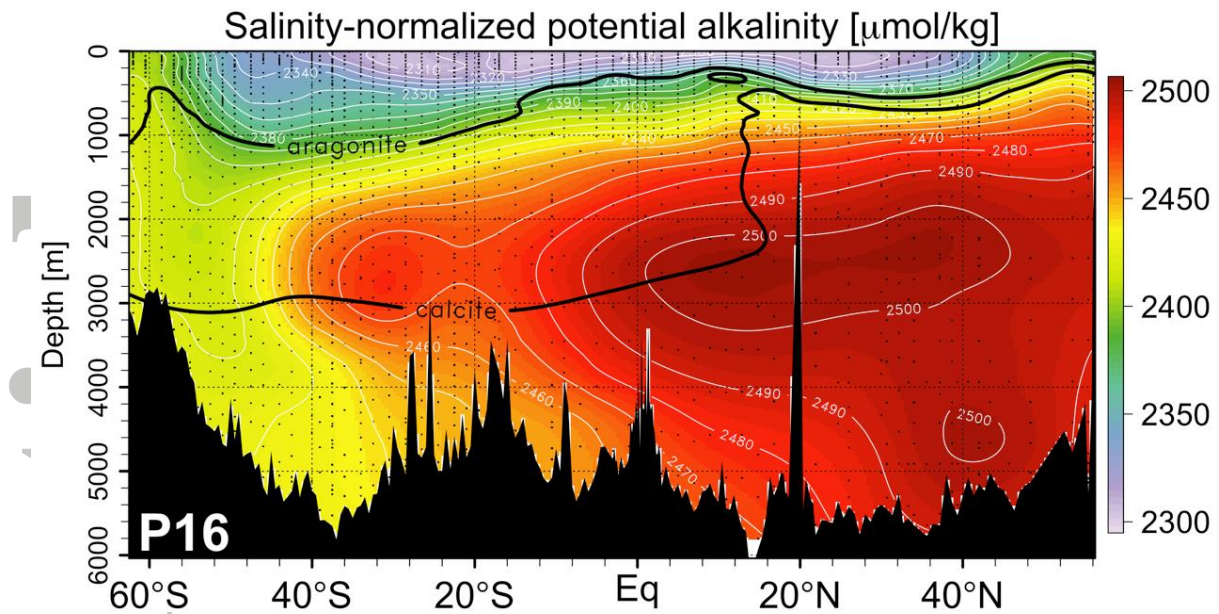
Figure 4: Salinity normalized potential alkalinity for the N-S P16 section in the central Pacific, defined according to *Carter et al.,* [2014] and using the GLODAP dataset. Note the significant increase in deep waters, particularly in the north where waters have been isolated from the atmosphere for more than 1 ka, accumulating respired organic carbon from above, and dissolved $CaCO_3$. Also shown are the depths of saturation for aragonite and calcite. Below these lines, the mineral is undersaturated (i.e. omega <1) and prone to dissolve. The lysocline and carbonate compensation depth - sedimentary features reflecting this change in saturation, are found slightly below the depth of calcite saturation. Units are microequivalents kg^{-1}.
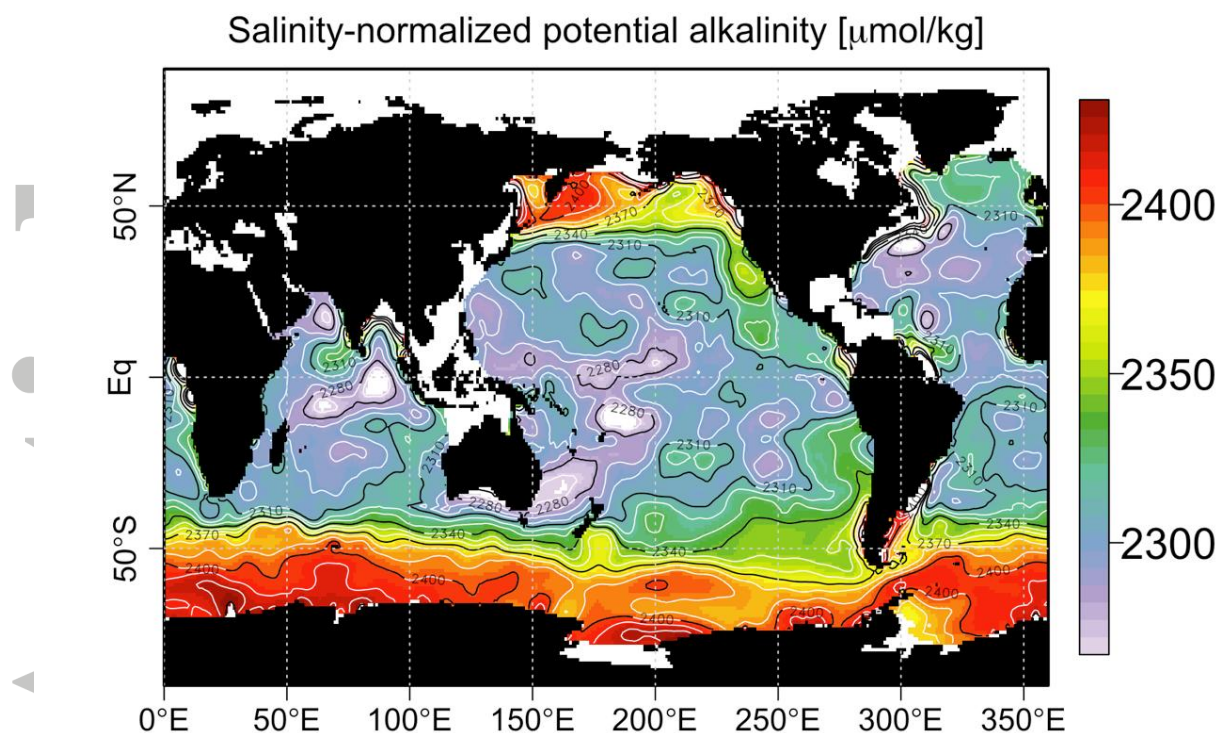
Figure 5: Salinity normalized alkalinity in the surface ocean (in microequivalents kg^{-1}) showing the range and pattern of natural variation using the GLODAP dataset.

No added alkalinity

With added alkalinity

Atmosphere cCO2

Surface, Middle and Deep Alkalinity

Effective Lysocline Depth

Surface, Deep pH

Saturation State
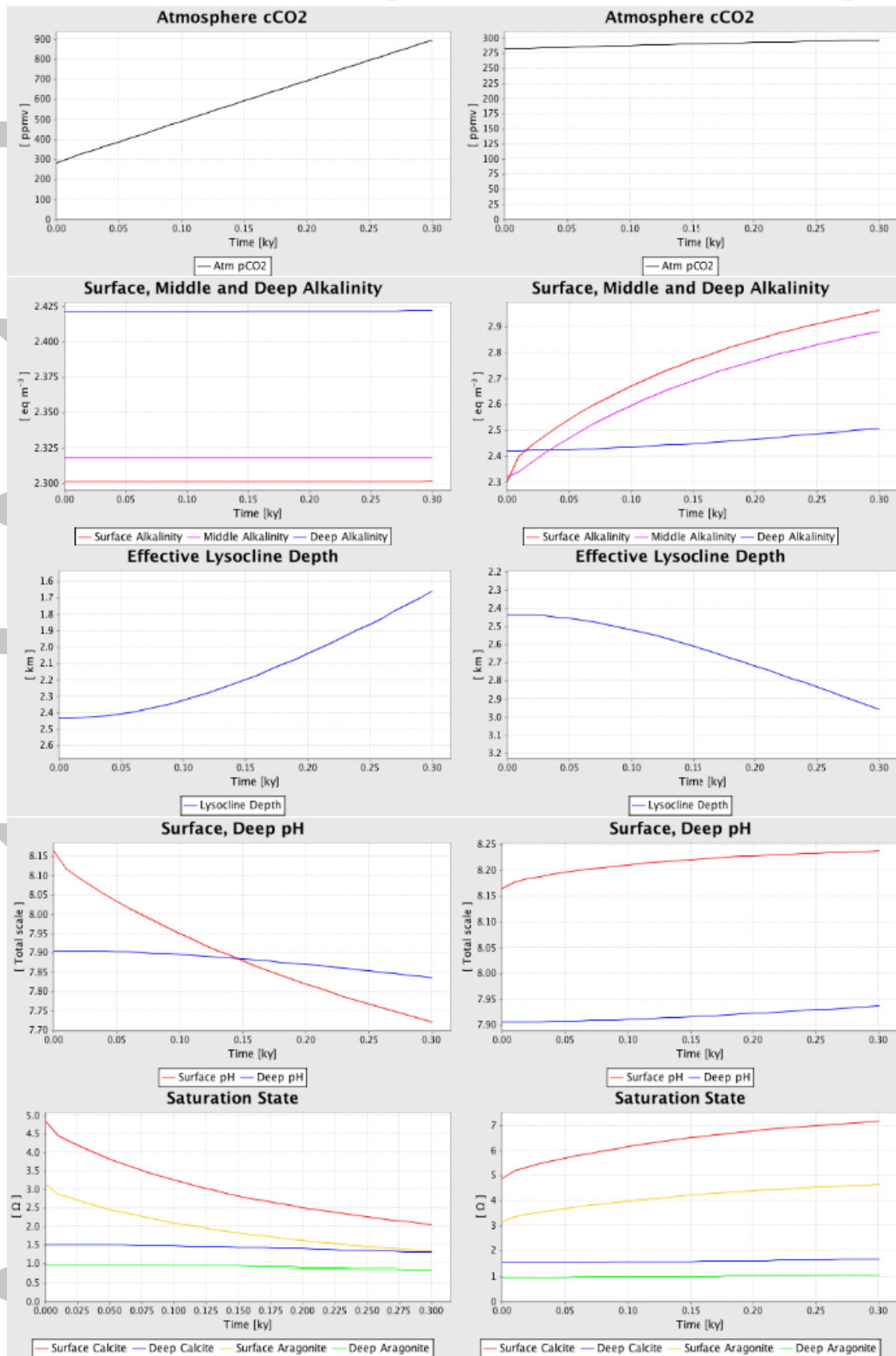
Figure 6: Output from a 3-box model mimicking significant features of the ocean carbon system (http://www.noc.soton.ac.uk/jmodels/; *Chuck et al.,* [2005]). Left hand panels take an initially equilibrium carbon cycle and perturbs it with a sufficient C flux to cause a 2 ppmV increase in atmospheric CO_2 a^{-1}, approximately equivalent to today's rate of CO_2 rise. Right hand panels impose the same C flux, but also increase the riverine alkalinity flux by a factor of 20 to increase C uptake to the ocean. 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 CO_2 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. These model results were previously presented in *Henderson et al.,* [2008].
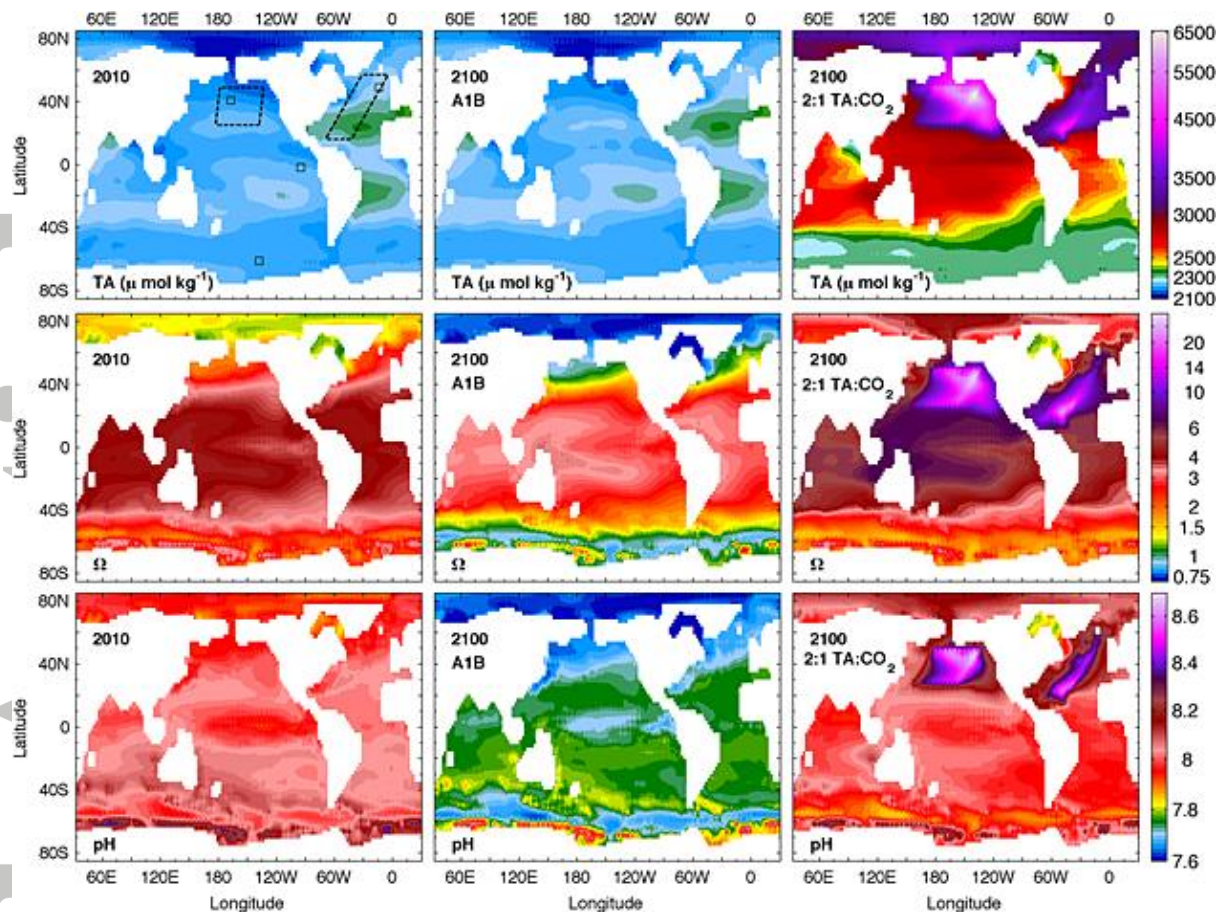
Figure 7: Model results to demonstrate the impact of alkalinity addition to one seventh of the surface ocean. Reprinted by permission from John Wiley Sons, Inc: Geophysical Research Letters [*Ilyina et al.,* 2013], copyright © 2013. Surface maps of alkalinity (top row), $\Omega_{calcite}$ (middle row) and pH (bottom row) are shown for three scenarios: 2010 (left column); 2100 following A1B CO_2 emission (middle column); 2100 with addition of alkalinity (right column). The dashed boxes in the upper left panel show the regions of alkalinity addition. Note that ocean saturation and pH are returned to broadly 2010 levels by alkalinity addition, but that there are very large changes in the system in the North Atlantic and North Pacific around the sites of alkalinity addition
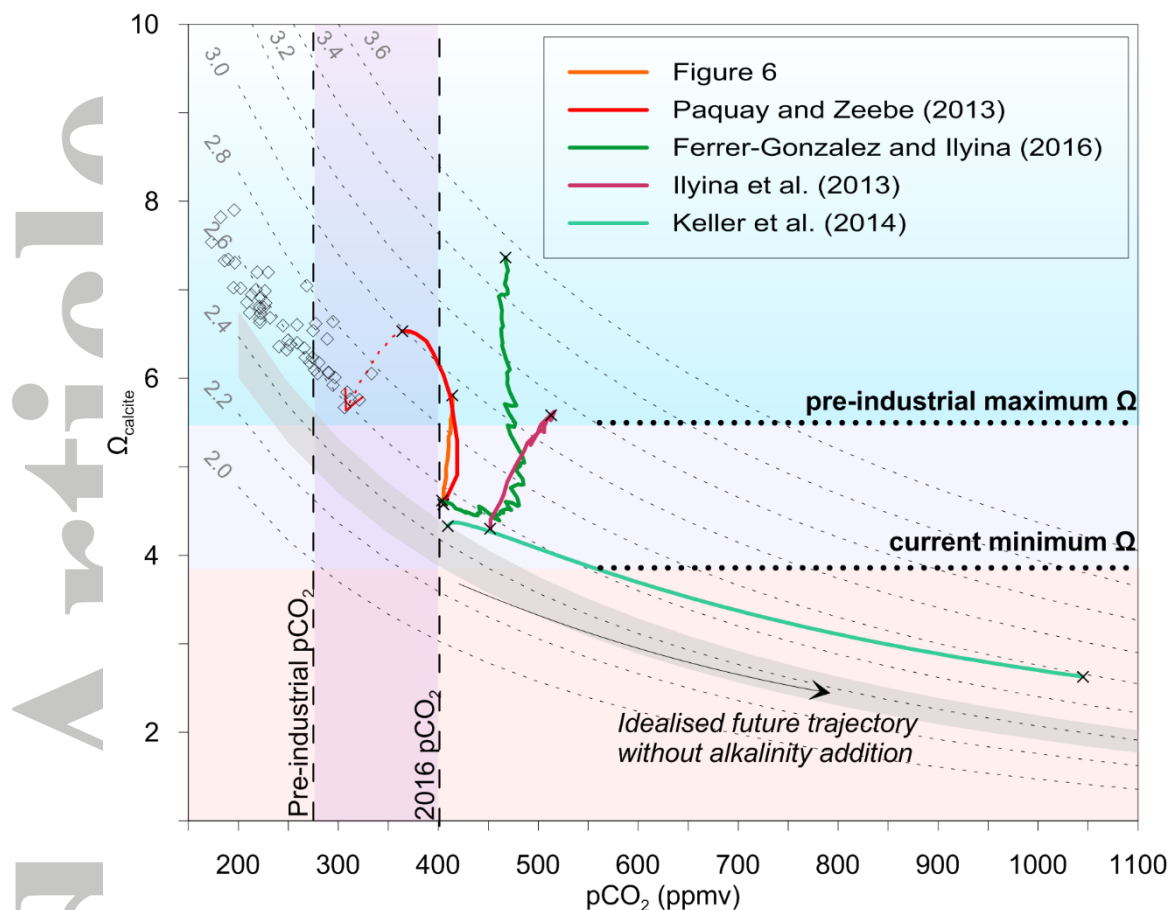
Figure 8: Results from modeling studies showing the relationship between $\Omega_{calcite}$ and pCO_2 for various alkalinity addition scenarios [*Ferrer-González and Ilyina* 2016; *Ilyina et al.,* 2013; *Keller et al.,* 2014; *Paquay and Zeebe* 2013]. The contours represent average surface ocean (0 – 100 m depth) A_T in mEq kg^{-1} at 16°C and 35% salinity, and the hatched region represents the 2 s.d. about the mean of modern surface ocean alkalinity. The open symbols represent ocean conditions reconstructed from *Hönisch et al.,* [2009] for the past 2 Ma.
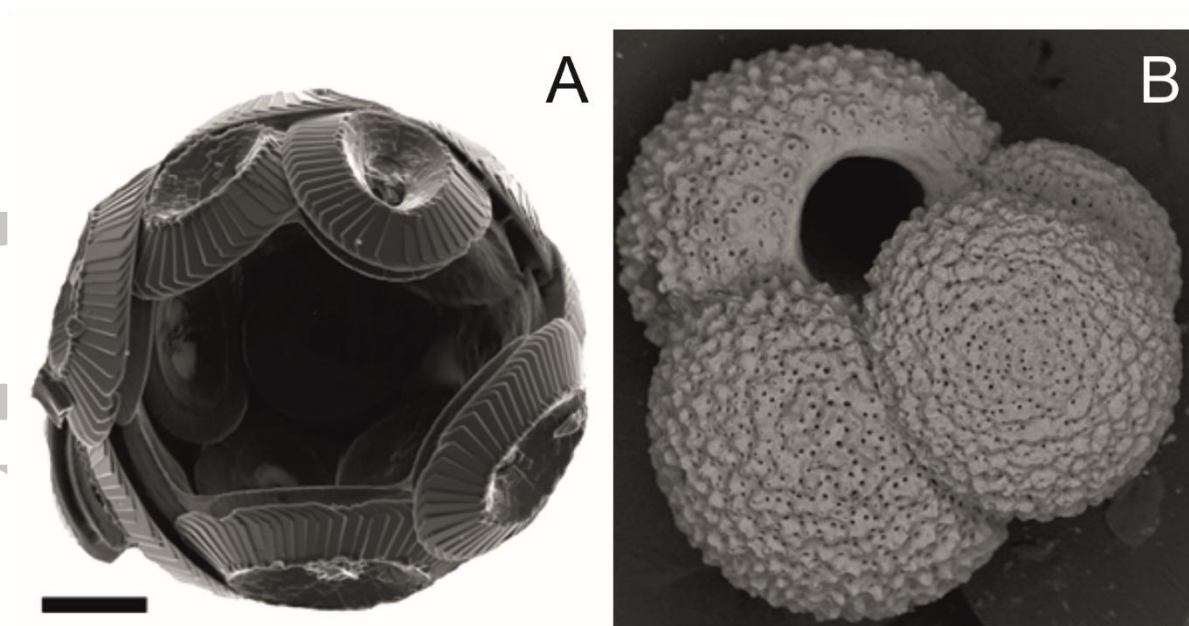
Figure 9: Scanning electron microscope images of A) A coccolithophore *Coccolithus pelagicus* ssp. *Braarudii* and B) a foraminifera *Globigerina bulloides*. Courtesy of Michaël Hermoso (University of Oxford). Approximate width is 10 μm and 30 μm for A and B respectively
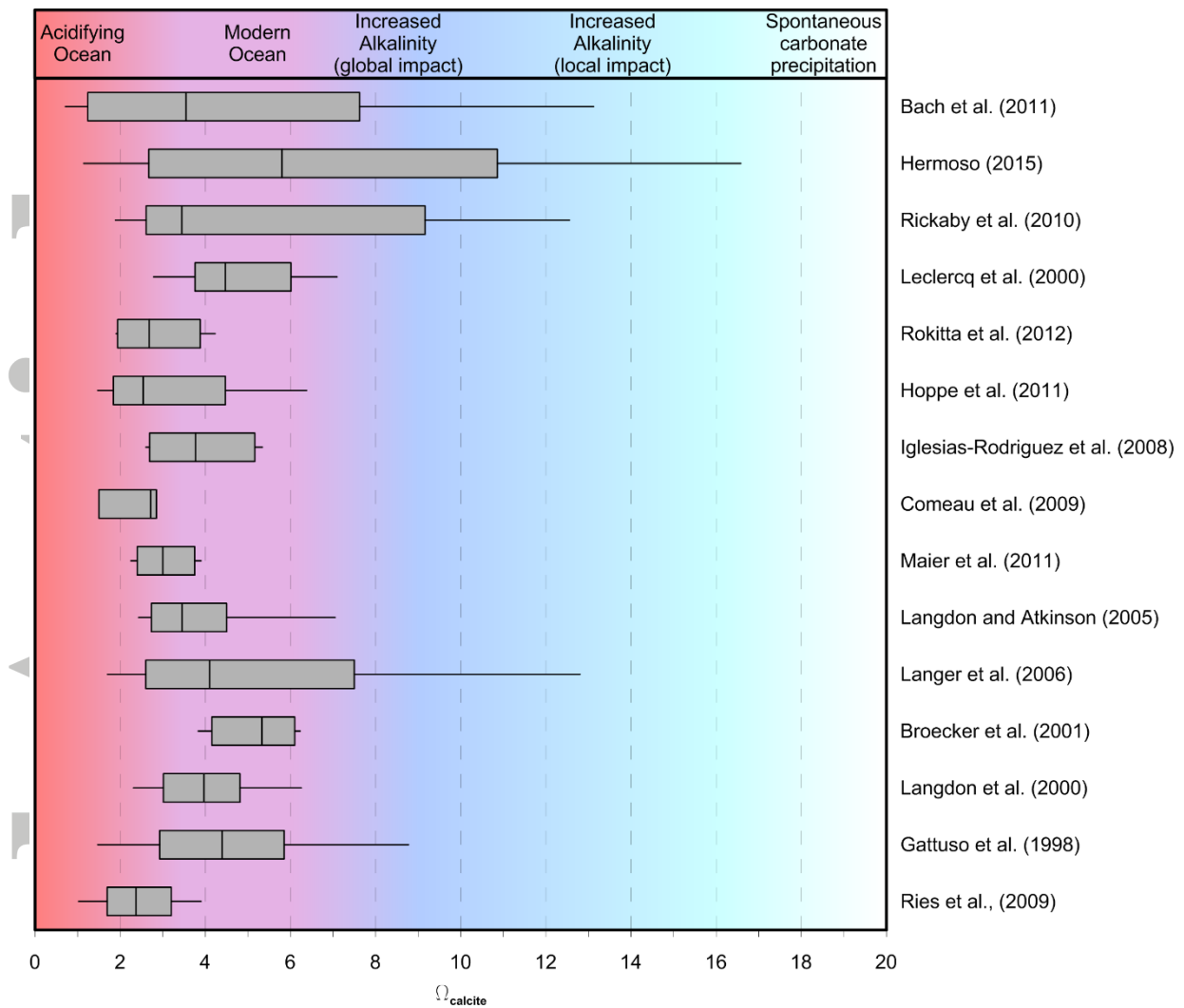
Figure 10: Indicative $\Omega_{calcite}$ ranges of culture experiments investigating calcification rate. [*Bach et al.,* 2011; *Broecker et al.,* 2001; *Comeau et al.,* 2009; *Gattuso et al.,* 1998; *Hermoso* 2015; *Hoppe et al.,* 2011; *Iglesias-Rodriguez et al.,* 2008; *Langdon et al.,* 2000; *Langdon and Atkinson* 2005; *Langer et al.,* 2006; *Leclercq et al.,* 2000; *Maier et al.,* 2011; *Rickaby et al.,* 2010; *Ries et al.,* 2009; *Rokitta et al.,* 2012].
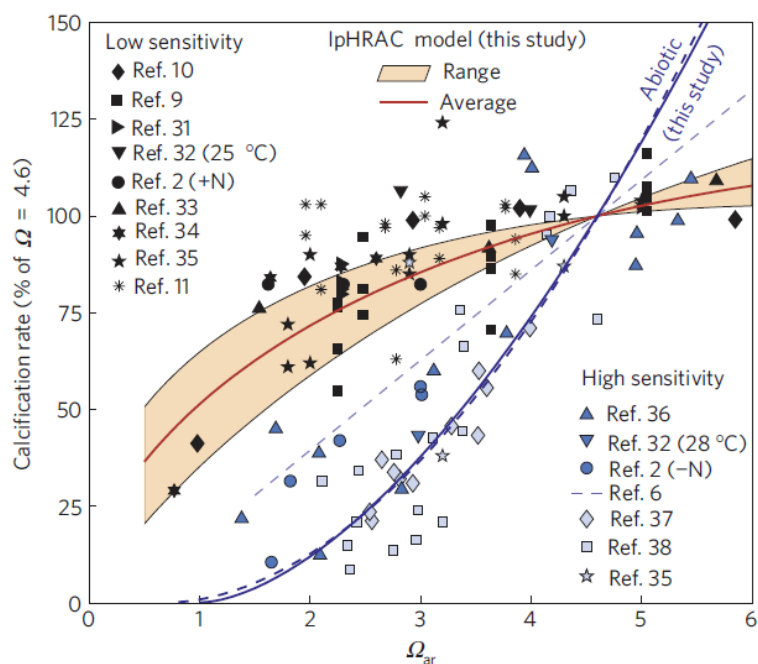
Figure 11: Percentage change in calcification rates (relative to $\Omega = 4.6$) plotted against seawater aragonite saturation states . Reprinted by permission from Macmillan Publishers Ltd: Nature Climate Change [*McCulloch et al.,* 2012], copyright © 2012. For embedded figure references see *McCulloch et al.,* [2012].
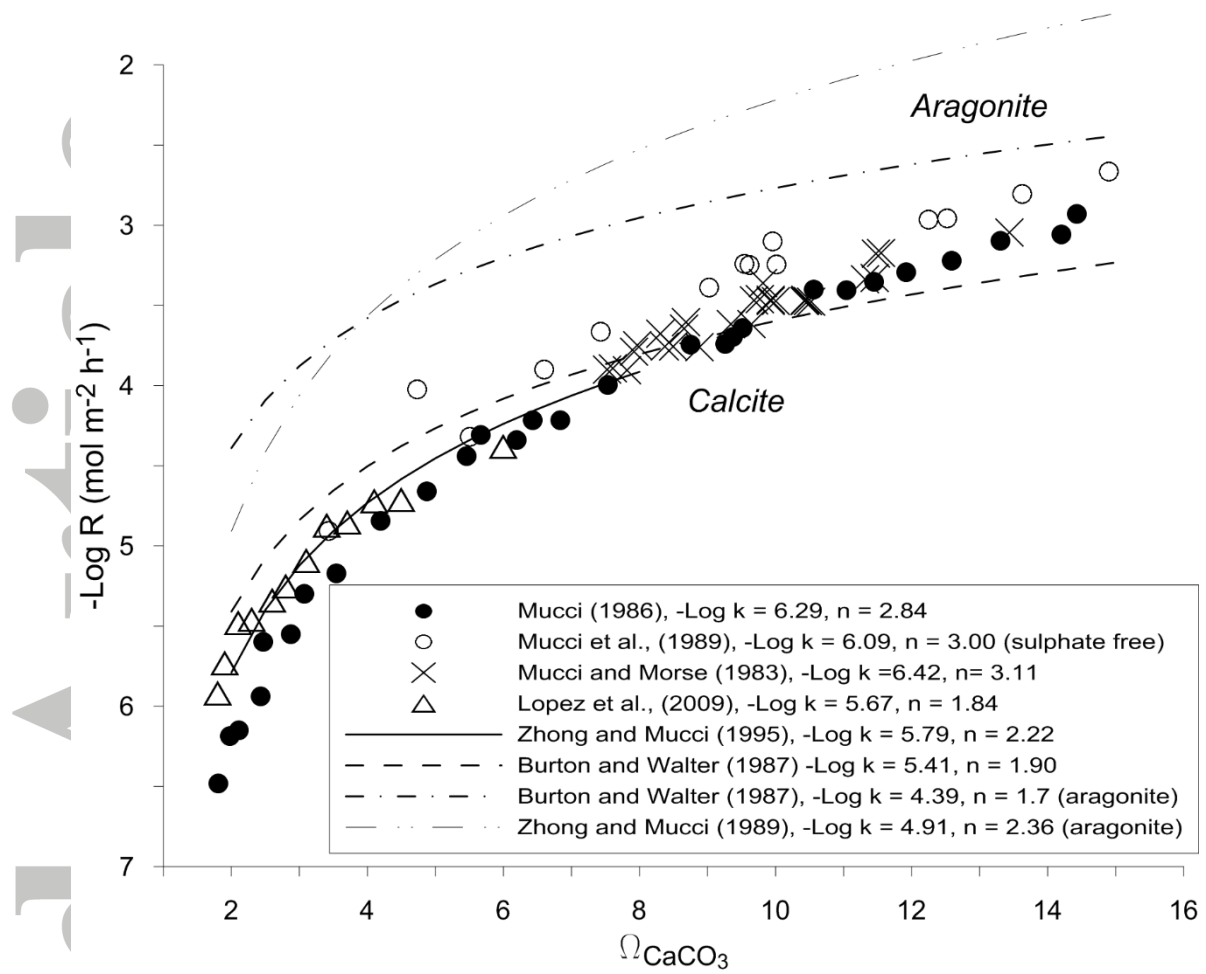
Figure 12: The relationship between saturation state and precipitation rate in natural and synthetic phosphate free seawater at 25°C. [*Burton and Walter* 1987; *Lopez et al.,* 2009; *Mucci* 1986; *Mucci et al.,* 1989; *Mucci and Morse* 1983; *Zhong and Mucci* 1995, 1989]
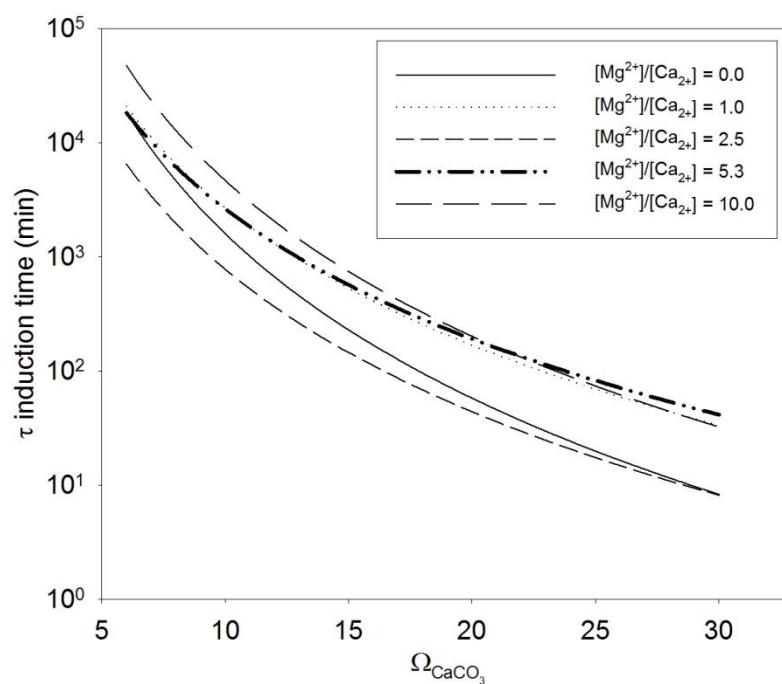
Figure 13: The relationship between homogenous nucleation induction time and carbonate saturation at 20°C [adapted from *Pokrovsky* 1998].
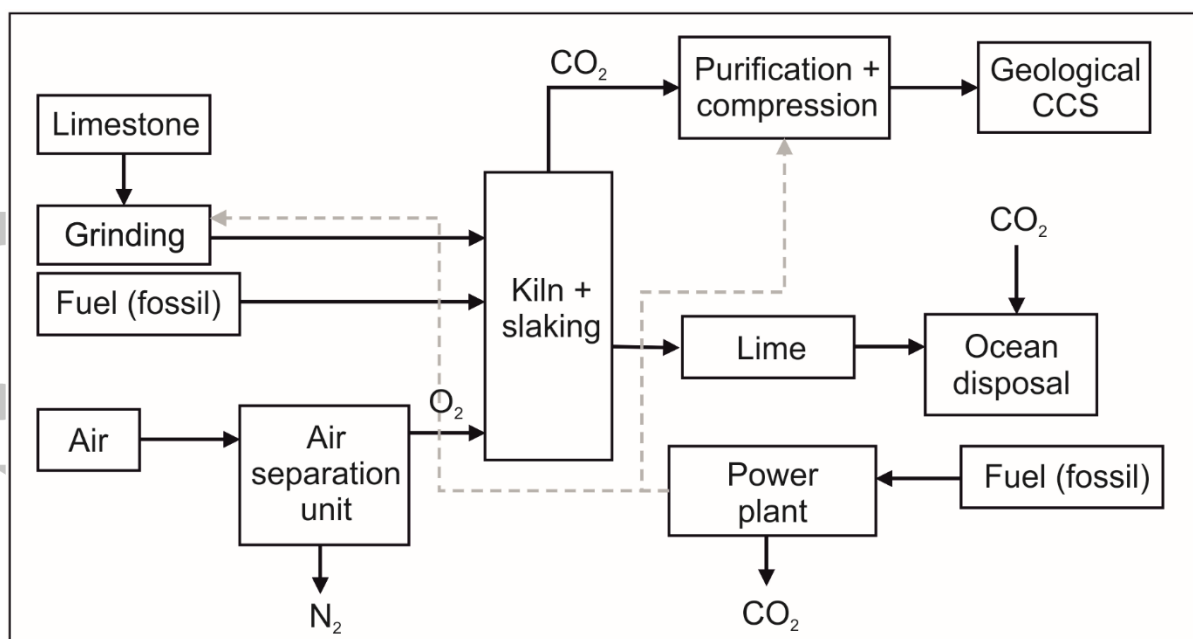
Figure 14: Schematic of lime production for ocean disposal. Developed from *Kheshgi* [1995] and *Renforth et al.,* [2013].
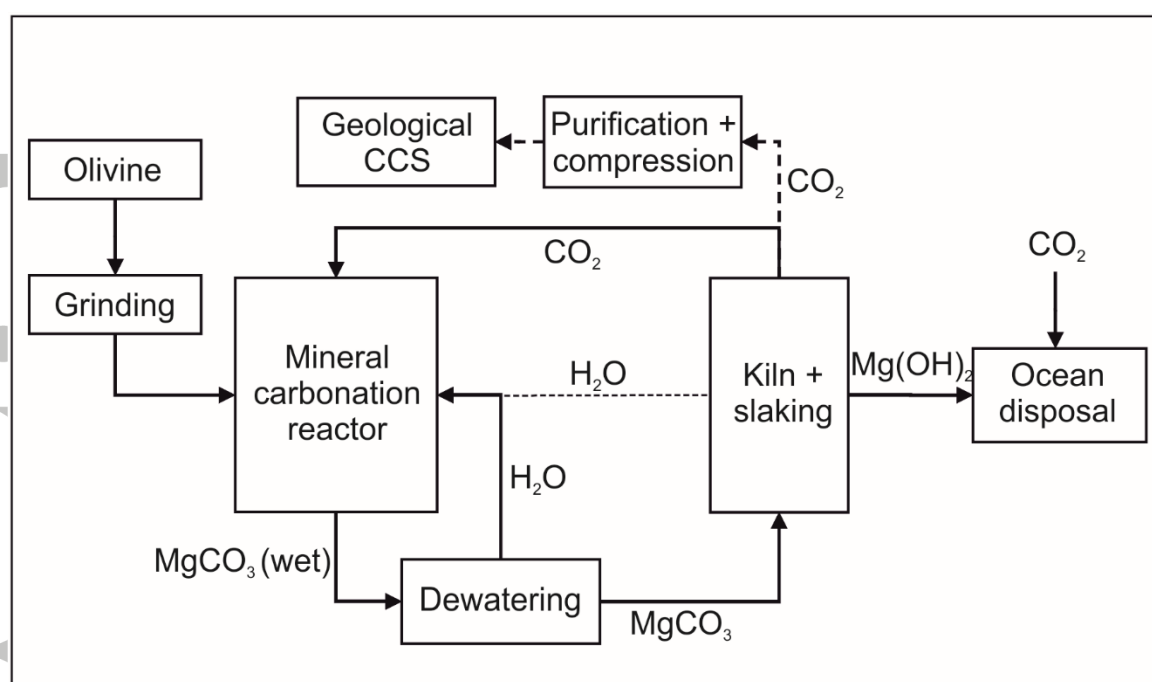
Figure 15: A simplified schematic of a coupled mineral carbonation ocean liming process. Adapted from *Renforth and Kruger* [2013].
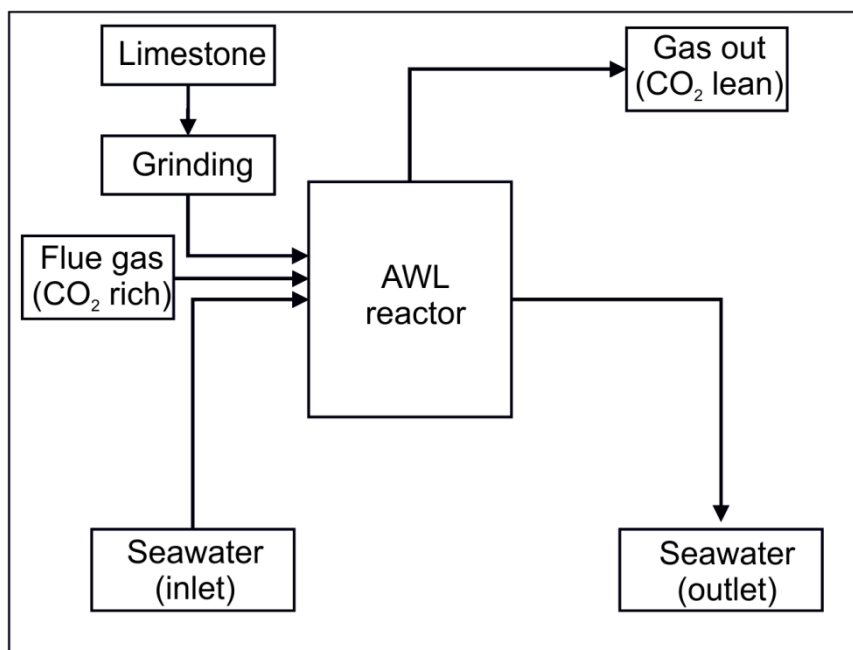
Figure 16: Schematic for the accelerated weathering of limestone.
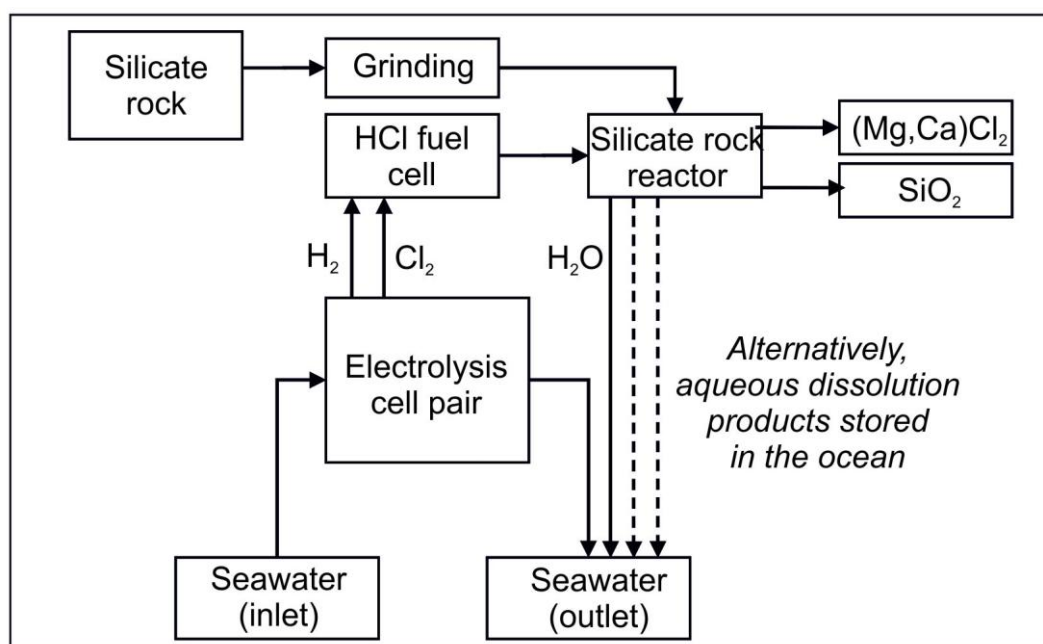
Figure 17: Direct electrolysis of seawater (adapted from *House et al.,* [2007])
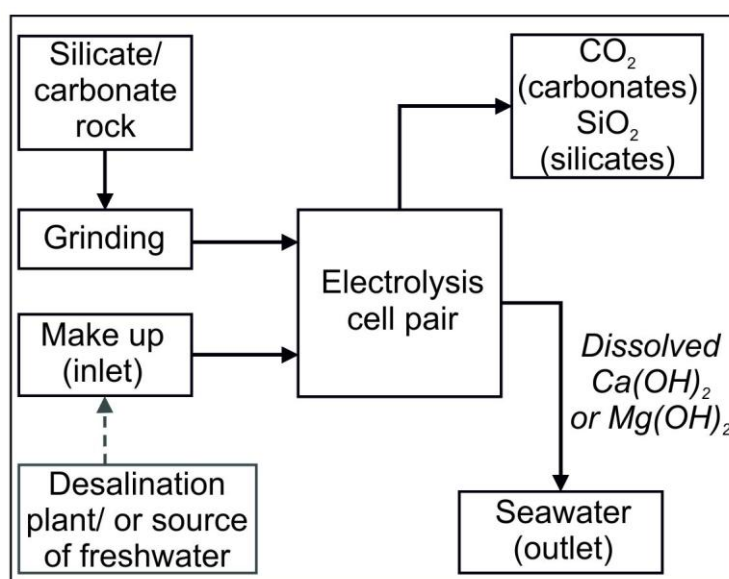
Figure 18: Electrochemical accelerated dissolution of minerals [*Rau* 2008; *Rau et al.,* 2013]. Seawater, natural or artificial brines could be the source of the electrolyte, which would negate the use of freshwater/desalination (although this would require the treatment of H_2 and Cl_2 produced)
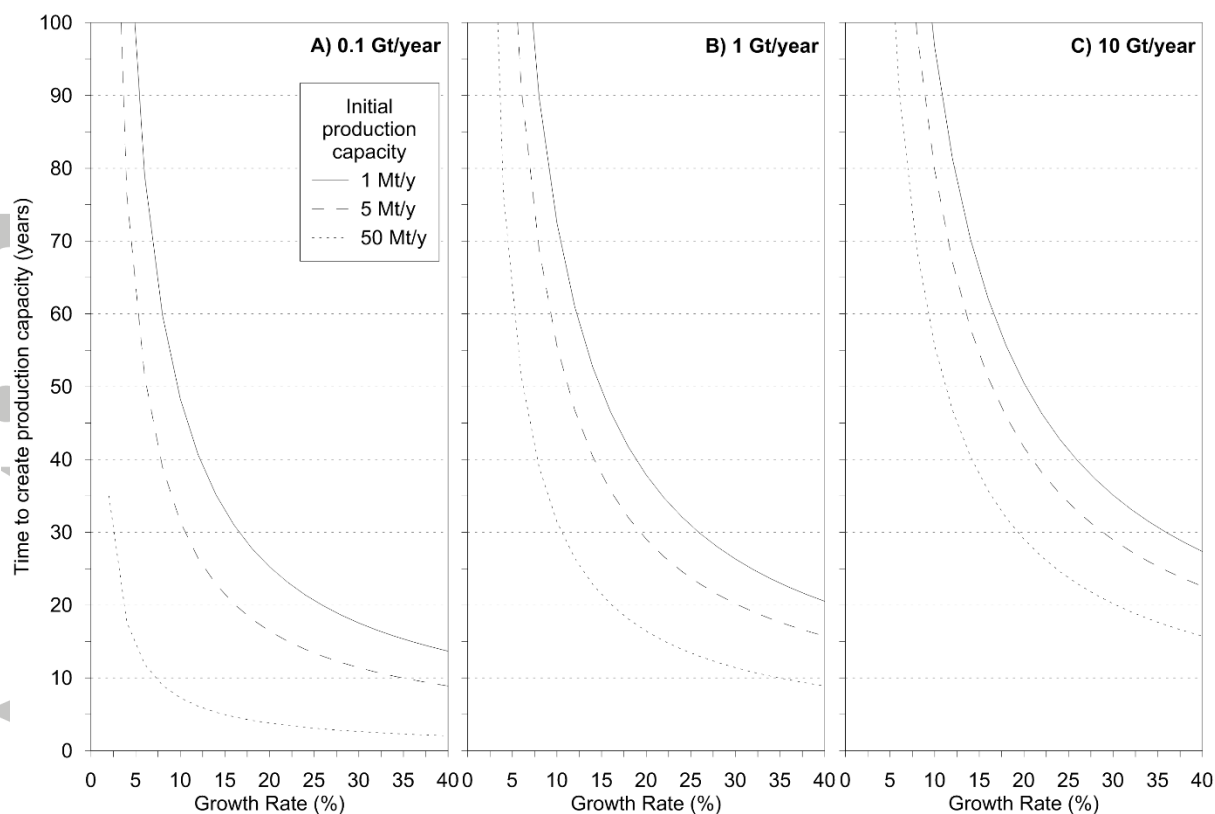
Figure 19: Time required to create A) 0.1 Gt, B) 1 Gt, and C) 10 Gt worth of production capacity as a function of technology growth rate (assuming an exponential growth). The different lines represent the initial capacity of 1 Mt a^{-1} and 5 Mt a^{-1} (which are broadly consistent with the minimum and maximum production capacity of a single cement plant), and 50 Mt a^{-1} which is (hypothetical/fictional) spare capacity present within existing industries.
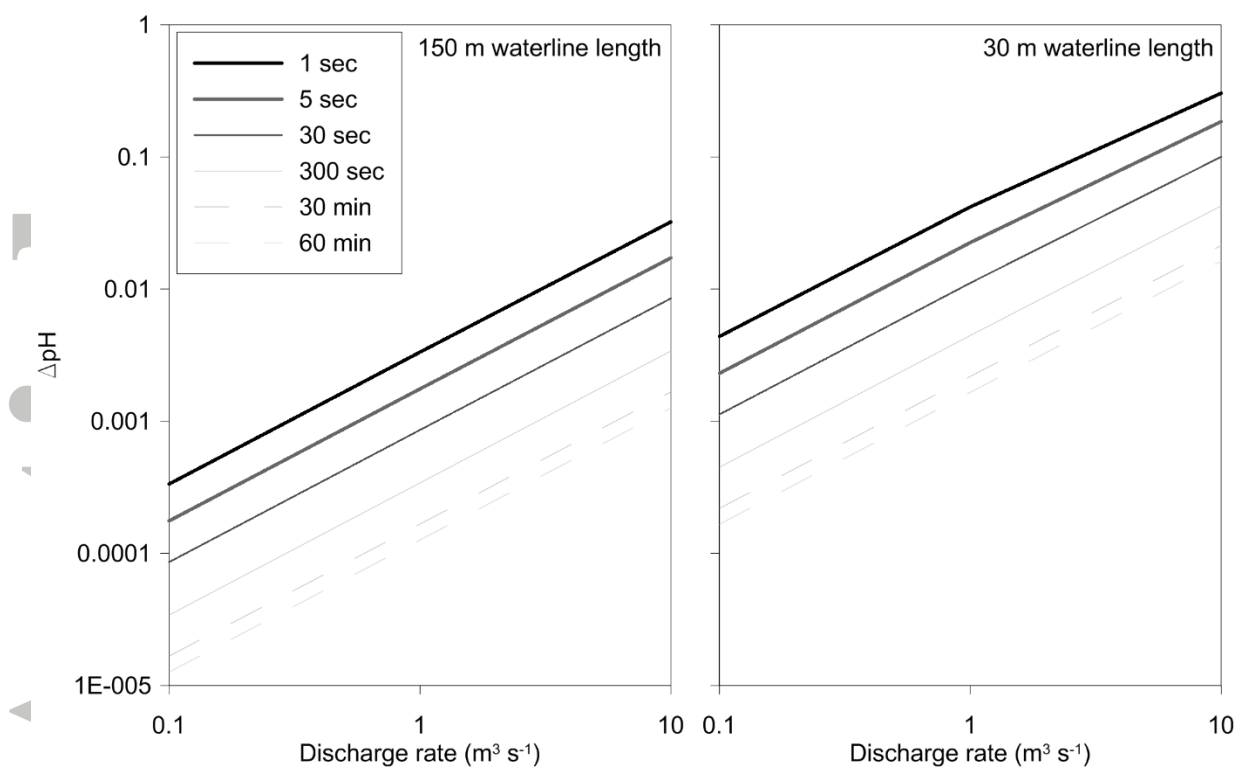
Figure 20: Change in pH from dumping of high pH solutions (or instantly dissolved particles) from the rear of a ship moving at 10 knots (18.5 km h^{-1}), derived from the IMO formula (see Box 2). Lines denote time after disposal. The model assumes no pH buffering.
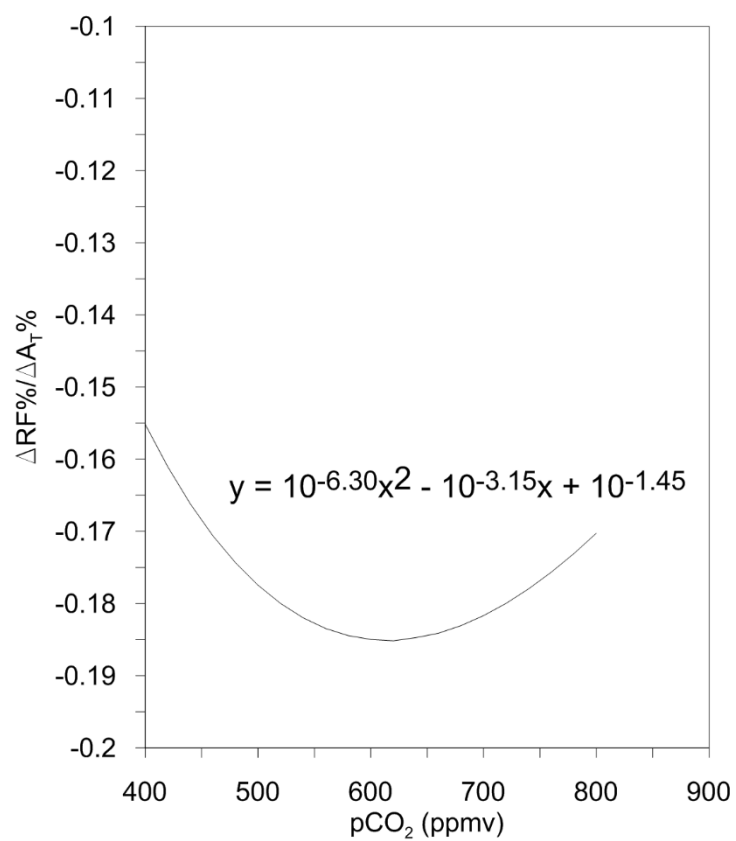
Figure 21: The proportional change in the Revelle Factor to total alkalinity increase.