Ocean alkalinity enhancement – avoiding runaway CaCO₃ precipitation during quick and hydrated lime dissolution

Charly A. Moras¹, Lennart T. Bach², Tyler Cyronak³, Renaud Joannes-Boyau¹, and Kai G. Schulz¹

¹Faculty of Science and Engineering, Southern Cross University, Lismore, NSW, Australia
²Ecology & Biodiversity, Institute for Marine and Antarctic Studies, University of Tasmania, Hobart, TAS, Australia
³Department of Marine and Environmental Sciences, Nova Southeastern University, Fort Lauderdale, FL, USA

Correspondence: Charly A. Moras (c.moras.10@student.scu.edu.au)

Received: 8 December 2021 – Discussion started: 10 December 2021
Revised: 19 June 2022 – Accepted: 26 June – Published: 1 August 2022

Abstract. Ocean alkalinity enhancement (OAE) is a method that can remove carbon dioxide (CO₂) from the atmosphere and counteract ocean acidification through the dissolution of alkaline minerals. Currently, critical knowledge gaps exist regarding the dissolution of different minerals suitable for OAE in natural seawater. Of particular importance is to understand how much alkaline mineral can be dissolved before secondary precipitation of calcium carbonate (CaCO₃) occurs, since secondary CaCO₃ precipitation reduces the atmospheric CO₂ uptake potential of OAE. Using two types of mineral proposed for OAE, quick lime (CaO) and hydrated lime (Ca(OH)₂), we show that both (<63 µm of diameter) dissolved in seawater within a few hours. No CaCO₃ precipitation occurred at a saturation state (Ωₐ) of ∼5, but CaCO₃ precipitation in the form of aragonite occurred above an Ωₐ value of 7. This limit is lower than expected for typical pseudo-homogeneous precipitation, i.e., in the presence of colloids and organic matter. Secondary precipitation at low Ωₐ (∼7) was the result of heterogeneous precipitation onto mineral surfaces, most likely onto the added CaO and Ca(OH)₂ particles. Most importantly, runaway CaCO₃ precipitation was observed, a condition where significantly more total alkalinity (TA) was removed than initially added. Such runaway precipitation could reduce the OAE CO₂ uptake efficiency from ∼0.8 mol of CO₂ per mole of added TA down to 0.1 mol of CO₂ per mole of TA. Runaway precipitation appears to be avoidable by dilution below the critical Ωₐ threshold of 5, ideally within hours of the mineral additions to minimise initial CaCO₃ precipitation. Finally, OAE simulations suggest that for the same Ωₐ threshold, the amount of TA that can be added to seawater would be more than 3 times higher at 5 °C than at 30 °C. The maximum TA addition could also be increased by equilibrating the seawater to atmospheric CO₂ levels (i.e., to a pCO₂ of ∼416 µatm) during addition. This would allow for more TA to be added in seawater without inducing CaCO₃ precipitation, using OAE at its CO₂ removal potential.

1 Introduction

Modern climate change is considered one of the greatest threats to humankind (Hoegh-Guldberg et al., 2019; IPCC, 2021; The Royal Society and Royal Academy of Engineering, 2018). Global mean temperature has increased by 1.0 °C since pre-industrial times and could reach +1.2–1.9 °C in the next 20 years and +2.1–5.7 °C by the end of this century (IPCC, 2021). Furthermore, about 26 % of all anthropogenic carbon dioxide (CO₂) emissions were taken up by the ocean through air–sea gas exchange between 1750 and 2020 (Friedlingstein et al., 2022). This has led to a decrease in the average open-ocean pH by 0.1 units in a process termed ocean acidification – OA (Bates et al., 2012; Canadell et al., 2007; Carter et al., 2019; Cyronak et al., 2014; Doney et al., 2009; Hoegh-Guldberg et al., 2007).

The aim of the 2015 Paris Agreement is to minimise the negative impacts of global warming and OA by limiting global warming to less than +2.0 °C, ideally below +1.5 °C, by the end of this century (Goodwin et al., 2018). However, the current and pledged reductions will likely not be enough, and additional CO₂ mitigation strategies are needed, such as ocean alkalinity enhancement – OAE (Gattuso et
OAE could be an efficient approach for CO₂ removal (current emissions of 40 Gt yr⁻¹), with models suggesting a potential of 165 to 790 Gt (1 Gt = 10¹² g) of atmospheric CO₂ removed by the year 2100 on a global scale if OAE were implemented today (Burt et al., 2021; Feng et al., 2017; IPCC, 2021; Keller et al., 2014; Köhler et al., 2013; Lenton et al., 2018). However, empirical data on OAE efficacies are limited, and safe thresholds for mineral dissolution are particularly lacking (National Academies of Sciences and Medicine, 2022).

OAE typically relies on the dissolution of alkaline minerals in seawater, releasing alkalinity similarly to natural rockweathering processes (Kheshgi, 1995). Suitable candidates are magnesium-rich minerals such as brucite, periclase or forsterite and calcium-rich minerals such as quick and hydrated lime (Renforth and Henderson, 2017). Quick lime and hydrated lime are of particular interest due to their high solubility in seawater and rapid dissolution. Quick lime, i.e. calcium oxide (CaO), is obtained by the calcination of limestone, composed primarily of calcium carbonate (CaCO₃), which is present in large quantities within the earth’s crust. Once heated to temperatures of ∼1200 °C, each molecule of CaCO₃ breaks down into one molecule of CaO and one molecule of CO₂ (Ilyina et al., 2013; Kheshgi, 1995). Hence, for maximum OAE potential, carbon capture during calcination and subsequent storage would be necessary (Bach et al., 2019; Ilyina et al., 2013; Kheshgi, 1995; Renforth et al., 2013; Renforth and Kruger, 2013). CaO can be hydrated into calcium hydroxide (Ca(OH)₂), also known as hydrated lime. The addition of either CaO or Ca(OH)₂ to seawater leads to the dissociation of Ca(OH)₂ into one calcium Ca²⁺ and two hydroxyl ions OH⁻ (Feng et al., 2017; Harvey, 2008). Ignoring the non-linearities of the seawater carbonate system (i.e. changes in total alkalinity, TA, and dissolved inorganic carbon, DIC, are not 1 : 1), the chemical reaction of CO₂ and Ca(OH)₂ dissolution and the subsequent uptake of atmospheric CO₂ can be written as

\[
(CaO + H₂O → Ca(OH)₂) + 2CO₂ → Ca^2+ + 2HCO₃^-. (1)
\]

The dissolution of CaO and Ca(OH)₂ and the subsequent addition of TA increase the pH of seawater, which changes the carbonate chemistry speciation (Zeebe and Wolf-Gladrow, 2001). DIC can be approximated as the sum of HCO₃⁻ and CO₃²⁻ (ignoring the small contribution by CO₂). Similarly, TA can be approximated as the sum of HCO₃⁻ and 2 CO₃²⁻ (ignoring the smaller contributions by boric and silicic acids and other minor components). Combining both DIC and TA equations reveals that CO₃²⁻ concentrations can be expressed as [CO₃²⁻] = TA – DIC. Hence, increasing TA at a constant DIC, e.g. by dissolving CaO or Ca(OH)₂, increases [CO₃²⁻], shifting the carbonate chemistry speciation towards a higher pH (Fig. A1) (Dickson et al., 2007; Wolf-Gladrow et al., 2007; Zeebe and Wolf-Gladrow, 2001). The subsequent shift in DIC speciation leads to a decrease in dissolved CO₂ concentrations, reducing the partial pressure of CO₂ (pCO₂) in seawater and increasing its atmospheric CO₂ uptake potential.

Depending on the amount of TA added and the initial seawater pCO₂, the TA-enriched seawater would either take up CO₂ from the atmosphere or reduce outgassing of CO₂. Factoring in the non-linearities of the carbonate system, about 1.6 mol of atmospheric CO₂ could be taken up per mole of dissolved CaO or Ca(OH)₂ (Köhler et al., 2010). Furthermore, dissolving CaO and Ca(OH)₂ can also counteract ocean acidification. During the dissolution of alkaline minerals, both pH and the CaCO₃ saturation state of seawater (Ω) increase through increasing Ca²⁺ and CO₃²⁻ concentrations. This makes OAE a dual solution for removing atmospheric CO₂ and mitigating OA (Feng et al., 2017; GESAMP, 2019; Harvey, 2008). However, there are important knowledge gaps in our understanding surrounding basic mineral dissolution in seawater (Feng et al., 2016; González and Ilyina, 2016; Mongin et al., 2021; Renforth and Henderson, 2017).

One knowledge gap is the critical Ω threshold beyond which CaCO₃ starts to precipitate inorganically. Such secondary precipitation constitutes the opposite of alkaline mineral dissolution and would decrease pH and Ω while simultaneously increasing the CO₂ concentration in seawater. This would decrease the ocean uptake’s capacity for atmospheric CO₂, causing the opposite of the intended effect. Additionally, if all added alkalinity were precipitated, only 1 mol of atmospheric CO₂ per mole of Ca²⁺ would be removed, instead of ∼1.6 mol in the absence of CaCO₃ precipitation. If even more CaCO₃ precipitated, the efficiency of OAE would be further reduced. Under typical seawater conditions, CaCO₃ precipitation does not occur due to the absence of mineral-phase precipitation nuclei and the presence of precipitation inhibitors such as dissolved organic compounds, magnesium (Mg) or phosphate (Chave and Suess, 1970; De Choudens-Sanchez and Gonzalez, 2009; Pytkowicz, 1965; Rushdi et al., 1992; Simkiss, 1964). There are three types of CaCO₃ precipitation, (1) homogeneous (in the absence of any precipitation nuclei), (2) heterogeneous (in the presence of mineral phases) and (3) pseudo-homogeneous (in the presence of colloids and organic materials) (Marion et al., 2009; Morse and He, 1993). For pseudo-homogeneous precipitation, the critical threshold at which calcite precipitates spontaneously is at a calcite saturation state (Ω_C) of ∼18.8 (at a salinity of 35 and at a temperature of 21 °C) (Marion et al., 2009). Assuming typical open-ocean carbonate chemistry (e.g. TA ~ 2350 μmol kg⁻¹ and DIC ~ 2100 μmol kg⁻¹), this threshold would be reached through an increase in TA of ~810 μmol kg⁻¹. This corresponds to a critical threshold for Ω with respect to aragonite, i.e. Ω_A, of ∼12.3. The two other types of precipitation (i.e. homogeneous and heterogeneous) are more poorly constrained (Marion et al., 2009). Importantly, at current dissolved Mg and Ca concentrations
in seawater, the CaCO₃ polymorph that is favoured during inorganic precipitation is aragonite rather than calcite (Morse et al., 1997; Pan et al., 2021). Therefore, aragonite saturation state Ω₄ may be a more important determinant of critical runaway precipitation thresholds. No matter what mineral phase is precipitating, a better understanding of CaCO₃ precipitation under conditions relevant to OAE is needed.

To gain a better understanding of the consequences of CaO and Ca(OH)₂ dissolution for OAE, we conducted several dissolution experiments with CaO and Ca(OH)₂ to determine (1) how much alkaline material can be dissolved without inducing CaCO₃ precipitation, (2) what causes secondary CaCO₃ precipitation and (3) how secondary precipitation can be avoided.

2 Material and methods

2.1 Experimental setup

Two different calcium minerals were used, CaO powder from Ajax Finechem (CAS no. 1305-78-8) and industrial Ca(OH)₂ powder (hydrated lime 20 kg, Dingo). The elemental compositions of these powders were analysed using an Agilent 7700 inductively coupled plasma mass spectrometer (ICP-MS), coupled to a laser ablation unit (NWR213, Electro Scientific Industries, Inc). Samples were embedded in resin and instrument readings calibrated against standard reference materials, batch nos. 610 and 612, from the National Institute of Standards and Technology.

All dissolution experiments were conducted in natural seawater. The seawater was collected between September 2020 and June 2021, about 200 to 300 m from the shore, avoiding suspended sand or silt, at Broken Head, New South Wales, Australia (28°42′12″ S, 153°37′03″ E). Seawater was stored for up to 14 d at 4 °C in the dark to slow bacterial metabolic activity and allow for all suspended particles to settle on the bottom before being sterile-filtered using a peristaltic pump, connected to a 0.2 µm Whatman Polycap 75 AS filter.

Salinity measurements, about 200 mL of seawater was placed in a gas-tight polycarbonate container and allowed to equilibrate to room temperature overnight. The sample’s conductivity and temperature were then measured with a Metrohm cell (6.017.080), connected to a 914 pH/Conductometer. The conductivity was recorded in millisiemens per centimetre (mS cm⁻¹) and the temperature in degrees Celsius (°C). Salinity was calculated according to Lewis and Perkin (1981) on the 1978 practical salinity scale. The salinity in each experiment is reported in Table A1.

2.2 OAE experiments

For each experiment, seawater was accurately weighed (in grams to 2 decimal places) into high-quality 2 L borosilicate 3.3 Schott DURAN beakers, and the temperature was controlled via a Tank chiller line TK-1000 set at 21 °C, feeding a re-circulation water jacket (Fig. A2). A magnetic stir bar was placed in the beaker, and the natural seawater was constantly stirred at ~ 200 rpm. To minimise gas exchange, a floating lid with various sampling ports was placed on top. Finally, after 1 h of equilibration, calculated quantities of weighed-in calcium alkaline compounds were added. Upon addition, samples for DIC and TA were taken at increasing time intervals to fully capture the dissolution kinetics and check for potential secondary precipitation. Furthermore, the pH was monitored at a frequency of 1 Hz for the first hour before alkalinity addition and over 4 h after addition to determine when alkalinity was fully released. Once the pH plateaued (corresponding to maximum TA release), the content of the beaker was carefully transferred to a clean Schott bottle to ensure that evaporation would not alter the DIC or TA concentrations. Bottles were kept in the dark for the duration of each experiment, i.e. up to 48 d, with the same constant stirring of ~ 200 rpm at 21 °C. Each bottle was exposed to UV light for at least 30 min after each sampling to inhibit bacterial growth.

2.2.1 CaO and Ca(OH)₂ dissolution

Following the beaker setup as described in Sect. 2.2, TA was added by sieving CaO and Ca(OH)₂ through a 63 µm mesh to avoid the formation of larger CaO or Ca(OH)₂ aggregates. The mesh was placed in a clean 50 mL upside-down Falcon tube cap to minimise the loss of material smaller than 63 µm, and the overall weight was recorded in milligrams. Then, the mesh was placed above the Schott bottle, and the mineral was added by gently tapping the side of the sieve. Finally, the sieve was placed in the same upside-down Falcon tube cap and weighed once again, thereby making sure that the desired amount had been added to the beaker. The weighing steps were carefully performed to avoid material loss between the bottle and the balance and were achieved in less than 5 min.

Two alkalinity additions, +250 and +500 µmol kg⁻¹ with each calcium mineral powder, were performed (Table 1).

2.2.2 Na₂CO₃ alkalinity, particles additions and filtration

Three further experiments assessed the role of mineral phases during secondary CaCO₃ precipitation observed in the previous experiments. The first experiment used a 1 M solution of sodium carbonate (Na₂CO₃, CAS number 497-19-8), freshly prepared on the day to limit CO₂ ingassing. Ultrapure Na₂CO₃ was accurately weighed (in mg with 2 decimal places) into a clean 100 mL Schott bottle and made up to 100 g with Milli-Q (18.2 MΩ). The solution was then sonicated for 15 min, with gentle mixing every 5 min. The amount of Na₂CO₃ to be added to seawater was calculated so that a similar maximum Ω₄ would be reached, i.e. ~ 7.7, as in the previous experiments with the highest addition of CaO and Ca(OH)₂. This required about twice
the alkalinity increase as before (Table 1) because Na$_2$CO$_3$ additions concomitantly increase DIC when dissociating in two sodium ions and one CO$_3^{2-}$ ion, making the $\Omega_A$ increase smaller. All carbonate chemistry calculations were performed in CO2SYS (see below).

In another experiment similar to the Na$_2$CO$_3$ addition, quartz powder was added after 2 d. Quartz powder was chosen as it does not dissolve on the timescales relevant for this study (Montserrat et al., 2017). The addition of quartz powder was similar to the sieved CaO and Ca(OH)$_2$ additions, i.e. through a 63 µm mesh. The mass of quartz particles added (in mg with 2 decimal places) was determined to provide the same mineral surface area as for the Ca(OH)$_2$ experiments with a TA increase of 500 µmol kg$^{-1}$. It was calculated using densities and masses of Ca(OH)$_2$ and quartz, assuming spherical particles with a diameter of 63 µm.

The third experiment followed the same experimental setup described in Sect. 2.2.1. Here, Ca(OH)$_2$ was added to increase TA by $\sim$500 µmol kg$^{-1}$ (Table 1). After 4 h of reaction, the entire content of the 2 L Schott beaker was filtered through a Nylon Captiva EconoFilter (25 mm) with a pore size of 0.45 µm into a clean 1 L Schott bottle using a peristaltic pump. The bottle was filled from bottom to top, with overflow to minimise gas exchange.

### 2.2.3 Dilution experiments

In a last set of experiments, alkalinity-enriched seawater was diluted with natural seawater to test if secondary precipitation could be avoided or stopped. Ca(OH)$_2$ powder was added to reach final alkalinity enrichments of 500 and 2000 µmol kg$^{-1}$, and dilutions were carried out at several time intervals.

For the experiment with a targeted TA increase of 500 µmol kg$^{-1}$, a larger quantity of TA-enriched seawater was required to perform all dilutions and sampling in comparison to the previous experiments. Therefore, two 5 L Schott bottles were filled with 5 kg of natural seawater and placed on a magnetic stirring platform. Calculated weighed-in masses of Ca(OH)$_2$ were added to the first bottle, as described in Sect. 2.2.1, using the 63 µm sieve, while the natural seawater in the second bottle was kept for subsequent dilutions. Both bottles were kept on the same bench under the same conditions, stirring at a rate of $\sim$200 rpm, for the duration of the experiment.

Following the Ca(OH)$_2$ addition, 1 : 1 dilutions (500 g TA-enriched seawater : 500 g natural seawater) were performed in clean 1 L Schott bottles that were kept in the dark and placed on a magnetic platform at a stirring rate of $\sim$200 rpm. After each sampling time, the bottles were exposed to UV light for at least 30 min. The second dilution experiment was...
set up like the first one, the only difference being that the targeted TA increase was 2000 µmol kg\(^{-1}\). The dilution ratio was 1 : 7 to reduce the targeted TA increase again to 250 µmol kg\(^{-1}\). All dilutions were performed 10 min, 1 h, 1 d and 1 week after Ca(OH)\(_2\) addition, leading to two TA-enriched and eight diluted treatments.

2.3 Carbonate chemistry measurements

Samples for TA and DIC measurements were filtered through a Nylon Captiva EconoFilter (0.45 µm) using a peristaltic pump to 100 mL borosilicate 3.3 Schott DURAN glass stopper bottles. The bottles were gently filled from the bottom to top, using a 14-gauge needle as described in Schulz et al. (2017), with at least half of their volume allowed to overflow, corresponding to \(\sim 150\) mL of seawater sampled per time point. After filling, 50 µL of saturated mercuric chloride solution was added to each sample before being stored without headspace in the dark at 4\(^\circ\)C.

TA was analysed in duplicate via potentiometric titrations by a Metrohm 848 Titrino plus coupled to an 869 Compact Sample Changer using 0.05 M HCl, with the ionic strength adjusted to 0.72 mol kg\(^{-1}\) using NaCl, corresponding to a salinity of 35. Titrations and calculations followed the open-cell titration protocols by Dickson et al. (2007). DIC was measured in triplicate using an Automated Infra-Red Inorganic Carbon Analyzer (AIRICA, Marianda) coupled to a LI-COR LI-7000 infra-red detector as described in Gafar and Schulz (2018). Measured values of TA and DIC were corrected using an internal standard prepared as described in Dickson (2010), calibrated against certified reference materials, batch nos. 175 and 190.

The overall instrument uncertainty for TA and DIC was calculated as follows. For each measurement, a standard deviation was calculated, from duplicates of TA and triplicates of DIC. The samples and reference material standard deviations were averaged, and an error propagation on these values were used to estimate average measurement uncertainty, i.e. ± 1.0 µmol kg\(^{-1}\) and DIC at ± 0.8 µmol kg\(^{-1}\), for TA and DIC, respectively.

2.4 Particulate inorganic carbon and scanning electron microscopy (SEM)

In cases where TA and DIC decreases were observed, indicative of CaCO\(_3\) precipitation, samples were taken at the end of the experiments for total particulate carbon (TPC), particulate organic carbon (POC) and scanning electron microscopy (SEM) analyses. TPC and POC samples were collected in duplicates on pre-combusted (450\(^\circ\)C) GF/F filters and stored frozen until analysis. Before analysis, POC filters were fumed with HCl for 2 h before drying overnight at 60\(^\circ\)C while TPC filters were dried untreated (Gafar and Schulz, 2018). The filters were wrapped in tin capsules and pressed into small 5 mm diameter balls. TPC and POC were quantified on a Thermo Fisher Flash Elemental Analyzer, coupled to a Delta V Plus isotope ratio mass spectrometer. Particulate inorganic carbon (PIC), or CaCO\(_3\), was calculated based on the difference between TPC and POC. The results are reported in µmol kg\(^{-1}\) of seawater with an uncertainty estimate by an error propagation of the square root of the sum of the squared standard deviations for TPC and POC.

For SEM analysis, 10 to 15 mL of the sample water was collected on polycarbonate Whatman Cyclopore filters with a 0.2 µm pore size and rinsed with 50 mL of Milli-Q. The filters were dried at 60\(^\circ\)C overnight and kept in a desiccator until analysis on a tabletop Hitachi TM4000 Plus scanning electron microscope. The microscope was coupled to an energy-dispersive X-ray (EDX) analyser, allowing us to identify the CaCO\(_3\) polymorph and elemental composition of precipitates. Finally, CaO and Ca(OH)\(_2\) powders were analysed for their carbon content. This analysis aimed to identify the presence and estimate the amount of particulate carbon, most likely CaCO\(_3\), in the respective mineral powders.

2.5 Carbonate chemistry calculations

Measured DIC, TA, temperature and salinity were used to calculate the remaining carbonate chemistry parameters with the CO2SYS script for MATLAB\textsuperscript{®} (MathWorks) (Sharp et al., 2021). The borate-to-salinity relationship and boric acid dissociation constant from Uppstrom (1974) and the carbonic acid dissociation constants of Lueter et al. (2000) were used. With two measured carbonate chemistry parameters, i.e. DIC and TA, the others can be derived. An important difference in our experiments was that the dissolution of CaO and Ca(OH)\(_2\) changed the calcium concentration, and hence the salinity-based \(\Omega\) calculated by CO2SYS is underestimated. \(\Omega\) is defined by the solubility product of CaCO\(_3\) as

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

where \([\text{Ca}^{2+}]\) and \([\text{CO}_3^{-2}]\) denote seawater concentrations of Ca\(^{2+}\) and CO\(_3^{-2}\) and \(K_{sp}\) is the solubility product for calcite or aragonite at the appropriate salinity and temperature. To calculate saturation states, the correct calcium concentration \([\text{Ca}^{2+}]_{\text{corr}}\) was estimated from measured salinity (Riley and Tongudai, 1967) and half the alkalinity concentration change, \(\Delta\text{TA}\), generated during CaO or Ca(OH)\(_2\) dissolution or loss due to CaCO\(_3\) precipitation:

\[
[\text{Ca}^{2+}]_{\text{corr}} = \frac{0.01028}{35} \times \text{salinity} + \frac{\Delta\text{TA}}{2},
\]

where 0.01028 is the molar Ca\(^{2+}\) concentration at a salinity of 35. \(K_{sp}\) was calculated from in situ temperature and salinity according to Mucci (1983). The correct \(\Omega_C\) and \(\Omega_A\) were then calculated according to Eq. (2). Please note that we have opted to report \(\Omega_A\) rather than \(\Omega_C\) since aragonite
is more likely to be precipitated in natural modern seawater (Morse et al., 1997).

2.6 OAE simulations

CO2SYS and the results from the various dissolution experiments were used to simulate three OAE scenarios (Table 3). Three alkalinity additions were simulated, +250, +500 and +1000 µmol kg\(^{-1}\). The starting parameters were TA = 2350 µmol kg\(^{-1}\), DIC = 2100 µmol kg\(^{-1}\), salinity = 35 and temperature = 19°C, using the same acid–base equilibrium constants as described in Sect. 2.5. In the first scenario, for all three additions, no CaCO\(_3\) precipitation was assumed. We then estimated the amount of CO\(_2\) taken up by the seawater after atmospheric re-equilibration, i.e. until a \(pCO_2\) of ∼416 ppm and recorded the changes in the carbonate chemistry parameters. Second, we assumed that as much CaCO\(_3\) precipitated as TA was added; e.g. after increasing the TA by 500 µmol kg\(^{-1}\), we assumed a loss of 500 µmol kg\(^{-1}\) of TA and 250 µmol kg\(^{-1}\) of DIC. We then simulated atmospheric re-equilibration until a \(pCO_2\) of ∼416 ppm and recorded the changes in the carbonate chemistry parameters. Second, we assumed that CaCO\(_3\) precipitated down to an \(\Omega\) of ∼2 as observed in our experiments.

After calculating full carbonate chemistry speciation in these various scenarios, the amount of CO\(_2\) taken up after atmospheric re-equilibration was determined using the same approach as described above.
3 Results

3.1 Chemical composition of CaO and Ca(OH)$_2$

The bulk chemical compositions of the CaO and Ca(OH)$_2$ powders were analysed. These consisted primarily of calcium, with minor contributions of magnesium and silicon (see Table A2 for a more comprehensive list). Furthermore, CaO and Ca(OH)$_2$ contained about 9.4 ± 0.1 and 18.0 ± 0.2 mg g$^{-1}$ of particulate carbon, respectively, i.e. ∼0.9 % and ∼1.8 % by weight.

3.2 CaO dissolution in filtered natural seawater

In the first CaO experiment with a targeted 250 µmol kg$^{-1}$ TA addition, TA increased by ∼200 µmol kg$^{-1}$ within the first 4 h (Fig. 1a). Following this increase, TA was stable over time. In contrast, DIC increased slowly, at about 1 µmol kg$^{-1}$ d$^{-1}$, reaching about +50 µmol kg$^{-1}$ on day 47 of the experiment (Fig. 1b). $\Omega_A$ reflected the trend observed for $\Delta$TA, increasing from ∼2.9 to ∼5.1 within the first 4 h before slowly decreasing to 5.0 on day 47 (Fig. 1c).

In the second CaO experiment with a targeted 500 µmol kg$^{-1}$ TA addition, TA increased by ∼410 µmol kg$^{-1}$ within the first 4 h before slowly decreasing on day 3 (Fig. 1a). This was followed by a rapid decrease over the following week, eventually reaching a steady state on day 20 at a final $\Delta$TA of about −540 µmol kg$^{-1}$. This corresponds to a total loss of TA of ∼950 µmol kg$^{-1}$, between the maximum measured TA and the final recorded TA. A small decrease in DIC of ∼10 µmol kg$^{-1}$ was observed over the first 2 d before a more significant reduction in the following week. Finally, $\Delta$DIC levelled off at about −465 µmol kg$^{-1}$ (Fig. 1b). $\Omega_A$ rapidly increased during the first 4 h of the experiment from 2.8 up to 7.6 (Fig. 1c). Following this quick increase, $\Omega_A$ decreased by 0.3 units by day 3. Afterwards, $\Omega_A$ dropped quickly to 2.4 on day 13, and reached ∼1.8 on day 47, corresponding to a reduction of 1.0 compared to the starting seawater value.

3.3 Ca(OH)$_2$ dissolution in filtered natural seawater

In the first Ca(OH)$_2$ experiment with a targeted TA addition of 250 µmol kg$^{-1}$, TA increased by ∼220 µmol kg$^{-1}$ after 4 h of reaction, before stabilising at a $\Delta$TA of ∼210 µmol kg$^{-1}$ for the rest of the experiment (Fig. 2a). The DIC concentration increased quickly over the first 6 d after the TA addition before slowing down, reaching about +70 µmol kg$^{-1}$ by the end of the experiment (Fig. 2b). Finally, $\Omega_A$ reached ∼4.1 after 4 h, slightly decreasing over time, reaching 3.3 on day 28 (Fig. 2c).

In the second Ca(OH)$_2$ experiment with a targeted TA addition of 500 µmol kg$^{-1}$, TA increased by ∼440 µmol kg$^{-1}$ within the first 4 h (Fig. 2a). This was followed by a steady decrease of ∼18 µmol kg$^{-1}$ d$^{-1}$ over the next 2 weeks, after which the decrease accelerated to ∼28 µmol kg$^{-1}$ d$^{-1}$ until day 35. Then, it levelled off at a $\Delta$TA of about −420 µmol kg$^{-1}$ towards the end of the experiment. Overall, ∼860 µmol kg$^{-1}$ of TA was lost compared to the highest TA recorded. The overall DIC concentration decreased in a similar fashion to TA, reaching a $\Delta$DIC of about −395 µmol kg$^{-1}$ compared to the initial DIC concentration (Fig. 2b). $\Omega_A$ increased from 2.5 to 7.4 in the first 4 h before decreasing, similarly to TA and DIC, reaching ∼2.0 on day 42 (Fig. 2c).

3.4 Na$_2$CO$_3$, particle addition and filtration

Three experiments assessed the influence of particles on CaCO$_3$ precipitation. In the first one, ∼1050 µmol kg$^{-1}$ of TA was added using a 1 M Na$_2$CO$_3$ solution, designed to obtain a similar maximum $\Omega_A$ to the previous experiments when TA decreased (Table 1). Upon addition, TA increased
Figure 4. Changes in TA (a and d), DIC (b and e) and $\Omega_A$ (c and f) following a TA addition of 500 and 2000\,µmol\,kg$^{-1}$, respectively, by Ca(OH)$_2$ (black line), as well as following a 1 : 1 dilution for the 500\,µmol\,kg$^{-1}$ TA addition (red and yellow lines) and a 1 : 7 dilution for the 2000\,µmol\,kg$^{-1}$ TA addition (blue lines). The dilutions were performed after 10 min, 1 h, 1 d and 1 week, and earlier dilutions are represented by lighter colours.
by ~1060 µmol kg\(^{-1}\) and DIC by ~530 µmol kg\(^{-1}\) within minutes. For the remainder of the experiment, ΔTA was fairly constant between 1060 and 1040 µmol kg\(^{-1}\) (Fig. 3a). In contrast, DIC slightly increased over 42 d from a ΔDIC of ~530 µmol kg\(^{-1}\) on day 1 to ~560 µmol kg\(^{-1}\) on day 42 (Fig. 3b). ΔA increased from ~2.3 to ~8.5 within minutes of the Na\(_2\)CO\(_3\) addition and slightly decreased to ~8.1 after 42 d of the experiment (Fig. 3c).

In the second experiment, the addition of 1 M Na\(_2\)CO\(_3\) solution (Table 1) increased TA by 1070 µmol kg\(^{-1}\), while DIC increased by ~540 µmol kg\(^{-1}\) within minutes and remained stable (Fig. 3a, b). After 2 d, quartz particles were added. Whereas ΔTA and ΔDIC remained invariant after 1 d, ΔTA decreased to ~220 µmol kg\(^{-1}\) and ΔDIC dropped to ~120 µmol kg\(^{-1}\) between day 5 and 12 (Fig. 3a, b). Over the next month, ΔTA and ΔDIC continued to decrease, although at a slowing rate, reaching about −200 and −110 µmol kg\(^{-1}\), respectively, on day 42. ΔA followed a similar trend, with an increase from ~2.8 up to ~9.2 within the first 1.5 h and a significant decline to ~3.9 between day 5 and day 12, before stabilising at around ~2.0 at the end of the experiment on day 48.

In the last experiment, Ca(OH)\(_2\) was added, aiming for a TA increase of 500 µmol kg\(^{-1}\) (Table 1), a level at which a significant TA decrease had been observed previously (Fig. 2a). In contrast to the previous experiment, after reaching ~470 µmol kg\(^{-1}\) at the 4 h mark, the content of the bottle was filtered and ΔTA remained relatively constant between 465 and 470 µmol kg\(^{-1}\) over the following 48 d of the experiment (Fig. 3a). Meanwhile, ΔDIC increased from ~5 to 55 µmol kg\(^{-1}\) after filtration (Fig. 3b). ΔA increased from ~2.8 to ~8.2 within the first 1.5 h after Ca(OH)\(_2\) addition and then slightly decreased to ~7.5 over the 48 d of the experiment (Fig. 3c).

### 3.5 Dilution experiments

#### 3.5.1 The 500 µmol kg\(^{-1}\) addition

In these experiments with a targeted TA increase of 500 µmol kg\(^{-1}\) by Ca(OH)\(_2\) addition, ΔTA increased to ~450 µmol kg\(^{-1}\) after 2 h (Fig. 4). These changes in TA were followed by a decline to ~320 µmol kg\(^{-1}\) after 14 d, although the latter was a slightly slower decrease than previously (Figs. 2, 4a). After a first increase in ΔDIC by ~10 µmol kg\(^{-1}\) on day 1, ΔDIC steadily decreased to about −20 µmol kg\(^{-1}\) after 2 weeks (Fig. 4b). Finally, ΔA increased from ~2.7 to ~7.8 after 2 h, before steadily decreasing to ~6.4 on day 14 (Fig. 4c).

In the diluted treatments, ΔTA remained relatively stable over time, until the end of the experiments on day 29, regardless of dilution time (Fig. 4a). Upon dilution, ΔTA was reduced, values of which were similar for the 10 min, 1 h and 1 d dilutions. Overall, in the 1-week dilution, ΔTA was slightly lower, i.e. ~205 µmol kg\(^{-1}\) instead of ~230 µmol kg\(^{-1}\) on average. In all dilutions, ΔDIC increased over time, ranging between ~20 and ~60 µmol kg\(^{-1}\), independently of dilution timing. Finally, ΔA showed similar trends to ΔTA, reaching between ~4.8 and ~5.2 and slightly decreasing over time until the end of the experiment.

#### 3.5.2 The 2000 µmol kg\(^{-1}\) addition

This set of experiments aimed for a TA increase of 2000 µmol kg\(^{-1}\) by Ca(OH)\(_2\) addition. However, TA only increased to approximately one-third of the targeted value, i.e. ~725 µmol kg\(^{-1}\) within the first 2 h (Fig. 4d). Following this increase, TA rapidly decreased during the first day, reaching a ΔTA of about −1260 and then −1440 µmol kg\(^{-1}\) in the following week (Fig. 4d). Over the second week of the experiment, TA appeared to stabilise before increasing until day 21. In contrast, ΔDIC decreased by ~580 µmol kg\(^{-1}\) within the first 2 h, before rapidly dropping to about −1590 µmol kg\(^{-1}\) on day 1 and −1660 µmol kg\(^{-1}\) after 7 d (Fig. 4e). Over the remaining 41 d, ΔDIC increased by ~210 µmol kg\(^{-1}\), remaining ~1450 µmol kg\(^{-1}\) below the starting DIC concentration. ΔA increased to ~16.7 after 2 h, followed by a rapid drop to ~3.2 on day 1 and ~2.0 on day 14 and slightly increasing over the following 34 d, varying between 2.0 and 2.1 (Fig. 4f).
With respect to $\Delta TA$, $\Delta DIC$ and $\Omega_A$, the 10 min and 1 h dilutions showed similar responses, as did the 1 d and 1-week dilutions. Upon dilution, $\Delta TA$ reached values of $\sim$240 µmol kg$^{-1}$ after the 10 min and 1 h dilutions and about $-160$ to $-190$ µmol kg$^{-1}$ after the 1 d and 1-week dilutions. With the exception of one data point in the 1-week dilution data, $\Delta TA$ remained relatively constant throughout all dilution experiments (Fig. 4d). DIC changes were similar to the TA changes, slowly increasing over time between 0.6 and 2.5 µmol kg$^{-1}$ d$^{-1}$, with very similar values reached for the 10 min and 1 h dilutions, as opposed to the 1 d and 1-week dilutions (Fig. 4e). Finally, $\Omega_A$ dropped from $\sim$5.0–5.1 to $\sim$4.0–4.1 over time in the 10 min and 1 h dilutions, while it decreased from $\sim$2.3–2.8 to $\sim$2.1–2.2 until day 21 in the 1 d and 1-week dilutions before increasing to $\sim$2.6–3.4 towards the end of the experiments (Fig. 4f).

### 3.6 Particulate inorganic carbon

With the exception of the $\sim$1050 µmol kg$^{-1}$ TA addition by Na$_2$CO$_3$ and quartz particles, measured PIC in experiments was always higher than estimates from measured $\Delta TA$ (Table 2). Furthermore, PIC estimated from the theoretical maximum TA increase upon full mineral dissolution, $\Delta TA_{\text{Theo}}$, was always higher than estimated PIC from $\Delta TA$, by about 7% to 14% in the $\sim$500 µmol kg$^{-1}$ TA additions with Ca(OH)$_2$ and CaO, respectively, and up to 67% in the experiment with $\sim$2000 µmol kg$^{-1}$ TA additions.

### 4 Discussion

This study presents the first results investigating the dissolution of CaO and Ca(OH)$_2$ in natural seawater in the context of OAE. In experiments with at least 500 µmol kg$^{-1}$ TA increase, secondary precipitation was detected through observed TA and DIC decreases, as well as PIC increases. More specifically, at TA additions leading to an $\Omega_A$ higher than 7 (in the +500 and +1000 µmol kg$^{-1}$ TA treatments), “run-away CaCO$_3$ precipitation” was observed, meaning that not only was the added TA completely removed but significant portions of residual seawater TA were as well, until a new steady state was reached. This vastly reduces the desired CO$_2$ removal potential by OAE and should therefore be avoided. In a subsequent set of experiments, we simulated ocean mixing to estimate the timescales required to avoid and/or stop secondary CaCO$_3$ precipitation for applications that initially have TA additions above the critical threshold.

#### 4.1 Identifying CaCO$_3$ precipitation, the problem of unmeasured precipitation, CO$_2$ gas exchange

CaCO$_3$ precipitation can occur via three pathways, i.e. heterogeneous, homogeneous and pseudo-homogeneous nucleation and precipitation (Chen et al., 2005; Marion et al., 2009; Wolf et al., 2008). Heterogeneous precipitation relies on the presence of existing solid mineral surfaces. This differs from homogeneous precipitation, characterised by the formation of CaCO$_3$ crystals from Ca$^{2+}$ and CO$_3^{2-}$ ions in the absence of any nucleation surfaces (Chen et al., 2005; Wolf et al., 2008). Finally, the last type of precipitation, termed pseudo-homogeneous, is similar to homogeneous nucleation, but it occurs on nuclei other than solid minerals such as colloids, organic particles or glassware in a laboratory setting (Marion et al., 2009). Concerning the $\Omega$ thresholds above which CaCO$_3$ precipitation is expected, the lowest threshold would be for heterogeneous and the highest for homogeneous, with pseudo-homogeneous nucleation in between. This is because nucleation sites effectively lower the activation energy required for CaCO$_3$ precipitation (Morse et al., 2007).

When 1 mol of CaCO$_3$ is precipitated, the TA of the solution decreases by 2 mol due to the removal of 1 mol of CO$_3^{2-}$ ions, accounting for 2 mol of TA (Zeebe and Wolf-Gladrow, 2001). Simultaneously, the loss of 1 mol of CO$_3^{2-}$ decreases the DIC concentration by 1 mol. Hence, any loss of TA and DIC following a 2 : 1 ratio can be linked to CaCO$_3$ precipitation (Zeebe and Wolf-Gladrow, 2001). Additionally, when CaCO$_3$ precipitation was suspected in our experiments, SEM and particulate inorganic carbon samples were taken to confirm the presence of CaCO$_3$ and to identify which polymorphs were predominant. In the +250 µmol kg$^{-1}$ TA additions by CaO and Ca(OH)$_2$, both appeared to fully dissolve without inducing CaCO$_3$ precipitation as TA and $\Omega_A$ quickly increased within minutes, similarly to what has been described in the literature (Chave and Suess, 1970; Rushdi et al., 1992), until reaching their respective maxima after about a day and remaining stable over weeks (Figs. 1a and c, 2a and c). A slight increase in DIC was observed over time as expected since atmospheric CO$_2$ was absorbed from the bottle headspace, created when 150 to 200 mL of solution was withdrawn at each sampling point. The measured TA increase was slightly below the theoretically expected increase, which is assumed to be due to a combination of impurities present (in the case of CaO, a significant fraction could be hydrated) and any loss of the finely ground material during the process of weighing and sieving. On average, $\sim$23% of alkalinity added was not detected in the experiments with CaO and about 14% for the experiments using Ca(OH)$_2$ (Table 1, Figs. 1 and 2).

In contrast, in the +500 µmol kg$^{-1}$ TA additions by CaO and Ca(OH)$_2$, TA started decreasing after about 1 d following the observed initial increase. If this TA loss was through CaCO$_3$ precipitation, DIC should be reduced by half this amount. The measured TA and DIC losses were very close to this 2 : 1 ratio for both the CaO and the Ca(OH)$_2$ experiments with a TA addition of 500 µmol kg$^{-1}$ (950 : 465 and 860 : 395 for CaO and Ca(OH)$_2$, respectively). This suggests that TA precipitated in the form of CaCO$_3$. The slight offset can be explained by ingassing of CO$_2$ from the headspace which lowers the TA/DIC ratio, becoming visi-
ble only when precipitation ceases towards the end (Fig. 1b). Another caveat is that the maximum increase in TA from full dissolution of CaO or Ca(OH)$_2$ cannot be measured in the presence of concurrent CaCO$_3$ precipitation. This is mostly evident in the +2000µmol kg$^{-1}$ TA addition (Fig. 4), where DIC decreases due to CaCO$_3$ precipitation yet TA increases due to higher Ca(OH)$_2$ dissolution rates. This also explains why estimated PIC calculated from measured TA changes is generally smaller than measured PIC concentrations (Table 2). In the experiment with 1 M Na$_2$CO$_3$ and quartz particles, the measured TA-based PIC estimates were larger than the measured PIC. This difference is difficult to explain and could be possibly linked to the observed white layer on the bottle walls, indicative of CaCO$_3$ precipitation. In any case, while being a laboratory artefact, this has no practical consequences as in a natural setting the TA would eventually precipitate in the water column. In summary, trying to estimate CaCO$_3$ precipitation from measured changes in TA, without knowing how much TA was actually generated by full mineral dissolution or actual PIC measurements, might underestimate total precipitation.

4.2 The presence of mineral phases triggers runaway CaCO$_3$ precipitation

An important finding in our experiments was that whenever CaCO$_3$ precipitation was observed, it continued even if the solution dropped below an $\Omega_A$ of $\sim$4–5, levels at which no precipitation was observed in the +250µmol kg$^{-1}$ TA addition experiments. Furthermore, in all these experiments, precipitation decreased and seemingly ceased at an $\Omega_A$ of $\sim$1.8–2.0. Therefore, it appears that when CaCO$_3$ is initially precipitated, CaCO$_3$ continues to precipitate in a runaway fashion, even if $\Omega_A$ drops below levels where precipitation would not be initiated in natural seawater. This is to be expected as CaCO$_3$ precipitates onto CaCO$_3$ mineral surfaces at any saturation state above 1, and the initial precipitation at high-saturation states provides new nucleation sites (Morse et al., 2003, 2007; Zhong and Mucci, 1989). The precipitation rate is directly proportional to $\Omega_A$, decreasing exponentially until reaching zero at an $\Omega$ value of 1 (Fig. A4). However, the question of why precipitation occurred at a much lower $\Omega$ than anticipated, i.e. $\Omega$ $\sim$7.5 vs. $\sim$12.3, remains (Marion et al., 2009).

It is known that the presence of particles in suspension can initiate and accelerate CaCO$_3$ precipitation (Millero et al., 2001; Morse et al., 2003; Wurgaft et al., 2021). It is unlikely that the presence of CaCO$_3$ impurities in CaO (less than 1 % carbon) and Ca(OH)$_2$ (less than 2 % carbon) from imperfect calcination would have caused precipitation as the presence of CaCO$_3$ mineral phases should have caused precipitation at any saturation state above 1, i.e. also in the +250µmol kg$^{-1}$ TA addition experiments. Furthermore, modelling precipitation using experimentally determined $\Omega_A$ and surface-area-dependent aragonite precipitation rates onto CaCO$_3$ mineral phases (Zhong and Mucci, 1989) suggests that once precipitation becomes analytically detectable, it should proceed very rapidly before levelling off (Fig. A5). Furthermore, while we expected CaCO$_3$ precipitation to stop at $\Omega_A$ $\sim$1, we observed it to stop at $\Omega_A$ $\sim$2. The presence of dissolved organic carbon and soluble reactive phosphate could have slowed down if not stopped CaCO$_3$ precipitation at an $\Omega_A$ higher than 1 (Chave and Suess, 1970; Pan et al., 2021). We also observed that the bulk of precipitation occurred over a period of at least a week, after which an equilibration was reached with apparent differences between the different dissolving minerals (i.e. CaO, Ca(OH)$_2$ and quartz, although it is acknowledged that the experiments were not replicated).

Another explanation for CaCO$_3$ precipitation is heterogeneous precipitation on not-yet-dissolved CaO and Ca(OH)$_2$ particles (or other impurities), leading to CaCO$_3$ crystal formation and initiating runaway precipitation. The $\Omega_A$ threshold for this process would depend on lattice compatibility of the mineral phases (Tang et al., 2020). For instance, CaCO$_3$ precipitation has been observed at any saturation state above 1 when introducing CaCO$_3$ seed particles. In contrast, Lioliou et al. (2007) did not report CaCO$_3$ precipitation onto quartz particles at an $\Omega_A$ lower than 3.5, and in order to trigger CaCO$_3$ precipitation onto quartz particles, $\Omega_A$ would need to be further increased. Here, we observed CaCO$_3$ precipitation on quartz particles at an $\Omega_A$ of $\sim$9.2 (Fig. 3). The reason for initially slower but then more rapid precipitation could be a combination of exponentially increasing CaCO$_3$ surface area while increasing lattice compatibility (Lioliou et al., 2007; Pan et al., 2021). The filtration of TA-enriched seawater supports this idea since not-yet-dissolved mineral phases that could facilitate early nucleation were removed, preventing runaway CaCO$_3$ precipitation (Fig. 3).

Needle-shaped aragonite precipitation onto quartz particles (Fig. 5c and d) was observed by SEM imaging. EDX analyses identified the larger mineral to be rich in silicon, a key characteristic of quartz, and the needle-shaped particles were composed of carbon, oxygen and calcium, indicative of CaCO$_3$ (Chang et al., 2017; Ni and Ratner, 2008; Pan et al., 2021). In contrast, direct aragonite precipitation onto quartz particles, although it could be facilitated by early nucleation, was not observed, preventing formation of CaCO$_3$ particles (Fig. 3).

4.3 Impacts of CaCO$_3$ precipitation on OAE potential

From an OAE perspective, CaCO$_3$ precipitation is an important chemical reaction that needs to be avoided. During CaCO$_3$ precipitation, dissolved [CO$_2$$^-$] and $\Omega$ decrease and [CO$_2$] increases, which reduces the ocean’s uptake capacity for atmospheric CO$_2$, hence impacting the OAE potential.
Considering typical open-ocean TA and DIC concentrations of 2350 and 2100 µmol kg$^{-1}$, respectively, at a salinity of 35 and a temperature of 19°C, this water mass would have a $p$CO$_2$ close to atmospheric equilibrium of 416 µatm, a pH$_T$ value (total scale) of 8.04 and an $\Omega_A$ of 2.80. Without CaCO$_3$ precipitation, an addition of 500 µmol kg$^{-1}$ TA would lower $p$CO$_2$ to $\sim$ 92 µatm while increasing pH$_T$ and $\Omega_A$ to about 8.61 and 8.45, respectively. If fully re-equilibrated with the atmosphere, DIC would increase by about 420 µmol kg$^{-1}$, leading to a pH$_T$ and $\Omega_A$ 0.07 and 1.10 higher, respectively, than prior to the addition (Table 3). The resulting OAE efficiency would be 0.83 mol of atmospheric CO$_2$ absorbed per mole of TA added, very similar to estimates by Köhler et al. (2010). Considering that CaCO$_3$ is the source material for CaO and Ca(OH)$_2$ and that 2 mol of TA is produced per mole of CaO or Ca(OH)$_2$ mineral dissolution, $\sim$ 0.7 t of CO$_2$ could be captured per tonne of source material, assuming CO$_2$ capture during the calcination process. At a global scale, using all available ship capacity and assuming a slow discharge of 1.7 to 4.0 Gt of Ca(OH)$_2$ per year (Caserini et al., 2021), between 1.2 and 2.8 Gt of CO$_2$ per year could be absorbed by the ocean. Including direct coastal TA discharge at a constant addition of Ca(OH)$_2$ of 10 Gt yr$^{-1}$ (Feng et al., 2016), we could expect to absorb an additional 7 Gt of CO$_2$ per year. To put these model-derived numbers into perspective, the global cement industry currently produces about 4.1 Gt of cement per year (Statista, 2021). Depending on whether hydraulic (4CaO · Al$_2$O$_3$ · Fe$_2$O$_3$) or non-hydraulic (Ca(OH)$_2$) cement is being produced and assuming a molar Ca$^{2+}$-to-CO$_2$ sequestration potential of 1.6, up to 3.9 Gt of atmospheric CO$_2$ could be captured per year. This is within the range required over the next 30 years to keep global warming below the 2°C target, as in the Representative Concentration Pathway (RCP) 2.6 scenario (Huppmann et al., 2018).

The above numbers can only be achieved if CaO or Ca(OH)$_2$ dissolution is complete without CaCO$_3$ precipitation. Hypothetically, when as much CaCO$_3$ precipitates as TA is added, i.e. 100 µmol kg$^{-1}$ of CaCO$_3$ precipitates after a TA increase of 100 µmol kg$^{-1}$, only 1 instead of 1.6 mol of DIC can be absorbed per 2 mol of TA, after equilibration with atmospheric $p$CO$_2$ (Table 3). This represents a decrease by nearly 40% in OAE potential. Similarly, runaway CaCO$_3$ precipitation until an $\Omega_A$ of 2.0, as observed here, decreases the OAE potential further by almost 90%. Consequently, only $\sim$ 0.1 mol of DIC would be absorbed per mole of TA added (Table 3). Furthermore, secondary CaCO$_3$ precipitation higher than TA addition will lead to pH$_T$ and $\Omega$ levels lower than the initial ones. For instance, runaway

### Table 3. Simulations of the changes in TA, DIC, $\Omega_A$, $p$CO$_2$ and pH$_T$ (total scale) after TA increases of 250, 500 and 1000 µmol kg$^{-1}$, assuming complete mineral dissolution without precipitation, a complete dissolution followed by as much CaCO$_3$ precipitated as the amount of TA added and a complete dissolution followed by CaCO$_3$ precipitation until reaching an $\Omega_A$ of 2.0, before CO$_2$ re-equilibration to initial $p$CO$_2$. For each scenario, the number of moles of CO$_2$ absorbed per mole of TA added has been calculated for comparison. The 500 µmol kg$^{-1}$ TA addition simulation is shown in Fig. A3 in the Appendix.

|                  | Starting conditions (salinity = 35, 19°C) | TA + 250 µmol kg$^{-1}$ without CaCO$_3$ precipitation | TA + 500 µmol kg$^{-1}$ | TA + 1000 µmol kg$^{-1}$ |
|------------------|------------------------------------------|--------------------------------------------------------|------------------------|--------------------------|
|                  | TA (µmol kg$^{-1}$)                       | TA + 250 µmol kg$^{-1}$                                 | TA + 500 µmol kg$^{-1}$ | TA + 1000 µmol kg$^{-1}$ |
|                  | 2350                                     | 2600                                                   | 2850                   | 2350                     | 2350                     | 1748                     |
|                  | 2100                                     | 5.53                                                   | 8.45                   | 2.80                     | 2100                     | 2100                     |
|                  | 416.2                                    | 175.1                                                  | 91.5                   | 29.6                     | 14.57                    | 1085                     |
|                  | pH$_T$ (µmol kg$^{-1}$)                   | pH$_T$                                                 | 8.38                   | pH$_T$                   | 8.73                     | 8.20                     |
|                  | $\Omega_A$ (µatm)                        | $\Omega_A$                                             | 2.80                   | $\Omega_A$               | 1.00$^*$                 |                           |
|                  | CO$_2$ uptake (mol mol$^{-1}$ TA)         | CO$_2$ uptake                                          | 0.84                   | CO$_2$ uptake            | 0.50                     | 0.13                     |

* Note the value for $\Omega_A$ is rounded to 1.00 but calculated at 0.997. n/a: not applicable.
precipitation for a TA addition of 500 µmol kg\(^{-1}\) will see pH\(_T\) drop by about 0.1 from 8.04 to 7.93 and \(\Omega_A\) from 2.80 to 1.66, significantly enhancing ongoing ocean acidification (Table 3). Runaway CaCO\(_3\) precipitation for a TA addition of 1000 µmol kg\(^{-1}\) (assumed to cease at an \(\Omega_A\) of 2 as observed here) would see a further drop in \(\Omega_A\), i.e. to below 1, upon CO\(_2\) re-equilibration with the atmosphere (Table 3). Under such conditions, aragonite would start to dissolve, impacting various marine organisms, especially carbonate-secreting organisms, e.g. sessile corals, benthic molluscs and planktonic pteropods (Riebesell et al., 2011; Zeebe and Wolf-Gladrow, 2001). In summary, runaway CaCO\(_3\) precipitation in OAE must be avoided as it will not only reduce CO\(_2\) uptake efficiency significantly but also enhance ocean acidification. Keeping track of OAE efficiency from changes in TA concentrations can be challenging as CaCO\(_3\) precipitation can be underestimated as described earlier, requiring new and clever monitoring strategies.

### 4.4 Avoiding CaCO\(_3\) precipitation by dilution and other TA addition strategies

An important aspect when it comes to avoiding CaCO\(_3\) precipitation is the dilution that would occur in the wake of ships releasing TA in the ocean or by natural mixing of TA-enriched water with surrounding seawater (Caserini et al., 2021; Feng et al., 2017; Mongin et al., 2021). In our experiments, a 1 : 1 dilution appeared to seemingly inhibit CaCO\(_3\) precipitation in seawater, even if performed only after 1 week for the +500 µmol kg\(^{-1}\) TA addition. At first glance, this comes as a surprise since precipitation nuclei would only be diluted by half, reducing surface area and precipitation rates by a factor of 2. However, as \(\Omega_A\) is simultaneously reduced, precipitation rates are further reduced by a factor of 10 (see Fig. A4). Hence, the overall precipitation rate would see a reduction by a factor of 20. This should slow down precipitation initiated upon the alkalinity addition if on CaCO\(_3\) particles but not completely inhibit it (Zhong and Mucci, 1989). A possible explanation could be that dilution lowers \(\Omega_A\) below the critical threshold, overcoming the lattice mismatch, as most of the aragonite precipitation appears to be on the original seed mineral itself rather than on the newly formed aragonite (compare Fig. 5c and d).

Overall, CaCO\(_3\) precipitation can be avoided if the TA + 500 µmol kg\(^{-1}\) enriched seawater is diluted 1 : 1, reaching an \(\Omega_A\) of ~5.0. The more quickly dilution takes place, the less CaCO\(_3\) would precipitate prior to dilution. Similar results were found for a TA addition of +2000 µmol kg\(^{-1}\), i.e. the ability to stop precipitation at an \(\Omega_A\) of ~5.0, after a 1 : 7 dilution. However, only the 10 min
and 1 h dilutions seem to be suitable in an OAE context as rapid aragonite precipitation at a higher initial $\Omega_A$ of about 16.7 would significantly reduce the CO$_2$ uptake efficiency. Furthermore, the difficulty in monitoring precipitation from simple TA measurements (as described above) would also mean that quantification of CO$_2$ removal is not straightforward. Therefore, in order to assign carbon credits, TA additions have to be done in a way that rule out or at least minimise secondary CaCO$_3$ precipitation. This is true for any type of TA addition and is not specific to additions of quick and hydrated lime.

Adding TA from land, as modelled by Feng et al. (2017), shows that as more TA is added, higher coastal $\Omega_A$ would be reached. By staying well below the $\Omega_A$ threshold identified here, i.e. limiting coastal $\Omega_A$ to only 3.2, up to $\sim$ 550 Gt of carbon in the form of CO$_2$ could be removed from the atmosphere between 2020 and 2100, corresponding to a reduction by about 260 ppm (Feng et al., 2017). The critical $\Omega_A$ threshold beyond which secondary CaCO$_3$ precipitation occurs could be higher for other alkaline minerals of interest for OAE, theoretically allowing for higher TA additions. However, it has to be kept in mind that in waters with high sediment load, often found in coastal settings, CaCO$_3$ could precipitate onto mineral particles other than those added to increase TA. This has been observed in river plumes (Wurgaft et al., 2021), on resuspended sediments of the Bahama Banks (Bustos-Serrano et al., 2009), and in the Red Sea following flash flood deposition of resuspended sediments and particles (Wurgaft et al., 2016). Even with minerals allowing for higher TA additions, an $\Omega_A$ threshold of 5 might be safer to adopt. Atmospheric CO$_2$ removal could be increased if TA were also added to the open ocean, e.g. on ships of opportunity. Here, additions could be much higher as ship movement and rapid mixing within a ship’s wake would significantly dilute added TA as opposed to coastal point sources (Caserini et al., 2021; Köhler et al., 2013).

Finally, another option to increase atmospheric CO$_2$ uptake would be to keep the seawater equilibrated with air or CO$_2$-enriched flue gases, during mineral dissolution. Firstly, an $\Omega_A$ of 3.3 would be reached as opposed to 5 in the +250 µmol kg$^{-1}$ TA scenario (Table 3), when equilibration occurs during instead of after the dissolution process. Secondly, when reaching an $\Omega_A$ of 5 with CO$_2$ equilibration, nearly 1000 instead of 250 µmol kg$^{-1}$ of TA could be added, allowing for almost 4 times the amount of atmospheric CO$_2$ to be removed (this number is highly sensitive to temperature and ranges between $\sim$ 3 and $\sim$ 6 between 30 and 5 °C). Unfortunately, this requires an extra step, which appears to be far more time-consuming and costly than a simple mineral addition. It should also be kept in mind that for the same $\Omega_A$ threshold, the amount of TA that can be added will increase at lower temperatures because of higher CO$_2$ solubility and, hence, naturally lower $\Omega_A$ in colder waters. Based on our $\Omega_A$ threshold of 5, at a salinity of 35 and at 5 °C, about 3 times as much TA can be dissolved than at 30 °C.

5 Conclusions

OAE is a negative-emission technology with large potential for atmospheric CO$_2$ removal (Caserini et al., 2021; Feng et al., 2016; Köhler et al., 2010). In order to maximise CO$_2$ uptake efficiency, secondary CaCO$_3$ precipitation has to be avoided. Here we show that an increase in TA by 500 µmol kg$^{-1}$ led to aragonite precipitation, reducing the CO$_2$ uptake potential from about 0.8 mol mol$^{-1}$ of TA added to nearly 0.1 mol. Precipitation most likely occurred on the CaO and Ca(OH)$_2$ mineral surfaces prior to their full dissolution. In contrast, an addition of 250 µmol kg$^{-1}$ of TA did not result in CaCO$_3$ precipitation, suggesting that an $\Omega_A$ of about 5 is a safe limit. This is probably the case for other minerals with even lower lattice compatibility for CaCO$_3$ since CaCO$_3$ could precipitate onto naturally present mineral phases in coastal settings, such as resuspended sediments. Safely increasing the amount of TA that could be added to the ocean could be achieved by (1) allowing for major mixing and dilution of enriched seawater by coastal tides or in the wake of ships, (2) equilibrating the seawater to atmospheric CO$_2$ levels prior to the addition during mineral dissolution, and/or (3) targeting low- rather than high-temperature regions.
Appendix A

Table A1. Seawater salinity in each experiment and phosphate concentrations in one of the batches.

| Alkaline mineral | TA increase (in µmol kg\(^{-1}\)) | Experiment details | Seawater salinity | Phosphate (in µmol kg\(^{-1}\)) |
|------------------|---------------------------------|-------------------|-----------------|-------------------------------|
| CaO              | 250 n/a                         |                   | 36.52           | Not measured                  |
|                  | 500 n/a                         |                   | 36.52           | Not measured                  |
| Ca(OH)\(_2\)    | 250 n/a                         |                   | 36.91           | Not measured                  |
|                  | 500 N/A                         |                   | 36.91           | Not measured                  |
|                  | 500 For dilutions               |                   | 35.46           | Not measured                  |
|                  | 500 For filtration              |                   | 36.52           | Not measured                  |
|                  | 2000 For dilution               |                   | 36.74           | 0.32 ± 0.03                   |
| Na\(_2\)CO\(_3\) | 1050 n/a                        |                   | 36.52           | Not measured                  |
|                  | 1050 With quartz particles      |                   | 36.52           | Not measured                  |

n/a: not applicable.

Table A2. Main chemical composition of the CaO and Ca(OH)\(_2\) feedstocks used for the TA increase experiments determined by ICP-MS analysis (expressed in mg g\(^{-1}\), with the corresponding standard deviation, SD).

| Element   | CaO powder mg g\(^{-1}\) | SD  | Ca(OH)\(_2\) powder mg g\(^{-1}\) | SD  |
|-----------|--------------------------|-----|----------------------------------|-----|
| Calcium   | 545.15                   | 70.92 | Calcium                         | 529.79 | 117.30 |
| Magnesium | 2.10                     | 0.23  | Magnesium                       | 6.87  | 1.98  |
| Silicon   | 2.02                     | 1.79  | Silicon                         | 2.70  | 1.12  |
| Aluminium | 0.50                     | 0.19  | Aluminium                       | 1.98  | 0.77  |
| Iron      | 0.32                     | 0.10  | Iron                            | 0.91  | 0.34  |
| Manganese | 0.11                     | 0.01  | Potassium                       | 0.43  | 0.23  |
| Potassium | 0.03                     | 0.00  | Titanium                        | 0.07  | 0.03  |
| Phosphorus| 0.02                     | 0.02  | Manganese                       | 0.05  | 0.01  |
| Titanium  | 0.02                     | 0.01  | Phosphorus                      | 0.04  | 0.01  |
| Chromium  | 0.01                     | 0.01  | Bromine                         | 0.03  | 0.01  |

Figure A1. Relative contribution of dissolved CO\(_2\), HCO\(_3^-\) and CO\(_3^{2-}\) to total dissolved inorganic carbon in seawater as a function of pH\(_T\) (total scale), also known as a Bjerrum plot (based on the carbonic acid equilibrium constant from Mehrbach et al., 1973, and refitted by Dickson and Millero, 1987), at 25 °C and a salinity of 35, with the current surface ocean pH average represented by the dashed vertical line (pH\(_T\) ~ 8.1).

https://doi.org/10.5194/bg-19-3537-2022 Biogeosciences, 19, 3537–3557, 2022
Figure A2. Conceptual diagram of the experimental setup used for the dissolution of alkaline minerals.

Figure A3. Simulation of the changes in TA, DIC, $\Omega_C$, $\Omega_A$, $p$CO$_2$ and pH$_T$ after addition of 500 $\mu$mol kg$^{-1}$ of alkalinity. Four important steps are presented: first, assuming the complete Ca(OH)$_2$ dissolution without CaCO$_3$ precipitation; second, assuming as much CaCO$_3$ precipitation as the amount of TA added; third, assuming CaCO$_3$ precipitation happening until reaching an $\Omega_A$ of 2; and fourth, CO$_2$ uptake until equilibrium is reached between atmosphere and seawater at a $p$CO$_2$ of $\sim$416 $\mu$ atm.
Figure A4. CaCO$_3$ precipitation rate onto aragonite seed crystals in µmol m$^{-2}$ h$^{-1}$ as a function of $\Omega_A$, based on the measurements of Zhong and Mucci (1989) at 25°C and for a salinity of 35. The $\Omega_A$ values for the starting conditions and following a +250, +500 and +1000 µmol kg$^{-1}$ TA increase are presented by the dashed grey lines, i.e. 2.8, 5.5, 8.5 and 14.6, respectively.

Figure A5. Simulations of TA loss due to aragonite precipitation after a TA addition of 500, 1000 and 2000 µmol kg$^{-1}$, based on $\Omega_A$ and surface-area-dependent precipitation rates shown in Fig. A4, assuming the initial presence of 2 % of CaCO$_3$ in our samples, i.e. $\sim$ 0.37, $\sim$ 0.74 and $\sim$ 1.48 mg kg$^{-1}$ for $\Delta$TA + 500, $\Delta$TA + 1000 and $\Delta$TA + 2000 µmol kg$^{-1}$, respectively. CaCO$_3$ mass was converted to a surface area as described in Zhong and Mucci (1989). The starting conditions were TA = 2300 µmol kg$^{-1}$, DIC = 2100 µmol kg$^{-1}$, salinity = 35 and temperature = 21°C.
**Data availability.** All data regarding the changes in TA and DIC were collected by Charly A. Moras and were publicly published on the 15 July 2022 by the Australian Ocean Data Network (AODN) under the name “Quick and hydrated lime dissolution for Ocean Alkalinity Enhancement” and can be found at https://doi.org/10.26198/8znv-e436 (Moras, 2022).

**Author contributions.** CM and KS designed the initial experiments. LB, TC and RJB contributed to designing the follow-up experiments after observing unexpected CaCO₃ precipitation. CM and RJB conducted the ICP-MS analyses of the various materials and, with the help of KS and TC, the identification and analyses of CaCO₃ using the SEM. CM and KS mainly wrote the paper, with inputs from all co-authors and specific inputs from LB for carbonate chemistry and TC for CaCO₃.

**Competing interests.** At least one of the (co-)authors is a member of the editorial board of Biogeosciences. The peer-review process was guided by an independent editor, and the authors also have no other competing interests to declare.

**Disclaimer.** Publisher’s note: Copernicus Publications remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

**Acknowledgements.** We would like to thank Marian Bailey for her help with ICP-MS sample preparation, as well as Nick Ward for his help with preliminary X-ray diffraction analyses of the calcium powders. We are also thankful to Matheus Carvalho de Carvalho for the particulate carbon analyses and Nadia Toppler for her help arranging the use of the SEM.

**Financial support.** This research is part of the PhD project of Charly A. Moras that is funded by a Cat. 5 – SCU Grad School scholarship from the Southern Cross University, Lismore, Australia. The ICP-MS analyses were made possible by Australian Research Council grants to Renaud Joannes-Boyau and Kai G. Schulz (grant no. LE200100022) and to Renaud Joannes-Boyau (grant no. LE120100201).

**Review statement.** This paper was edited by Jean-Pierre Gattuso and reviewed by Daniel Burt and one anonymous referee.

**References**

Bach, L. T., Gill, S., Rickaby, R., Gore, S., and Renforth, P.: CO₂ removal with enhanced weathering and ocean alkalinity enhancement: Potential risks and co-benefits for marine pelagic ecosystems, Front. Clim., 1, 7, https://doi.org/10.3389/fclim.2019.00007, 2019.

Bates, N. R., Best, M. H. P., Neely, K., Garley, R., Dickson, A. G., and Johnson, R. J.: Detecting anthropogenic carbon dioxide uptake and ocean acidification in the North Atlantic Ocean, Biogeosciences, 9, 2509–2522, https://doi.org/10.5194/bg-9-2509-2012, 2012.

Burt, D. J., Fröb, F., and Ilyina, T.: The sensitivity of the marine carbonate system to regional ocean alkalinity enhancement, Front. Clim., 3, 624075, https://doi.org/10.3389/fclim.2021.624075, 2021.

Bustos-Serrano, H., Morse, J. W., and Millero, F. J.: The formation of whittings on the Little Bahama Bank, Mar. Chem., 113, 1–8, 2009.

Canadell, J. G., Le Quéré, C., Raupach, M. R., Field, C. B., Buitenhuis, E. T., Ciais, P., Conway, T. J., Gillett, N. P., Houghton, R., and Marland, G.: Contributions to accelerating atmospheric CO₂ growth from economic activity, carbon intensity, and efficiency of natural sinks, P. Natl. Acad. Sci. USA, 104, 18866–18870, 2007.

Carter, B. R., Feely, R. A., Wanninkhof, R., Kouketsu, S., Sonnerup, R. E., Pardo, P. C., Sabine, C. L., Johnson, G. C., Sloyan, B. M., and Murata, A.: Pacific anthropogenic carbon between 1991 and 2017, Global Biogeochem. Cy., 33, 597–617, 2019.

Caserini, S., Pagano, D., Campo, F., Abbà, A., De Marco, S., Righi, D., Renforth, P., and Grosso, M.: Potential of Maritime Transport for Ocean Liming and Atmospheric CO₂ Removal, Frontiers in Climate, 3, 575900, https://doi.org/10.3389/fclim.2021.575900, 2021.

Chang, R., Kim, S., Lee, S., Choi, S., Kim, M., and Park, Y.: Calcium carbonate precipitation for CO₂ storage and utilization: a review of the carbonate crystallization and polymorphism, Frontiers in Energy Research, 5, 17, https://doi.org/10.3389/fengr.2017.00017, 2017.

Chave, K. E. and Suess, E.: Calcium Carbonate Saturation in Seawater: Effects of Dissolved Organic Matter 1, Limnol. Oceanogr., 15, 633–637, 1970.

Chen, T., Neville, A., and Yuan, M.: Calcium carbonate scale formation – assessing the initial stages of precipitation and deposition, J. Petrol. Sci. Eng., 46, 185–194, 2005.

Cyronak, T., Schulz, K. G., Santos, I. R., and Eyre, B. D.: Enhanced acidification of global coral reefs driven by regional biogeochemical feedbacks, Geophys. Res. Lett., 41, 5538–5546, 2014.

De Choudens-Sanchez, V. and Gonzalez, L. A.: Calcite and aragonite precipitation under controlled instantaneous supersaturation: elucidating the role of CaCO₃ saturation state and Mg/Ca ratio on calcium carbonate polymorphism, J. Sediment. Res., 79, 363–376, 2009.

Dickson, A. G.: Standards for ocean measurements, Oceanography, 23, 34–47, 2010.

Dickson, A. G. and Millero, F. J.: A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media, Deep-Sea Res., 34, 1733–1743, 1987.

Dickson, A. G., Sabine, C. L., and Christian, J. R.: Guide to best practices for ocean CO₂ measurements, PICES Special Publication 3, IOCCP Report 8, Sidney, British Columbia, North Pacific Marine Science Organization, 191 pp., https://doi.org/10.25607/OPB-1342, 2007.

Doney, S. C., Fabry, V. J., Feely, R. A., and Kleypas, J. A.: Ocean acidification: the other CO₂ problem, Annual Rev. Mar. Sci., 1, 169–192, 2009.
Hoegh-Guldberg, O., Jacob, D., Taylor, M., Bolaños, T. G., Bindi, M., Brown, S., Camilloni, L., Diedhiou, A., Djilani, R., and Ebi, K.: The human imperative of stabilizing global climate change at 1.5°C, Science, 365, eaaw6974, https://doi.org/10.1126/science.aaw6974, 2019.

Huppmann, D., Kriegler, E., Krey, V., Riahi, K., Rogelj, J., Rose, S. K., Weyant, J., Bauer, N., Bertram, C., and Bosetti, V.: IAMC 1.5°C Scenario Explorer and Data hosted by IIASA, International Institute for Applied Systems Analysis & Integrated Assessment Modeling Consortium, https://doi.org/10.22022/SR15/08-2018.15429, 2018.

Ilyina, T., Wolf-Gladrow, D., Munhoven, G., and Heinze, C.: Assessing the potential of calcium-based artificial ocean alkalization to mitigate rising atmospheric CO$_2$ and ocean acidification, Geophys. Res. Lett., 40, 5909–5914, 2013.

IPCC: Summary for Policymakers, in: Climate Change 2021: The Physical Science Basis, Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change, edited by: Masson-Delmotte, V., Zhai, P., Pirani, A., Connors, S. L., Péan, C., Berger, S., Caud, N., Chen, L., Goldfarb, M. I., Gomis, M., Hansen, K., Leitzell, K., Lonnoy, J. B. R., Matthews, Y., Maycock, T. K., Waterfield, T., Yelekçi, O., Yu, R., and Zhou, B., Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 3-32, https://www.ipcc.ch/report/ar6/wg1/downloads/report/IPCC_AR6_WGI_SPM.pdf, https://doi.org/10.1017/9781009157896.001, 2021.

Keller, D. P., Feng, E. Y., and Oschlies, A.: Potential climate engineering effectiveness and side effects during a high carbon dioxide-emission scenario, Nat. Commun., 5, 1–11, 2014.

Kheshgi, H. S.: Sequestering atmospheric carbon dioxide by increasing ocean alkalinity, Energy, 20, 915–922, 1995.

Köhler, P., Hartmann, J., and Wolf-Gladrow, D. A.: Geoengineering potential of artificially enhanced silicate weathering of olivine, P. Natl. Acad. Sci. USA, 107, 20228–20233, 2010.

Köhler, P., Abrams, J. F., Völker, C., Hauck, J., and Wolf-Gladrow, D. A.: Geoengineering impact of open ocean dissolution of olivine on atmospheric CO$_2$, surface ocean pH and marine biology, Environ. Res. Lett., 8, 014009, https://doi.org/10.1088/1748-9326/8/1/014009, 2013.

Lenton, T. M. and Vaughan, N. E.: The radiative forcing potential of different climate geoengineering options, Atmos. Chem. Phys., 9, 5539–5561, https://doi.org/10.5194/acp-9-5539-2009, 2009.

Lenton, A., Matear, R. J., Keller, D. P., Scott, V., and Vaughan, N. E.: Assessing carbon dioxide removal through global and regional ocean alkalization under high and low emission pathways, Earth Syst. Dynam., 9, 339–357, https://doi.org/10.5194/esd-9-339-2018, 2018.

Lewis, E. and Perkin, R.: The practical salinity scale 1978: conversion of existing data, Deep-Sea Res., 28, 307–328, 1981.

Liouliou, M. G., Paraskeva, C. A., Koutsokou, P. G., and Payatakes, A. C.: Heterogeneous nucleation and growth of calcium carbonate on calcite and quartz, J. Colloid Interf. Sci., 308, 421–428, 2007.

Luecker, T. J., Dickson, A. G., and Keeling, C. D.: Ocean pCO$_2$ calculated from dissolved inorganic carbon, alkalinity, and equations for K1 and K2: validation based on laboratory measurements of CO$_2$ in gas and seawater at equilibrium, Mar. Chem., 70, 105–119, 2000.
Marion, G. M., Millero, F. J., and Feistel, R.: Precipitation of solid phase calcium carbonates and their effect on application of seawater $S_A = T - P$ models, Ocean Sci., 5, 285–291, https://doi.org/10.5194/os-5-285-2009, 2009.

Mehrbach, C., Culberson, C., Hawley, J., and Pytkowicz, R.: Measurement of the apparent dissociation constants of carbonate ions in seawater at atmospheric pressure 1, Limnol. Oceanogr., 18, 897–907, 1973.

Millero, F., Huang, F., Zhu, X., Liu, X., and Zhang, J.-Z.: Adsorption and desorption of phosphate on calcite and aragonite in seawater, Aquat. Geochem., 7, 33–56, 2001.

Mongin, M., Baird, M. E., Lenton, A., Neill, C., and Akl, J.: Reversing ocean acidification along the Great Barrier Reef using alkalinity injection, Environ. Res. Lett., 16, 064068, https://doi.org/10.1088/1748-9326/ac002d, 2021.

Montserrat, F., Renforth, P., Hartmann, J., Leermakers, M., Knops, P., and Meysman, F. J.: Olivine dissolution in seawater: implications for CO$_2$ sequestration through enhanced weathering in coastal environments, Environ. Sci. Technol., 51, 3960–3972, 2017.

Moras, C. A.: Quick and hydrated lime dissolution for Ocean Alkalinity Enhancement, Australian Ocean Data Network [data set], https://doi.org/10.26198/8vm-e436, 2022.

Morse, J. W. and He, S.: Influences of T, S and pCO$_2$ on the pseudo-homogeneous precipitation of CaCO$_3$ from seawater: implications for whitation formation, Mar. Chem., 41, 291–297, 1993.

Morse, J. W., Wang, Q., and Tsio, M. Y.: Influences of temperature and Mg: Ca ratio on CaCO$_3$ precipitates from seawater, Geology, 25, 85–87, 1997.

Morse, J. W., Gledhill, D. K., and Millero, F. J.: CaCO$_3$ precipitation kinetics in waters from the great Bahama bank: Implications for the relationship between bank hydrochemistry and whittings, Geochem. Cosmochim. Ac., 67, 2819–2826, 2003.

Morse, J. W., Arvidson, R. S., and Lüttinge, A.: Calcium carbonate formation and dissolution, Chem. Rev., 107, 342–381, 2007.

Mucci, A.: The solubility of calcite and aragonite in seawater at various salinities, temperatures, and one atmosphere total pressure, Am. J. Sci., 283, 780–799, 1983.

National Academies of Sciences, Engineering, and Medicine: A Research Strategy for Ocean-based Carbon Dioxide Removal and Sequestration, The National Academies Press, Washington, DC, 322 pp., https://doi.org/10.17226/26278, 2022.

Ni, M. and Ratner, B. D.: Differentiating calcium carbonate polymorphs by surface analysis techniques – an XPS and TOF-SIMS study, Surf. Interface Anal., 40, 1356–1361, 2008.

Pan, Y., Li, Y., Ma, Q., He, H., Wang, S., Sun, Z., Cai, W.-J., Dong, B., Di, Y., and Fu, W.: The role of Mg$^{2+}$ in inhibiting CaCO$_3$ precipitation from seawater, Mar. Chem., 237, 104036, https://doi.org/10.1016/j.marchem.2021.104036, 2021.

Pytkowicz, R. M.: Rates of inorganic calcium carbonate nucleation, The Journal of Geology, 73, 196–199, 1965.

Renforth, P. and Henderson, G.: Assessing ocean alkalinity for carbon sequestration, Rev. Geophys., 55, 636–674, 2017.

Renforth, P. and Kruger, T.: Coupling mineral carbonation and ocean liming, Energ. Fuel., 27, 4199–4207, 2013.

Renforth, P., Jenkins, B., and Kruger, T.: Engineering challenges of ocean liming, Energy, 60, 442–452, 2013.

Riebesell, U., Fabry, V. J., Hansson, L., and Gattuso, J.-P.: Guide to best practices for ocean acidification research and data reporting, Office for Official Publications of the European Communities, Luxembourg, 258 pp., https://doi.org/10.2777/66906, 2011.

Riley, J. and Tonguid, M.: The major cation/chlorinity ratios in sea water, Geol. Geophys., 2, 263–269, 1967.

Rushdi, A., Pytkowicz, R., Suess, E., and Chen, C.: The effects of magnesium-to-calcium ratios in artificial seawater, at different ionic products, upon the induction time, and the mineralogy of calcium carbonate: a laboratory study, Geol. Rundsch., 81, 571–578, 1992.

Schulz, K. G., Bach, L. T., Bellerby, R. G., Bermúdez, R., Büdenbender, J., Boxhammer, T., Czerny, J., Engel, A., Ludwig, A., and Meyerhöfer, M.: Phytoplankton blooms at increasing levels of atmospheric carbon dioxide: experimental evidence for negative effects on pynmenesisis and positive on small picoeukaryotes, Frontiers in Marine Science, 4, https://doi.org/10.3389/fmars.2017.00064, 2017.

Sharp, J. D., Pierrot, D., Humphreys, M. P., Epitals, J.-M., Orr, J. C., Lewis, E. R., and Wallace, D. W. R.: CO2SYSv3 for MATLAB (Version v3.2.0), Zenodo, https://doi.org/10.5281/zenodo.3950562, 2021.

Simkiss, K.: The inhibitory effects of some metabolites on the precipitation of calcium carbonate from artificial and natural sea water, ICES J. Mar. Sci., 29, 6–18, 1964.

Statista: Global cement industry – Statistics & Facts, https://www.statista.com/topics/8700/cement-industry-worldwide/ (last access: 23 March 2022), 2021.

Tang, H., Wu, X., Xian, H., Zhu, J., Wei, J., Liu, H., and He, H.: Heterogeneous Nucleation and Growth of CaCO$_3$ on Calcite (104) and Aragonite (110) Surfaces: Implications for the Formation of Abiotic Carbonate Cements in the Ocean, Minerals, 10, 294, https://doi.org/10.3390/min10040294, 2020.

The Royal Society and Royal Academy of Engineering: Greenhouse Gas Removal, https://royalsociety.org/-/media/policy/projects/greenhouse-gas-removal/royal-society-greenhouse-gas-removal-report-2018.pdf (last access: 7 May 2022), 2018.

Uppstrom, L.: The boron/chlorinity ratio of deep-sea water from the Pacific Ocean, Deep-Sea Res., 21, 161–162, 1974.

Wolf-Gladrow, D. A., Zeebe, R. E., Klaas, C., Körtzinger, A., and Dickson, A. G.: Total alkalinity: The explicit conservative expression and its application to biogeochemical processes, Mar. Chem., 106, 287–300, 2007.

Wolf, S. E., Leiterer, J., Kappl, M., Emmerling, F., and Tremel, W.: Early homogenous amorphous precursor stages of calcium carbonate and subsequent crystal growth in levitated droplets, J. Am. Chem. Soc., 130, 12342–12347, 2008.

Wurgaf, E., Steiner, Z., Luz, B., and Lazar, B.: Evidence for inorganic precipitation of CaCO$_3$ on suspended solids in the open water of the Red Sea, Mar. Chem., 186, 145–155, 2016.

Wurgaf, E., Wang, Z., Churchill, J., Dellapenna, T., Song, S., Du, J., Ringham, M., Rivlin, T., and Lazar, B.: Particle triggered reactions as an important mechanism of alkalinity and inorganic carbon removal in river plumes, Geophys. Res. Lett., 48, e2021GL093178, https://doi.org/10.1029/2021GL093178, 2021.

Zeebe, R. E. and Wolf-Gladrow, D.: CO$_2$ in seawater: equilibrium, kinetics, isotopes, 65, Gulf Professional Publishing, 360 pp, ISBN 9780444509468, 2001.
Zhong, S. and Mucci, A.: Calcite and aragonite precipitation from seawater solutions of various salinities: Precipitation rates and overgrowth compositions, Chem. Geol., 78, 283–299, 1989.