

Biogeosciences Discuss., community comment CC1

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Comment on bg-2021-330

Anonymous Referee #2

Referee comment on "Ocean Alkalinity Enhancement – Avoiding runaway CaCO₃ precipitation during quick and hydrated lime dissolution" by Charly Andre Moras et al., Biogeosciences Discuss., <https://doi.org/10.5194/bg-2021-330-RC2>, 2021

General Comments:

Overall, this Reviewer finds this study to be an important contribution to the field and the manuscript is well-structured. However, the Reviewer has some major concerns about the study and minor concerns regarding the manuscript.

The primary concern this Reviewer has is the lack of replication of experiments and the absence of justification for this. This concern is compounded by the differences between the 500 $\mu\text{mol kg}^{-1}$ hydrated lime incubations presented in Figures 2 and 4; furthermore, the end-points of these incubations cannot be compared because the second experiment was not continued for the same length of time. The inconsistent length of experiments and frequencies of sampling/ measurements is noted across the reported experiments. Additionally, the range of TA additions tested is limited for the broad conclusions given. The result of these concerns leaves the Reviewer with a strong feeling that there is insufficient evidence for the conclusions presented.

The individual experiments were not replicated as the main goal was not to infer dissolution kinetics of the two minerals. However, when all of the individual experiments are viewed together, the various additions of 250 and 500 $\mu\text{mol kg}^{-1}$ of TA paint a coherent image of OAE related Ω thresholds, which is our main conclusions. Furthermore, two similar pre-experiments with the 500 $\mu\text{mol kg}^{-1}$ of TA by Ca(OH)₂ were conducted. The first was only conducted for 5 days, and a second for 40 days, however

no stirring was applied. In both cases, the TA decreased, indicating CaCO₃ precipitation as shown in our manuscript.

The +250 μmol kg⁻¹ TA addition with Ca(OH)₂ was stopped after 28 days as no changes were observed for over more than 3 weeks after TA addition. Hence, a stable end-point for TA had been reached.

Concerning the frequency of sampling, sticking to a strict schedule was not considered to be important, as we were not interested in the dissolution kinetics but the final outcomes of Ca-rich mineral dissolution, i.e., the point at which precipitation stabilised.

We agree that a finer resolution of TA additions would be desirable to pinpoint the exact threshold at which CaCO₃ precipitation occurs (and that could be done in follow-up experiments). From a practical perspective for OAE implementation, the 250 μmol kg⁻¹ TA threshold is one below which it is a safe option (as opposed to 500 μmol kg⁻¹).

Regarding the manuscript itself, the author has a tendency to use vague and non-specific language at points, contrasting with the majority of the manuscript which is meticulously and clearly written. Additionally, the in-text citations are not systematically organised, it would be useful if these could be organised in a consistent manner (e.g. youngest to oldest).

We agree that there are some confusing sections and these will be re-written (see responses to the specific comments below). We apologize for the inconsistency in in-text citations and organise them from youngest to oldest, as suggested.

In section 1, a lot of background information is given before the author indicates the significance and focus of the current study; it would be advantageous to the reader if this was indicated earlier.

We will add the following to the first paragraph: “However, there is no empirical database on OAE efficacies, in particular regarding safe thresholds for mineral dissolution”.

The methods presented in section 2 vary between thorough and detailed descriptions and vague indications, the Reviewer would like this to be more consistent throughout.

We will make sure that all necessary details will be provided in section 2 (see also our responses to the detailed reviewer comments below).

The Reviewer found some inconsistency between the motivation given in Section 1 and the results presented in Section 3, particularly that there are no quantifications of the influence of CaCO₃ on pH. The author also presents results as approximations (i.e. using tilde) where no replicates were performed and some values were not consistently used throughout the manuscript. In Section 3.5, the author refers to pairs of subfigures from Fig. 4 which does not always appear relevant when the context suggests one subfigure is being discussed. It could also be more clear to the reader, if the changes discussed in Section 3.5 were relative to the initial state before dilution. Section 3.6 also feels abrupt and it is not clear how much the particulate organic carbon investigation contributes to the manuscript.

Concerning the CaCO₃ comment, we will add the following information to the text: “Such secondary precipitation constitutes the opposite of alkaline mineral dissolution and would decrease the pH (as Ω_{CaCO_3}), simultaneously increasing seawater [CO₂].”

We decided to report the results as approximations as there was no replication, as noted previously by the reviewer. Therefore, the finding that TA decreased by, for instance, 542.1 $\mu\text{mol kg}^{-1}$ at day 47 of the experiment with a TA increase of 500 $\mu\text{mol kg}^{-1}$ with CaO, would be misleading, and we hence rounded to $\sim 540 \mu\text{mol kg}^{-1}$ instead.

Concerning referring to subfigures in the text, we will carefully check for correctness.

When it comes to the initial state before the dissolution, that is shown in Figure 4, i.e., one can see that in the 1:7 dilution of the +2000 $\mu\text{mol kg}^{-1}$ TA addition, where about 150 $\mu\text{mol kg}^{-1}$ of TA was lost when dilution was not carried out immediately, i.e., after 10 minutes or 1 hour.

Concerning PIC measurements, they are important as they show that measured changes in TA are not necessarily a perfect indicator of how much CaCO₃ precipitates. The implications (e.g., monitoring and accounting) are presented in the discussion.

The first paragraph of Section 4.1 is a good paragraph which clearly explains the precipitation pathways and therefore what the author was investigating as sources of precipitation. However, this information may have benefited the reader earlier in the manuscript to justify the methods used.

We will move this information to the introduction.

In Section 5, the author gives both the expanded and abbreviated form of terms that were defined through the paper and it is not clear why this is necessary.

We will correct this mistake.

Finally, regarding figures and tables, it would be useful to the reader if the measured/ actual TA addition was also included in Table 1. The author also divides the temporal resolution of Figures 1-3 and Figure 4 differently, which is not immediately clear to the reader. This difference should be clarified in the Figure 4 caption to prevent confusion.

The actual TA addition was not added to the table as the figures were thought to be sufficient. However, we will add this information to a table in the appendix. The figures have slightly different temporal resolutions, as for logistical reasons initial sampling frequencies were different. No data point was collected on day 1 for experiments shown in Figures 1 to 3. Similarly, no samples were taken after 0.2 days for experiments shown in Figure 4.

Specific Comments:

Line 13: Does “their” refer to alkaline minerals in general or specifically to the investigated minerals, quick and hydrated lime?

We will reformulate the sentence.

Line 14: “...how much...” is again rather vague, is the author referring to mass of alkaline mineral or only the investigated minerals?

We will reformulate the sentence.

Line 19: The author uses “so-called” here but later in the discussion at line 292 indicates that this is an established form of CaCO_3 precipitation described in multiple literature sources; unclear why it is referred to in this manner in the abstract.

It is an established technical term, but probably not widely known amongst the readers. Hence, we used the term so-called.

Line 21: “...until Ω_{Ar} reached levels below 2.”; Does this mean that the runaway precipitation spontaneously stops at this threshold but does not start again until the threshold of 5?

CaCO_3 will stop precipitating onto existing calcite nuclei at an Ω_{CaCO_3} of 1. The reason that it seemingly stops at a higher threshold of 2, is because of the exponential nature of precipitation rate in relation to the saturation state. As shown in Figure 4 in the appendix, below an Ω_{Ar} of 2, precipitation rates become so small that it seemingly stops. Furthermore, dissolved organic matter in natural seawater can inhibit precipitation. The latter will be discussed in a revised version. And yes, adding more alkalinity beyond the Ω_{Ar} threshold of 5 would initiate precipitation again.

Line 23: “...ideally within hours of the addition...” is vague and the significance of the statement to the work is not made clear in the abstract (i.e. that the authors investigated the significance of dilution at different timescales.)

We feel that from a practical OAE aspect, the term “within hours” is not vague and clearly distinguish the timescale required, i.e., not minutes or seconds, but also not days.

Line 24: The term “...model considerations...” is unclear and no description of any modelling is given in Section 2 and the model results presented in Table 3 are only discussed in Section 4. More detail should be included about what was modelled and how, if the author wants to include these results. Furthermore, “considerations” does not indicate if the authors considered using models or whether simulations were performed.

We will reformulate “model considerations” to “OAE simulations”. Regarding the simulations in section 4, the following paragraph will be added to the methods:

“2.6 OAE simulations

Using CO₂SYS and the results from the various dissolution experiments, three OAE scenarios were simulated (Table 3). For those, three alkalinity additions were performed, +250, +500 and +1000 μmol kg⁻¹. The starting parameters were TA = 2350 μmol kg⁻¹, DIC = 2100 μmol kg⁻¹, salinity = 35, temperature = 19 °C, using the same acid-base solubility constants as described in section 2.5. In a first scenario, for all three simulations, no CaCO₃ precipitation was assumed, and the amount of CO₂ taken up after atmospheric re-equilibration was calculated. For the +500 and +1000 μmol kg⁻¹ TA increases, two additional simulations were performed: first we assumed that as much CaCO₃ precipitated as TA was added, and second, it was simulated that CaCO₃ precipitated down to an Ω_{Ar} of ~2 as observed in our experiments. Again, next to calculating full carbonate chemistry speciation in these various scenarios, the amount of CO₂ taken up after atmospheric re-equilibration was calculated.”

Line 26: The authors indicate that equilibration of seawater to atmospheric CO₂ mixing ratios would enhance mineral dissolution but do not indicate what CO₂ partial pressures are being referenced or what the factors given are in reference to.

We will add the following information: “to atmospheric CO₂ levels, i.e., to a pCO₂ of ~416 μatm, “.

Line 36: “...ideally around +1.5°C...” makes it sound as though, even if less were possible, that Governments should still aim for +1.5°C because of the use of “ideally”

This sentence will be reformulated as “ideally below +1.5 °C”.

Line 39: “...one...” is vague, can the author be more specific as to what OAE is one of the highest of...? e.g. “...additional mitigation strategies...”

“One with” refers to the mitigation strategies mentioned in the previous sentence: “ However, current and pledged reductions will likely not be enough and additional mitigation strategies are being discussed, such as ocean alkalinity enhancement – OAE”

Line 40: The authors give an extreme example of OAE (Feng et al., 2017) and do not address other examples of OAE discussed in literature with arguably more realistic application strategies i.e. Köhler et al. (2013), Keller et al. (2014), Lenton et al. (2018) or Burt et al. (2021)

We will add the other studies as suggested.

Line 42: Is the use of “...typically...” appropriate? Are there OAE methods which do not use alkaline minerals?

OAE can also be implemented with alkaline solutions, but most studies consider the direct dissolution of minerals in seawater. However, we will also mention the first option, e.g., via the separation of water into protons and hydroxide (alkalinity) via electrolysis (de Lannoy et al. 2018).

Line 43: “In this regard...” is vague and not clear that the author is introducing alkaline minerals which are considered for AOE.

This will be reformulated to “Suitable candidates are magnesium-rich minerals such as brucite, periclase or forsterite, and calcium-rich minerals such as quick and hydrated lime.”.

Line 44: “The last two minerals...” is vague and could be replaced with “Quick and hydrated lime...” for greater clarity.

This will be changed.

Line 47: Is the additional release of CO₂ considered with respect to the final CO₂ drawdown?

For optimal efficiency, it is assumed that there is a CO₂ capture during limestone calcination. We added the following information “Once heated to temperatures of ~1200 °C, each molecule of CaCO₃ breaks down into one molecule of CO₂—hence for maximum OAE potential, carbon capture and storage would be advisable (Bach et al., 2019; Renforth et al., 2013; Renforth and Kruger, 2013) – and one molecule of CaO (Ilyna et al., 2013; Kheshgi, 1995).”

Line 51: Is it appropriate to state that the non-linearities of the seawater carbonate system are ignored as Equation 1 gives the bicarbonate ion which is only the major dissociation product at typical seawater conditions due to the non-linearities?

We have clarified our point by stating “Including the subsequent oceanic uptake of atmospheric CO₂, and 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), a conceptual model of CaO and Ca(OH)₂ dissolution can be summarised as per:”.

Line 56-58: Is the repetition of the equation explanation required? Furthermore, the DIC concentration only remains unchanged if there is no uptake of atmospheric CO₂ while the statement at line 51 “Including the subsequent oceanic uptake of atmospheric CO₂...” indicates that Equation 1 considers atmospheric CO₂ rather than aqueous CO₂. How did the author intend the understanding of these statements be reconciled?

Please see our comment above.

Line 58: “This increases the pH...”, the author does not explain why this is the case and neither does Equation 1 explicitly indicate the change which produces the reduction in H⁺ ions.

We will add the following explanation: “The dissolution of CaO and Ca(OH)₂ and subsequent the addition of TA increases seawater pH. This can be conceptually understood by remembering that DIC can be approximated by being the sum of HCO₃⁻ and CO₃²⁻ (ignoring the relatively small contribution by CO₂), and TA as being the sum of HCO₃⁻ and 2 CO₃²⁻ (ignoring the relatively small contributions by boric and silicic acid, and other minor components). Combining both equations reveal that CO₃²⁻ concentrations can be expressed as [CO₃²⁻] = TA-DIC. Hence, increasing TA at constant DIC, e.g., by

dissolving CaO or Ca(OH)₂, increases [CO₃²⁻], shifting carbonate chemistry speciation towards higher pH (Figure A 1) (Dickson et al., 2007; Wolf-Gladrow et al., 2007; Zeebe and Wolf-Gladrow, 2001).”

Line 60: Is it appropriate to consider that the reduction in partial pressure of CO₂ in seawater is the result of the reduction of CO₂ rather than being concurrent?

At constant temperature, pressure and salinity, pCO₂ and [CO₂] are linearly correlated.

Line 65-67: Repetition; the authors state twice that OAE counters two aspects of OA

This will be removed.

Line 70: The author is not specific about what is being constrained.

The major constraint is to keep Ω_{CaCO_3} below a threshold above which it CaCO₃ would instantly precipitate, later explained using the work from Marion et al.

Line 71: The author does not indicate why the reduction in carbonate ions increases the aqueous CO₂ concentration rather than following Le Chatelier’s principle to replace the precipitated carbonate ions.

See comment above. Furthermore, a Bjerrum plot will be added in appendix.

Line 72: The author does not explain why the precipitation of native Ca²⁺ and CO₃²⁻ ions further reduces the effectiveness of the added alkalinity.

This is because the removal of alkalinity by the precipitation of CaCO₃ shifts carbonate chemistry speciation towards a lower pH and higher CO₂ concentration, reducing ocean’s uptake capacity. This will be added.

Line 77: Does the indicated increase in TA to reach the described critical threshold hold if a non-lime alkalinity source such as olivine were used? If the estimate is specific to quick/ hydrated lime, can the author specify this when the estimate is stated.

These values were determined using CO₂SYS and are not mineral dependant.

Line 78: Is the critical threshold given here calculated by the author or given in Marion et al. (2009)? The citation location and the previous postulation leaves this ambiguous.

We will clarify this issue by “There are three types of precipitation, i.e., 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). The critical precipitation threshold for calcite (at a salinity of 35 and at a temperature of 21 °C) is at a saturation state (Ω_{Ca}) of ~18.8 (Marion et al., 2009).”

Line 91: Acronym “ESI” is used without prior definition; is this familiar to all relevant members of field?

ESI is the company that provided the ablation unit and not an acronym.

Line 94: The author describes how the seawater samples were stored to reduce bacterial metabolic activity before being sterilised; why were the samples not sterilised before storage?

The seawater was stored in a fridge for several days, prior to sterile filtration, to remove particles by sedimentation and facilitate the filtration process.

Line 102: The author describes the seawater as being “accurately weighed” without indicated the degree of accuracy used; please clarify.

We will add the following: “accurately weighed (in grams to 2 decimal places)”.

Line 102: The beakers are referred to as “high-quality”; what is the metric used to determine the quality of the beakers?

This name was used to differentiate normal glass from borosilicate 3.3 glass which does not leak alkalinity, as other types can do.

Line 105: The term “floating lid” is unfamiliar and it was unclear how this minimised gas exchange. The discussion indicates that while this apparatus minimised gas exchange at the beginning of the experiment, a gaseous head space was created with subsequent sampling and therefore the lid did not float on the surface of the reduced fluid level. Can the apparatus and its function be described more clearly?

The experimental setup is presented in Figure 2A, and the term “floating lid” refers to the behaviour of the lid. As gas exchange is directly proportional to the surface area of water exposed to the atmosphere, a lid covering it minimise gas exchange. During sampling and associated decreasing water levels in the beaker, the floating lid still covers the surface.

Line 106: Amounts is vague; were the alkaline minerals added in masses or a different metric? What masses were added?

We will add the following to the Method section “calculated amounts of weighed-in alkaline compounds...”. The unit, i.e., mg, will be mentioned in the following paragraph while explaining the alkalinity weighing and addition processes.

Line 106: The author refers to “alkaline compounds” in general while the context of the paper indicates that only quick and hydrated lime were used, were other compounds used in the experiments?

While quick and hydrated lime were of prime interest in this research, a 1M solution of Na_2CO_3 was also used. That's why we use the more general term, "alkaline compounds".

Line 106: "...taken in increasing time intervals..."; can the author give the specific time intervals used in the experiments?

Since the time intervals could be slightly different according to the experiment, the authors preferred using this term while providing the exact sampling time intervals in the figures.

Line 108: The author does not indicate how the pH monitoring was performed such as if the monitoring was continuous or periodic; please clarify

We will clarify with: "the pH was monitored at a frequency of 1 Hertz for the first hour before alkalinity...".

Line 109: The contents of the beaker were "carefully transferred" but there is no indication of how care was taken or why the contents of the beaker were transferred; please clarify

We will change to "Once the pH plateaued (corresponding to maximum TA release), the content of the beaker was carefully transferred to a clean Schott bottle of the corresponding volume (see below), avoiding any spill. Bottling ensured that evaporation would not play a role in changing DIC and TA."

Line 110: What was the "corresponding" volume? This is not specific

The volumes varied between experiments and are described later in the text (see also our previous comment).

Line 114: It is not immediately clear that these are details of the descriptions of "alkalinity addition" given in the previous paragraph; make this clearer

We will clarify the issue by: "Following the previously described setup, TA was added by sieving CaO and $\text{Ca}(\text{OH})_2$ through a 63 μm mesh, avoiding the formation of larger CaO or $\text{Ca}(\text{OH})_2$ aggregates."

Line 114: Why was this mesh size selected or why were these particles sizes selected for the described experiments?

In preliminary experiments, we observed aggregates forming when the powders were not sieved directly above the seawater, resulting in a less efficient, but most importantly, not reproduceable dissolution. In order to avoid this phenomenon, we decided to sieve the alkaline materials through a mesh. The pore size was chosen as being the cut-off between sand and silt, and in the size range previously considered in modelling studies.

Line 115: Why was it important to mass particles smaller than 63 μm when the experimental design was only for the addition of particles larger than 63 μm ?

Only particles that passed the sieve, i.e., smaller than 63 μm , were added. And as about 2 meters were separating the experimental setup and the weighing balance, it was important to not lose any particles during the process, but capture them in the upside-down falcon tube cap to get a correct reading of the amount added.

Line 119: Why is it pertinent that the massing steps were performed in less than 5 minutes?

To get accurate information on dissolution kinetics, i.e., how quickly certain minerals dissolve, it is important to add them in one go. However, this is technically impossible as of the weighing and sieving steps. Hence, we provided the time required, which allows the reader to put it into perspective, i.e., as opposed to full dissolution within several hours.

Line 119: Why were these addition concentrations used? What do these addition concentrations represent?

These two additions were determined in preliminary experiments. The initial design was to add either 500 or 1000 $\mu\text{mol kg}^{-1}$ of alkalinity, corresponding to one lower and one higher addition than the theoretical amount needed to trigger CaCO_3 precipitation for pseudo-homogeneous precipitation. However, preliminary experiments showed CaCO_3 precipitation at TA+500 $\mu\text{mol kg}^{-1}$, leading to a redesign of the addition towards +250 and +500 $\mu\text{mol kg}^{-1}$ over +500 and +1000 $\mu\text{mol kg}^{-1}$.

Line 121: The author has not prepared the reader for this set of experiments. There is no apparent preceding justification or explanation how these experiments tie into the three research questions posed in section 1

We will clarify this issue by adding the following: "Three experiments assessed the role of mineral phases during CaCO_3 precipitation in the previous experiments. The first experiment made use of a 1M solution of sodium carbonate (Na_2CO_3 , CAS number 497-19-8) which was freshly prepared before the experiment."

Line 123: The author describes the weighing as accurate without indicating the degree of accuracy

We will add: "Ultrapure Na_2CO_3 was accurately weighed, i.e., in mg (with 4 decimal places), into a clean 100 mL Schott bottle and made up to 100 g with MilliQ (18.2 M Ω)".

Line 124: "sonicated for 15 minutes with gentle shaking" is vague; unclear how ultrasonic vibrations can be applied gently, can the author give the frequency or some other metric?

We will clarify by: "The solution was then sonicated for 15 minutes, and gentle mixing every five minutes."

Line 126: “almost twice the alkalinity increase” is vague; in the first, “almost” indicates a concentration less than double while Table 1 indicates the target was higher in both instances and theoretically lower in one instance, and in the second, it would be clearer if the specific concentration was given instead

We changed the sentence to: “This required about twice the alkalinity increase as before (Table 1), because Na_2CO_3 additions concomitantly increase DIC when dissociating in two sodium and one CO_3^{2-} ion, making the Ω_{CaCO_3} increase smaller. Calculations were done in CO_2SYS (see below).”

Line 129: The author does not explain why quartz powder was added until section 4; please indicate the justification earlier

To clarify this issue, we will add the following to the paragraph: “Quartz powder was chosen as it does not dissolve on the timescales used in this study (Montserrat et al., 2017)”.

Line 130: “amount” is vague; was a specific mass of quartz particles added?

We clarify by: “The mass of quartz particles added, recorded in mg, was determined to provide the same mineral surface area as for the $\text{Ca}(\text{OH})_2$ experiments with a TA increase of $500 \mu\text{mol kg}^{-1}$.”

Line 131: “amount” is vague; context suggests area is an appropriate metric?

Please see comment above.

Line 132: This assumption seems unavoidable; is it possible to assess the errors from this assumption?

It is difficult to assess potential errors, but the spherical assumption gives the lowest, while a cubic one the highest surface area. The difference between them is about a factor of 2. However, as the shape assumption was applied to all minerals equally, the surface areas should have been very similar as it is highly unlikely that particles of one mineral were cubic while those of another spherical.

Line 135: Is “particle filtering experiment” a fixed term? Please give more detail

We will change to “Finally, a third experiment was carried out in which all particles were removed by filtration, using $\text{Ca}(\text{OH})_2$ as the alkaline compound and following the same setup as described above (sections 2.2.1 and 2.2.2).”

Line 135: “following the same setup as described above”; does the author refer to the setup described in 2.2.1 or 2.2.2 here?

Please see comment above.

Line 136: Why was a 4 hour period selected for the reaction? This contrasts with the 5 hours allocated in 2.2.1

Thanks for pointing this out. There was a typo in section 2.2.1 which now will read: “. Furthermore, the pH was monitored at a frequency of 1 Hertz for the first hour before alkalinity addition, and over 4 hours after addition to get an estimate for when alkalinity was fully released.”

Line 137: Here it is indicated that a “2L Schott beaker” was used but in 2.2 this is vaguely given that either 2L or 5L beakers were used; can the author describe which experiments used which volume and justify why different volumes were used?

Since various dilutions were performed in a 1:1 ratio, at least 4 x 500mL of initial sample water was needed for the 10 minutes, 1 hour, 1 day and 1 week dilution points. Therefore, more volume was required in the dilution experiments as opposed to the previously explained ones, we will add this piece of information in the respective methods sections.

Line 143: The acronym “NSW” is used without introduction; please clarify

Thanks for pointing this out, this is an artefact from an older manuscript version and will be changed to “natural seawater”.

Line 143: Is it necessary to tell the reader that something will be described rather than moving on to the description?

We will remove “as described in the following”.

Line 145: “amounts”; was hydrated lime added in masses or another metric?

We will change to “Calculated weighed-in masses of $\text{Ca}(\text{OH})_2$ were added to the first bottle as described earlier using the 63 μm sieve, while the natural seawater in the second bottle was left for future dilutions.”.

Line 147: The description of how the hydrated lime powder was added is given here after a vague “added” at line 145; why is a vague term used and detail given later when the detail could be given in the first instance?

As suggested, we will move this sentence up.

Line 148: The author does not explain how the dilutions were performed? Was the solution transfer performed following the method given at line 109 or 137?

We will add the following information: “Following the $\text{Ca}(\text{OH})_2$ addition, 1:1 dilutions (500 g TA enriched seawater:500 g natural seawater) were performed in clean 1L Schott bottles that were then kept in the dark and placed on a magnetic platform at a stirring rate of ~200 rpm.”

Line 151: Why were these time intervals selected?

These time intervals were selected to cover the full range of CaCO_3 precipitation observed in the previous experiments.

Line 165: Why were samples collected at the end of some of the experiments? Which experiments were sampled and why?

When no CaCO_3 precipitation was expected, i.e., no drop in TA nor DIC, no samples for PIC or SEM were taken.

Line 166: Is this a standard protocol? If so, please indicate reference, if not, please justify. Furthermore, why were TPC and POC samples treated differently?

Yes, this is a standard protocol, as CaCO_3 has to be removed from the POC samples. We will provide a reference here, i.e., Gafar and Schulz, 2018.

Line 170: Please explain how standard deviations were calculated without replication

We will add the information that duplicate TPC and POC filters were collected in the respective treatments.

Line 174: Why was CaCO_3 precipitation “suspected”, this indicates to the reader that there was insufficient evidence to support the conclusion

We will add the following information: “In case where TA and DIC decreased were detected, indicative of CaCO_3 precipitation, several samples were taken for total particulate carbon (TPC), particulate organic carbon (POC) and SEM analysis. TPC and POC samples were collected in duplicates at the end of some experiments on pre-combusted (450 °C) GF/F filters, and stored frozen until analysis. “

Line 175: Why were samples taken in a 10-15 mL range of volumes and not a more consistent and precise volume?

The SEM analysis was not quantitative regarding the concentration of CaCO_3 in seawater. Therefore, an exact amount is not required.

Line 180: “Most” indicates that not all parameters were calculated; which were/ were not calculated and why?

We will change to: “Using the measured DIC and TA, the remaining carbonate chemistry parameters were calculated for in-situ temperature and salinity using the CO_2SYS script for MATLAB® (MathWorks).”

Line 182: Which parameters were calculated and why? What could not be calculated?

In our case, the relevant calculated parameters were the $p\text{CO}_2$, pH, Ω_{Ca} and Ω_{Ar} values.

Line 189: “amount”; was alkalinity added in concentrations or another metric?

We will change amount to concentration.

Line 203: The author states that a “~250 $\mu\text{mol kg}^{-1}$ TA addition” was performed for the first quicklime experiment but Table 1 describes a Theoretical TA addition which exceeds this target by 9.6%; calling the experiments by the target TA addition is then misleading given that the Theoretical and Actual TA additions varied significantly from these targets; name the experiments in a clearer and more consistent manner.

It was chosen to stick to the theoretical TA additions for all experiments, as the measured increase in TA is not necessarily a perfect measure for the TA addition (e.g., the problem of precipitation, counteracting the increase), as discussed later on.

Line 204: The author describes an increase in DIC concentration in the seawater incubations despite using a “floating lid” to minimise gas exchange (Section 2.2 and Fig. A2), this is not appropriately addressed in Section 4. Was there a port for gas exchange in the “floating lid”? If the volume of the gas phase in the beaker changed, what was the CO_2 mixing ratio of the introduced gas? How comparable is the CO_2 uptake with a system of free gas exchange?

The floating lid design was only a temporary setup for the alkaline mineral addition and the first 5 hours of experiment, to minimise gas exchange, but also evaporation, which would otherwise have changed DIC and TA. Then, the content of the beaker was transferred to a Schott bottle (as described in the methods section), where inevitably, a headspace was created after several sampling sessions. Hence, CO_2 from lab air (~465 μatm) which was introduced each sampling time was dissolving in the seawater which had a much lower $p\text{CO}_2$.

In an open system with constant stirring, the gas exchange would have been much higher, however, the closed system here is more representative to an open and ‘unstirred’ oceanic environment, where gas exchange occurs on the order of months.

Line 204: “slowly” is vague and subjective; please quantitatively indicate the rate of change of DIC concentration

The rate will be added to the sentence: “In contrast, DIC increased slowly over time, about 1 $\mu\text{mol kg}^{-1}$ per day, reaching about +50 $\mu\text{mol kg}^{-1}$ on day 47 of the experiment (Figure 1b).”

Line 208: “...before slowly decreasing two days later...” indicates that there is no change between the first 4 hours until after 48 hours while Fig. 1 suggests a decline over the 48 hours and a greater rate of change 6th and 8th sampling points; can the author clarify this discrepancy between description and illustration?

We will clarify the point with: “In the second CaO experiment with about 500 $\mu\text{mol kg}^{-1}$ TA addition, TA increased by $\sim 410 \mu\text{mol kg}^{-1}$ within the first 4 hours before slowly decreasing the next two days later (Figure 1a), followed by a more rapid decrease over the following week, before slowing down and eventually reaching a steady state on day 20 at a final ΔTA of about $-540 \mu\text{mol kg}^{-1}$.”

Line 209: “eventually” is vague and subjective; specify when this ΔTA was recorded

Please see comment above.

Line 210: “slight” is vague and subjective

We will change to: “relatively small”

Line 210-211: “much more considerable” is vague and subjective

We will change to: “a much more significant”.

Line 211: The ΔDIC is given as approximately $465 \mu\text{mol kg}^{-1}$ but Fig. 1b indicates that this should be a negative value

Thanks for pointing out this typo, it has to read “about $-465 \mu\text{mol kg}^{-1}$ ”.

Line 213: “rapidly” is vague and subjective

We will change to: “before relatively quickly dropping to 2.4”.

Line 217: The sentence beginning “The DIC concentration...” indicates a constant rate of increase to a total of $70 \mu\text{mol kg}^{-1}$ but Fig 2b indicates a greater rate of change between the 6th and 9th sampling intervals; please clarify

This will be clarified with: “The DIC concentration increased relatively quickly over the first 6 days after the TA addition before slowing down, reaching $\sim 70 \mu\text{mol kg}^{-1}$ by the end of the experiment (Figure 2b).”

Line 221: “relatively steady” is vague and subjective; what was the rate of decrease?

This will be clarified with “This was followed by a relatively steady decrease by $\sim 18 \mu\text{mol kg}^{-1}$ per day over the next 2 weeks, after which the decrease accelerated to $\sim 28 \mu\text{mol kg}^{-1}$ per day until day 35, before levelling off at a ΔTA of about $-420 \mu\text{mol kg}^{-1}$ towards the end of the experiment.”

Line 221: “decrease accelerated” is vague; by how much? From what to what?

Please see our previous response.

Line 222: Why is the TA loss smaller with Ca(OH)₂ than with CaO?

The difference in ΔTA between CaO and Ca(OH)₂ is about 100 $\mu\text{mol kg}^{-1}$. The seawater was sampled at two different times of the year, having different initial Ω_{Ar} values. In the case of Ca(OH)₂, the seawater Ω_{Ar} was around 2.5, while for CaO, Ω_{Ar} was 2.8. Therefore, more CaCO₃ was precipitated in the latter. The important point here is that in both treatments a very similar saturation state was reached at the end.

Line 223: Does the DIC concentration drop “in a similar fashion as TA”? Fig. 2 indicates these were measured at different frequencies; what caused the difference in sampling frequency?

The samples for DIC were taken at the same time as for TA. However, due to a machine malfunction, several DIC samples were lost during analysis. Therefore, some data points are missing.

Line 227-229: The first two sentences of section 3.4 are the preparation that was missing from section 2.2.2

As suggested, we will move this information up.

Line 228-229: “...designed to result... precipitated (Table 1).”; 1) Table 1 does not indicate the aragonite saturation state so the reader cannot confirm that these states are comparable; 2) After being presented with figures 1 and 2, the reader notes that the aragonite saturation states produced by this set of experiments significantly exceeds any of the previous sets of experiments, how can comparison be made?; 3) According to Table 1 the Na₂CO₃ solutions were precisely comparable to 0.02 mg kg⁻¹ and 0.16 $\mu\text{mol kg}^{-1}$ TA and yet produced significantly different aragonite saturation states illustrated in Fig. 3; can the author address this disparity?

There are two reasons. One (as discussed above) is that the various seawater batches had different initial aragonite saturation states, and the second, that for various reasons outlined in the discussion we did not measure the maximum theoretical TA increase in experiments shown in Figures 1 and 2.

Concerning comparability, the important point here is that even though the saturation state in the Na₂CO₃ addition experiment and in the Ca(OH)₂, in which particles were filtered out, was higher than in the previous ones, TA was stable. Hence, our conclusion that precipitation on mineral phases of CaO and Ca(OH)₂ in these previous experiments is justified.

Line 233-234: there is repetition of methods here

We will shorten the description.

Line 235: “about a week later” is vague; what period does this include? 6-8 days? 5-9 days? Please clarify

We will change to: “between day 5 and day 12”.

Line 238: “pronounced decline” is vague and author does not indicate rates; Fig. 3 indicates the majority of the decline occurred in the first 20 days

This will be reformulated as “Finally, Ω_{Ar} followed a similar trend, with an increase from ~ 2.8 up to ~ 9.2 within the first 1.5 hours, and a pronounced decline from 9.2 at day 2 to 2.3 at day 19, before stabilizing around ~ 2.0 at the end of the experiment.”

Line 239: further repetition of method

The repetition will be removed.

Line 241: What is the variable with concentration of $470 \mu\text{mol kg}^{-1}$?

ΔTA

Line 245: 1) Section 2.2.3 description was insufficient to prepare the reader for Figure 4; it was not clear that each dilution was performed ONCE at different times and that five solutions were subsequently incubated. 2) Section 2.2.3 also does not address how the author ensured that the particles from the parent solution were proportionately included in the diluted solution. Was it assumed that the stirring was sufficient to maintain a homogeneous suspension? 3) It needs to be more clearly stated that it is not a single solution diluted multiple times but that it is a source solution diluted a single time at multiple instances.

We will add the following to section 2.2.3: “All dilutions were performed 10 minutes, 1 hour, 1 day and 1 week after $\text{Ca}(\text{OH})_2$ addition, leading to 2 TA-enriched and 8 diluted treatments.”

Line 249: Is it intended that the reader should compare figure 4a with figure 4d?

Thanks for pointing out the typo. It should read: “These changes in TA were followed by a decline to $\sim 320 \mu\text{mol kg}^{-1}$ after 14 days, although the latter being a slightly slower decrease than previously (Figure 4a).”

Line 252: repetition of method

Any repetition will be removed.

Line 255: “slightly lower” is vague; what was the difference?

We will clarify with: “Overall, ΔTA in the 1 week dilution, however, was slightly lower, i.e., $\sim 205 \mu\text{mol kg}^{-1}$ instead of $\sim 230 \mu\text{mol kg}^{-1}$ on average.”

Line 255-256: sentence starting “In all dilutions...”; while the direction of change appears independent of dilution timing, the magnitude appears to vary; replication may have provided more information

The Δ DIC increase was very similar in three dilutions, but one was higher. This could have been caused by a faulty cap, enhancing gas exchange. However, this does not pose a problem to any of our interpretations.

Line 260: This is the first instance where the author refers to the Theoretical TA addition from Table 1; it would be insightful for the reader to see both Actual and Theoretical TA additions in Table one for comparison

We will add measured TA to Table 1.

Line 262: sentence beginning “From then on...” is vague

We will change to: “Over the second week of experiment, TA appeared to stabilise up to day 14, before slightly increasing until day 21.”

Line 264-265: Can the author address the source of DIC increase given the use of the “floating lid” to minimise gas exchange?

In these experiments, the floating lid was not used as the experiments were conducted in Schott bottles as described on lines 144 and 150.

Line 266: “up to ~16.7”; the author uses “up to” indicating a maximum and then gives an approximation, is the approximation a rounding of the maximum value? Why use an approximation?

The calculated Ω_{Ar} value was 16.73253. However, given measurement uncertainties for DIC and TA, it only makes sense to report 1 decimal place. Hence, the value was rounded to ~16.7.

Line 268: repetition of method

Any repetition will be removed.

Line 273: repetition of lines 269-270

Any repetition will be removed.

Line 274: “slowly increased over time” is vague

This will be changed to “DIC changes were similar to the TA changes, slowly increasing over time between 0.6 and 2.5 $\mu\text{mol kg}^{-1}$ per day on average, with very similar values reached for the 10 minutes and 1 hour dilutions, as opposed to the 1 day and 1 week ones (Figure 4e).”

Line 274: “~5.0-5.”; what value is being presented here? It reads as approximately 5.0 to 5.0, which would not appear to be correct. Please clarify

Thanks for pointing out this typo, it should read “~5.0-5.1”

Line 275: states where the aragonite saturation state drops to but not where from; please expand

This sentence can be reformulated as “Finally, Ω_{Ar} dropped from ~5.0-5.1 to ~4.0-4.1 over time in the 10 minutes and 1 hour dilutions, while it initially decreased from ~2.3-2.8 to ~2.1-2.2 until day 21 in the 1 day and 1 week dilution, before increasing to ~2.6-3.4 toward the end of the experiments (Figure 4f).”

Line 275: “ Ω_{Ar} decreased slightly over time after dilutions”; both the 1 day and 1 week dilutions appear to exhibit an increase before the final sampling?

This issue has been corrected in the response above.

Line 278: Can the author address the difference between the estimated and measured PIC?

This part is explained (or at least theorised) in the discussion from line 323 to 331. We will refer to the respective section.

Line 280-281: Source of percentages unclear; reviewing Table 2 indicates a 14% and a 7% overestimation respectively in the 500 $\mu\text{mol kg}^{-1}$ cases and 67% overestimation in the the 2000 $\mu\text{mol kg}^{-1}$ case; can the author explain the source of the given percentages?

Thanks for pointing this issue. The authors reviewed the calculations and agree that theirs were wrong. After recalculations, the corresponding percentages should have been:

Experiment	$\Delta\text{TA Theo}$	$\Delta\text{TA Meas}$	$\% = (\Delta\text{TA Theo} - \Delta\text{TA Meas})/\Delta\text{TA Meas}$
500 TA – CaO	543.24	476.38	14.04
500 TA – Ca(OH) ₂	462.28	430.51	7.38
500 TA – Ca(OH) ₂ Dil.	107.05	66.20	61.71
2000 TA – Ca(OH) ₂ Dil.	1718.83	1030.74	66.76

These recalculated values will be changed as: “Furthermore, PIC estimated from the theoretically maximum TA increase upon full mineral dissolution, $\Delta\text{TA}_{\text{Theo}}$, was always higher than estimated PIC from ΔTA , by about 7 to 14% in the ~500 $\mu\text{mol kg}^{-1}$ TA additions with Ca(OH)₂ and CaO respectively, and around 64% in the dilution experiments with ~500 and ~2000 $\mu\text{mol kg}^{-1}$ TA additions.”

Line 284: "In some..." is vague; which experiments?

This will be changed to ". In some of our experiments, secondary precipitation was detected via TA and DIC decreases, as well as PIC built-up."

Line 285: "...TA additions equal to or higher than 500 $\mu\text{mol kg}^{-1}$ " seems misleading as these refer only to target or theoretical TA additions while the results indicate that the experiments with target TA additions of 500 $\mu\text{mol kg}^{-1}$ had lower measured TA changes; please clarify

We will clarify our point here and refer to the actual saturation state, ultimately governing precipitation, by changing to: "More specifically, we observed "runaway CaCO_3 precipitation" at TA additions yielding to an Ω_{Ar} higher than 7 (in the +500 and +2000 $\mu\text{mol kg}^{-1}$ TA treatments), i.e., not only was the added TA completely removed, but significant portions of residual seawater TA as well, until a new steady state was reached."

Line 287: "...we simulated ocean mixing..."; how do the dilutions represent ocean mixing timescales? Please clarify

Ocean mixing occurs on various timescales, and depending on the system settings, e.g., tidal coastal or open ocean, they can vary by orders of magnitude. We clarify that we make a general point by changing to: "Hence, in a set of experiments, we simulated the process of ocean mixing for in situ OAE experiments."

Line 290: Subsection 4.1 also addresses errors including CO_2 invasion from the headspace beyond precipitation which are not indicated by the title

We will change the section name to: "Identifying CaCO_3 precipitation, the problem of unmeasured precipitation, and CO_2 gas exchange"

Line 297: Section 2.5 state that only aragonite saturation states were reported and all Figures present aragonite saturation states. Is the author able to discuss calcium carbonate saturation state thresholds in general given the reported data?

What we have stated on line 297 applies to both, aragonite and calcite saturation states, or any other morphotype of CaCO_3 .

Line 300: Reference to Eqn. 1; The statement is not disputed. However, the relevance of the citation to Eqn. 1 to explain how the change in carbonate ions accounts for a change in TA is questioned. The equation expressed in Eqn. 1 does not describe the contributions to TA.

We will remove the reference to Equation 1.

Line 301: sentence beginning "Hence, any loss..." is well established in literature; would a citation not be appropriate?

We will add the following reference: Zeebe and Wolf-Gladrow, 2001.

Line 302: “suspected” suggests a lack of evidence. If the author detected a 2:1 ratio of TA to DIC changes and then investigated to confirm if this was precipitation, then the authors’ actions are based on empirical evidence rather than a feeling or thought. Please clarify.

Here we will reformulate as “When TA and DIC decreased close to this 2:1 ratio, CaCO_3 precipitation was suspected in our experiments and SEM and particulate inorganic carbon samples were taken ...”

Line 306: addresses comment at line 204: No information is given in section 2.2 regarding sample collection. What volume of samples were taken? Does this mean that the headspace volume increased with each sampling? What was the ambient CO_2 mixing ratio in the room during sampling? Was the floating lid removed completely for sampling? If so, how long for? Was a port in the floating lid used for sampling? Figure A2 does not indicate an additional port to allow gas into the vessel during sampling.

Section 2.2 will be amended, and the following sentence will be added to section 2.3: “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 overflow, corresponding to ~150 mL of seawater sampled per time-point (Dickson et al., 2007).”

Line 309: “a significant fraction could be hydrated” is given as a reason for lower efficiency, could this have been prevented or quantified; please clarify.

Our ICPMS analysis is only picking up the ionic composition and not able to tell apart CaO from $\text{Ca}(\text{OH})_2$. Also, EDX analysis can have problems. Hence, we are not aware of a method that would have distinguished CaO from $\text{Ca}(\text{OH})_2$. More importantly, however, it does not change any of our conclusions.

Line 310: see comment at line 203: In section 3.2 the target TA values are given for the additions and compared with the measured TA increase. When comparing the TA target with the Theoretical TA addition being discussed here; there are significant deviations of 8-10% in the CaO experiments. The measured TA values are reported as approximates but comparing the Theoretical TA increase and the measured TA increase (as indicated at line 308) these deviations appear to be 35% and 33% and not the 25-27% reported at line 310. Where does this discrepancy come from?

We have now added the theoretically expected and actually measured TA values to Table 1, which should clarify our calculations.

Line 311: see previous; these percentages also appear to be underestimated.

Please see our previous comment.

Line 314: “same conclusions”; there is no apparent conclusion in the following statement to qualify this aside; please clarify

We will move the “same conclusions” statement to the following sentence: “If this TA loss would be by CaCO_3 precipitation, DIC should be reduced by half this amount.”

Line 314: repetition of results

We will remove any repetition.

Line 315: “about $-970 \mu\text{mol kg}^{-1}$ ” this value deviates from the $-950 \mu\text{mol kg}^{-1}$ given in the results; please clarify which is the correct concentration

Thanks for pointing out this typo. We will change to $-950 \mu\text{mol kg}^{-1}$.

Line 317: “Although a perfect match”; an absolutism and not technically accurate; for CaO with a reported TA loss of $-950 \mu\text{mol kg}^{-1}$ this would reflect a change in DIC loss of $475 \mu\text{mol kg}^{-1}$ rather than the reported $465 \mu\text{mol kg}^{-1}$; similarly, for the Ca(OH)_2 this would be $430 \mu\text{mol kg}^{-1}$ rather than the reported $395 \mu\text{mol kg}^{-1}$; the absolute statements appear misleading

We will change to: “And indeed, measured DIC loss in both experiments was very close to this 2:1 ratio ($950:465$ and $860:395$ for CaO and Ca(OH)_2 , respectively), suggesting that TA was precipitated in the form of CaCO_3 .”

Line 320-323: sentence beginning “This discrepancy...” to “...dissolution rates.”; not clear how the statement follows; The discrepancy described until this point is the invasion of CO_2 from the headspace which mitigated the DIC loss. It is not clear how this is explained by an inability to measure full dissolution in the presence of concurrent precipitation?

The fact that CaCO_3 might precipitate at the same time as CaO and Ca(OH)_2 dissolve might reflect our inability to quantify the exact amount of TA produced by dissolution, and hence the discrepancy with the theoretical maximum. We will clarify this issue by adding this sentence before: “Hence, the DIC loss should have been higher. Another caveat is the fact 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.”

Line 323: “It also explains...”; what is the “it” in this context? Is the author arguing that the concurrent dissolution and precipitation prevents a true maximum ΔTA and therefore explains the lower PIC estimate?

Yes, the PIC estimate from measured TA is incomplete as what appears to be the maximum TA we measure is actually the difference between the fully dissolved mineral and the early precipitated CaCO_3 .

Line 325: “This could be explained...”; this reads as speculation? Was there no way to verify this? Was there visible precipitation on the bottle walls? Why would this particular experiment be influenced by bottle wall-precipitation to such a significant degree compared to the other experiments?

In each experiment where CaCO_3 precipitation was observed, we noted some white layer on the bottle walls. This layer was very likely to be CaCO_3 . Hence, this could at least partially explain differences between theoretical and measured PIC values. Unfortunately, the total amount of CaCO_3 precipitated onto the walls could not be measured.

Line 326: “In this sense”; in which sense? Please clarify

We will change to: “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.”

Line 327: “theoretical TA generation by dissolution”; why would dissolution generate theoretical TA? Please clarify

Please see comment above.

Line 329: “in between the other estimates”; which estimates are being referred to here?

We will clarify the point by: “Finally, next to impurities, issues with mineral handling, and initial TA removal by CaCO_3 precipitation disguising overall TA release by mineral dissolution, the reason why measured seawater PIC concentrations are in between the other estimates, i.e., $\Delta\text{TA}_{\text{Theo}}$ and measured ΔTA , lies in the fact that a small portion of the CaCO_3 precipitated on the bottle walls, particularly in the $2000 \mu\text{mol kg}^{-1}$ TA experiment, and visible as a white layer.”

Line 329: “lies in the fact...”; appears to be a repetition of the speculation at line 326

This sentence has been reformulated.

Line 333: “An interesting finding” is subjective

We will adopt the reviewer’s suggestion and change to: “An important finding”.

Line 335-337: “in all these experiments... initiated in natural seawater”; this conclusion is supported by 4 incubations in different experimental conditions and is not convincing

In all 4 experiments with CaCO_3 precipitation, it ceased at a similar Ω_{Ar} .

Line 327-329: sentence beginning “This is to be”; how does this follow? If precipitation occurs more readily at higher saturation states, why does a non-linear relationship between precipitation rate and

saturation state explain the continued precipitation at saturation states where precipitation is not naturally initiated?

We realised that there is a typo here, it has to read: "This is to be expected when CaCO₃ precipitates onto CaCO₃ mineral phases at any saturation state above 1 (Zhong and Mucci, 1989; Morse et al., 2007). The rate is directly proportional to Ω_{CaCO_3} , decreasing exponentially until reaching zero at an Ω_{CaCO_3} value of 1 (Figure A 4)."

Line 344: "modelling precipitation"; there is no explanation of modelling in the method section. Is this from Zhong and Mucci (1989)? It is set in the text and phrased as though it were part of this work. Please clarify

Thanks for pointing this out. This sentence is not based on Figure A4 but on a model that was not included in the manuscript. We will add the model in appendix as Figure A5.

Line 349: "...experiments were not replicated." This is a key concern of this Reviewer over the strength of the manuscript's conclusions and further justification to this lack of replication is required

The main focus of the manuscript was to provide insights for the initiation of CaCO₃ precipitation as well as the endpoints, in terms of when it ceases. And all 4 experiments in which precipitation was encountered paint a consistent picture. We agree with the reviewer that if we would have been interested in teasing out the exact time required to initiate and end precipitation under the various conditions, i.e. full kinetic information, replication would have been required. And that's why we mentioned the lack of replication here.

Line 353: "In contrast"; is this comparing the results of this manuscript with the results of Lioliou et al. (2007) or is this work from Lioliou et al. (2007); please clarify

We will clarify with: "In contrast, Lioliou et al (2007) did not report CaCO₃ precipitation onto quartz particles at an Ω_{Ar} lower than 3.5"

Line 354: "For that to occur"; what is the purpose of this statement? The next statement states that the experiments do increase the aragonite saturation state.

We will change to: "In order to trigger CaCO₃ precipitation onto quartz particles, Ω_{Ar} would need to be further increased."

Line 355: "above an Ω_{Ar} of ~9.2 CaCO₃ precipitation did actually occur"; This statement is factually correct but incomplete as no tests were performed at lower aragonite saturation states to determine if precipitation occurred.

We will change to: "Here, we indeed observed CaCO₃ precipitation above an Ω_{Ar} of ~9.2 (Figure 3)."

Line 357: “this idea” is vague; which idea? How does it support the idea? If anything it does not refute the hypothesis of heterogeneous precipitation e.g. an unfiltered sample which exhibits natural precipitation would be required to test the hypothesis

The particle filtration experiment supports the hypothesis that the presence of particles leads to CaCO_3 precipitation in our experiments.

Line 360: first reference to Figure 5; if the figure is important enough to be included, why are they not described in Section 3?

Figure 5 is exclusively used for interpreting the results presented in section 3.

Line 366: “Early CaCO_3 precipitation...”; Repetition. Early precipitation during dissolution was discussed at length in the previous subsection.

We will remove this sentence.

Line 370: “When CaCO_3 precipitates...” is repetition

We will remove this sentence.

Line 372: it is not explained how the changes described are “impacting OAE potential”; this should be stated explicitly

We will clarify this point by: “During CaCO_3 precipitation, dissolved $[\text{CO}_3^{2-}]$ and Ω_{CaCO_3} are decreasing, and $[\text{CO}_2]$ is increasing, which reduces the ocean’s uptake capacity for atmospheric CO_2 , hence impacting OAE potential.”

Line 375: sentence beginning “If fully...”; Why would a DIC increase further increase the pH? Are the numbers cumulative with the 8.61 and 8.45 reported on line 375? After reading Table 3, are these numbers after subsequent reductions in pH and aragonite saturation state during equilibration? If so, this should be clarified in text

Here we compare the final pH_T and Ω_{Ar} values after re-equilibration following OAE to the starting values before addition. The final pH_T is 8.11, 0.07 unit higher than the starting pH_T value of 8.04, and Ω_{Ar} is estimated at 3.90, 1.10 unit higher than the starting Ω_{Ar} value of 2.80.

Line 379: It was not clear how the author arrived at this value. Given that the author describes the use of quick and hydrated lime in the manuscript, these materials would sequester ~ 1.30 and ~ 0.99 tonnes of CO_2 respectively at the efficiencies described. The mixed use of “base material” and “source material” did not associate that the author intended this estimate to be based on CaCO_3 masses; please clarify in the text if this is the case. Additionally, does this estimate include the effects of mining, processing and transportation on the estimate of CO_2 sequestered per tonne of source material mined? If not, these estimates could be misleading

We will clarify this point by only using the term “source material”.

Line 381-382: Please explain the source of these sequestration estimates. Caserini et al. (2021) only indicate the given annual discharge rate of $\text{Ca}(\text{OH})_2$ but estimate a CO_2 uptake of 1.5-3.3 Gt a⁻¹. What is the source of the 1.2-2.8 Gt a⁻¹ CO_2 given in the text? Please clarify the arrangement of the citation to indicate the correct sources of information

We will clarify this issue by: “At a global-scale, using all available ship capacity and assuming a slow discharge of 1.7 to 4.0 Gt of $\text{Ca}(\text{OH})_2$ per year (Caserini et al., 2021), between 1.2 and 2.8 Gt of CO_2 per year could be absorbed by the ocean.”

Line 382-384: c.f. comment for Line 40; the author addresses the Caserini et al. (2021) estimate but also includes the extreme input rate discussed by Feng et al. (2016) without acknowledging the extreme nature of the latter estimate

The Feng et al. (2016) modelling does not rely on ships for distribution but utilises direct coastal addition. We will clarify this issue by: “Including direct coastal TA discharge at a constant addition of $\text{Ca}(\text{OH})_2$ at 10 Gt.year⁻¹ (Feng et al., 2016), we could expect to absorb an additional 7 Gt of CO_2 per year.”

Line 385-392: “If as much... drop below 1.”; This is difficult to follow and the Reviewer is not convinced there is sufficient evidence to support these conclusions. 1) It does not appear that the results shown indicate an experimental case where “as much CaCO_3 precipitates as TA was added”. In cases where precipitation occurred, “runaway CaCO_3 precipitation” also appeared to occur? 2) If all of the TA added precipitates; how can the alkalinity of the ocean be enhanced at all, let alone by 10-60%? 3) This is the first time that “secondary CaCO_3 precipitation” has been mentioned; please define in more detail what is meant by this term. 4) How reliable is the DIC uptake of restricted gas exchange experiments with open ocean implementations?

These are thought experiments. We will clarify this by changing to: “Hypothetically, if as much CaCO_3 precipitates as TA was added, only 0.5 instead of 0.8 mole of DIC can be absorbed per mole of TA after equilibration with atmospheric pCO_2 (Table 3). This represent a decrease by nearly 40% in OAE potential. Similarly, runaway CaCO_3 precipitation until $\Omega_{\text{Ar}} = 2.0$, as observed here, decreases the OAE potential further by almost 90%. Then, only ~0.11 mole of DIC would be absorbed per mole of TA added (Table 3). Finally, secondary CaCO_3 precipitation higher than TA addition will lead to pH_T and Ω_{CaCO_3} levels lower than initial ones. For instance, runaway precipitation for a TA addition of 500 $\mu\text{mol kg}^{-1}$ will see pH_T drop by about 0.1 from 8.04 to 7.93 and Ω_{Ar} from 2.80 to 1.66, significantly enhancing ongoing ocean acidification (Table 3). Runaway CaCO_3 precipitation for a TA addition of 1000 $\mu\text{mol kg}^{-1}$ (assumed to cease at an Ω_{Ar} of 2 as observed here) would even see Ω_{Ar} drop further, i.e., to below 1, upon CO_2 re-equilibration with the atmosphere (Table 3).”

Line 399: “While above considerations stress...” is vague, which “considerations” does the author mean? Further, how has this been stressed? 4.1 describes errors of unmeasured precipitation, 4.2 describes the influence of undissolved mineral phases on heterogeneous precipitation, 4.3 discusses

the impact of precipitation on OAE. There has been no or very limited stress on the importance of monitoring; please clarify

We will change to: “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.”

Line 399: Please clarify what is meant by “natural” here; ships and their wakes are not natural phenomena?

We will remove “natural”.

Line 401: It is unclear why Feng et al. (2016), Caserini et al. (2021) and Mongin et al. (2021) are cited here as the statement made appears to be regarding the assumptions of the present work?

Here, these citations are used to reference the different means to release alkalinity, highlighted in their respective works.

Line 401: “In our experiments...”; How does mixing after 10 minutes, 1 hour, 1 day or 1 week simulate dilution in wakes or natural mixing? Ship wakes would have a limited surface mixing effect in the short-term. Natural mixing would have a longer term and extremely regional impact c.f. Burt et al. (2021). Both approaches neglect continuous diffusion.

We are not simulating mixing by ship wakes or tidal cycles, yet diffusion in our experiments. What we can say is that whatever the mixing process, if the dilution of a +500 TA addition to an Ω_{Ar} of below 5 is performed within 1 week, precipitation will be stopped.

Line 403: “at a surprise”; why is this surprising? Following the arguments and work discussed in this manuscript; no significant precipitation was reported for the 250 $\mu\text{mol kg}^{-1}$ CaO or $\text{Ca}(\text{OH})_2$ experiments (Fig. 1 and 2) and dilution of particles to that concentration could be expected to respond in a similar manner.

This came as a surprise as after a day or a week of alkalinity addition, CaCO_3 particles would already be present in suspension. We have seen that the presence of particles, and particularly CaCO_3 , enhance further precipitation. When proceeding to the dilutions in 1L Schott bottles, CaCO_3 seeds were also transferred in these bottles. Yet, even though CaCO_3 particles were present and Ω_{Ar} values were higher than 1, i.e., ~ 5 , no precipitation was triggered. We will reformulate as: “At a first glance, this comes at a surprise as precipitation nuclei would only be diluted by half, hence reducing surface area and precipitation rates by a factor of 2.”

Line 403: Is dilution by half not the intention of the 1:1 dilution? Please clarify

Here we highlight the fact that despite a dilution, there will be precipitation nuclei present. Yet, CaCO_3 stopped precipitating.

Line 404: “precipitation rates...”; this is not apparent from Fig. A4. Fig. 4c indicates a change from aragonite saturation state of 7-8 between the 4 dilutions to approx. 4-5. Fig. A4 indicates an aragonite saturation state of 7-8 would have a precipitation rate of 800-1100 to a precipitation rate of 200-400?

Here we refer to Figure A 4, in the appendix.

Line 409: How is a comparison of Fig. 5c and Fig. 5d relevant here? The author appears to be discussing the precipitation response of $\text{Ca}(\text{OH})_2$ dilutions from 500 $\mu\text{mol kg}^{-1}$ to comparing Na_2CO_3 experiments with quartz seed minerals rather than comparing precipitation between quartz seed minerals?

As we do not have SEM images of CaCO_3 precipitates on CaO or $\text{Ca}(\text{OH})_2$ at an early stage, but only after more than 4 weeks, where a complete overgrowth is likely, we used the SEM images for quartz as an analogy.

Line 410: “precipitation can be avoided”; there seems insufficient evidence to support that a 1:1 dilution is required as no other dilution ratios were tested at this concentration; please clarify

It is most likely that a 1:1 dilution will be required, as otherwise, the saturation state will still be above the threshold of 5.

Line 411: “The quicker dilution...”; the similarity indicated appears limited; perhaps only to the aragonite saturation state achieved within the first day? Plot axes make comparison difficult for the reader

We agree that the differences in ΔTA between the various dilutions are difficult to differentiate. However, the important part is that the longer one waits, the more CaCO_3 precipitates. This can be seen in the undiluted case (black line).

Line 415: “that verification... problematic”; it is unlikely that measurements of TA additions would be used to monitor CO_2 sequestration in the long term and “permanent” sequestration is difficult to define; please clarify what is meant by “TA measurements” and “permanent” in this context

We agree with the reviewer and will clarify this issue by: “Furthermore, the difficulty to monitor precipitation from simple TA measurements (as described above) would also mean that quantification of CO_2 removal is not straight-forward.”

Line 419: “Staying clearly...” is ambiguous; in what context is “clear” being used here?

We will clarify our point here by: “Staying clearly below the Ω_{Ar} threshold identified here, i.e., limiting coastal Ω_{Ar} to only 3.2, up to ~ 550 Gt of carbon in the form of CO_2 could be removed from the atmosphere by 2100 (using olivine sand, with a grain size of $\sim 10 \mu\text{m}$), corresponding to a reduction by about 260 ppm (Feng et al., 2017).

Line 419-420: The author should address the fact that Feng et al. (2017) consider olivine rather than CaO or Ca(OH)₂ and that the drawdown the author indicates were modelled using less than 10 µm grain sizes compared to the greater than 63 µm grain sizes used in this study

Please see comment above.

Line 425: “Hence, even with...”; the Reviewer finds insufficient evidence to conclude that this is the optimum threshold

It is not the optimum threshold, but considering potential precipitation onto mineral phases naturally occurring in seawater, it might be safer. Obviously, more research is needed.

Line 431: “equilibrate it with air”; this reads that the mineral must first be equilibrated with air? Please clarify

We will clarify this by: “Finally, another option to increase atmospheric CO₂ uptake would be to not adding minerals to seawater directly, but to keep the seawater equilibrated with air or CO₂ enriched flue gases, during minerals dissolution.”

Line 431: “CO₂ enriched flumes”; unclear what the author means by this term

Thanks for pointing out the typo and please see response above.

Line 431: “This would allow... passive”; does the author mean that excessive aragonite saturations be permitted such that a rapid equilibration with air and CO₂ uptake would reduce the aragonite concentration again? What conditions could permit this in the ocean?

Equilibrating the seawater to atmospheric CO₂ during mineral dissolution is a step that would need to be done on land, before pumping the water into the ocean. We will also reformulate our statements as: “Firstly, this would allow reaching an Ω_{Ar} of 5 as opposed to 3.3 in the +250 µmol kg⁻¹ TA scenario (Table 3), when equilibration is occurring after instead of during the dissolution process. And secondly, reaching an Ω_{Ar} of 5 with CO₂ equilibration, nearly 1000 instead of 250 µmol kg⁻¹ of TA could be added, allowing for almost 4 times the amount of atmospheric CO₂ to be removed (this number is highly sensitive to temperature, and ranges between ~3 and ~6 between 30 and 5 °C).”

Line 433-438: From “In this case...” all reads as speculation and feels “tacked on” to the end of the manuscript. Is this what is referred to in the subsection title as “and other TA additional strategies”? How viable would these strategies be in terms of equilibration times? The author expresses that this extra step is time and cost intensive; is the trade-off worth discussing?

These are part of the other TA additional strategies. Using microbubble airstones, the process would be relatively fast, particularly if CO₂-enriched flue gases are used. Concerning potential costs and viability, we decided not to make technology assumptions, but to only provide the chemical basis.

Line 440: “promising” is subjective and reader may not agree

We will change to: “Ocean alkalinity enhancement is a negative emission technology with relatively large potential for atmospheric CO₂ removal.”

Line 444-445: “suggesting... of about 5” reads as speculation and the breadth of the experiments described in this study appear insufficient to support this conclusion

We agree that the upper limit could be higher, but an Ω_{Ar} value of 5 appears to be a safe one. We will also change “safe upper limit” to “safe limit”.

Line 447: Is this intended to build upon the condition of the previous statement which referred to coastal settings? i.e. expanding beyond coastal settings into the open ocean? Please clarify

The reviewer is correct that we had a coastal setting in mind for our first statements, which does not make sense. Hence, we will reformulate as: “Safely increasing the amount of TA that could be added to the ocean involves allowing for major mixing and dilution of enriched seawater by coastal tides or in the wake of ships, equilibrating the seawater to atmospheric CO₂ levels prior to the addition during mineral dissolution, and targeting low rather than high temperature regimes.”

Line 448: What is meant by “major mixing”, please clarify

Please see our response above.

Line 448: “equilibrating the seawater... mineral dissolution”; unclear why this is stated. Surface water should always be in or approaching equilibrium with the surface atmosphere. What situations would this not occur?

When alkaline minerals dissolve, the [CO₂] decrease. If we could concomitantly equilibrate the seawater while increasing the TA, we could theoretically dissolve more alkaline mineral, as described in the previous paragraph. We will also add the following: “equilibrating the seawater to atmospheric CO₂ levels prior to the addition during mineral dissolution, and targeting low rather than high temperature regimes.”

Technical Corrections:

Line 16: In what way does the sentence beginning “However, ...” contrast or oppose the preceding sentence?

We will change to: “However, CaCO_3 precipitation, in the form of aragonite, was found to occur at a saturation (Ω_{Ar}) threshold of about 5.”

Line 16: “...dissolved...” could be used in the present tense here as the results should hold constant in time

We opted to keep the description of our results in past tense.

Line 20: the use of “...by which...” and the sentence structure of the statement makes the sentence feel unnecessarily complex and slows reading

We will change to: “Most importantly, this led to runaway CaCO_3 precipitation, i.e. significantly more alkalinity (TA) was removed than initially added, until Ω_{Ar} reached levels below 2.”

Line 25: Why is a comma used after the temperatures are given?

This comma will be removed.

Line 31: Capitalise “IPCC” in the given citation

This will be done.

Line 38: Why is “ocean alkalinity enhancement” italicised and the acronym given after a dash rather than in parenthesis?

We will remove the Italic font. The reason for the dash rather a parenthesis was to avoid a closing and opening parenthesis next to each other.

Line 42: “...similar to what occurs...” is vague; what occurs during rock weathering? The sentence structure can be made more concise and less vague.

We will change to: “OAE typically relies on the dissolution of alkaline minerals in seawater, releasing alkalinity like during natural rock weathering.”

Line 51: The sentence structure here is complicated by the mixture of multiple comma-enclosed parentheses and comma-separated clauses. The sentence should be simplified

We will put the explanation in parentheses: "Including the subsequent oceanic uptake of atmospheric CO₂, and 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), a conceptual model of CaO and Ca(OH)₂ dissolution can be summarised as per:"

Line 58-59: "This" is vague, clarify what is increasing the pH i.e. the addition of quick/ hydrated lime. Additionally, "lowering" and "increasing" are nouns describing the actions rather than the verb forms "lowers" and "increases" which are indicated contextually.

This refers to the increase in TA, while DIC is unchanged as described in the previous sentence. We will also use the verb forms as suggested.

Line 60: "This in turn..." is vague, what it turn?

We will change to: "The shift in DIC speciation leading to the decrease in [CO₂] also reduces the partial pressure of CO₂ (pCO₂) in seawater."

Line 70: Why is the symbol Ω introduced here in the second use of CaCO₃ saturation state rather than the first use at line 66?

Thanks for pointing this out, it will be amended.

Line 74-81: The paragraph structure here is meandering; the author begins on the topic of the critical threshold for precipitation and then go on to postulate about the TA change to achieve this threshold before returning to introduce the reader to other types of precipitation. The paragraph should be restructured to more clearly make the author's intended point.

We will consolidate the structure as suggested: "There are three types of precipitation, i.e., 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)."

Line 90: missing article before "Agilent"; grammar indicates plural but noun is used in the singular without article.

Thanks for pointing this out, we will add an 'an'.

Line 115: the sentence beginning "The mesh..." is written in the past tense but the present tense "avoiding" is used, to be correct this should be changed to "to avoid"

We will address this issue by: “The mesh was placed in a clean upside-down 50 mL Falcon tube cap, to minimise the loss of material smaller than 63 μm , and the overall weight was recorded.”

Line 122 and 123: the author repeats the CAS number information; is this necessary?

Thanks for pointing this out, the second CAS number will be removed.

Line 129: “identical” is an absolutism; Table 1 indicates that the experiments were similar but not identical

Here we can change to “similar”.

Line 142: There is a mixture of singular and plural in the statement beginning “ $\text{Ca}(\text{OH})_2$ was added”; “final alkalinity enrichments” in the plural should be used

We will change to: “ $\text{Ca}(\text{OH})_2$ powder was added...”

Line 147: please add space between value and unit for “200 rpm”

Noted.

Line 154: Incomplete statement or missing word; “Samples for TA and DIC...” context suggests the author intended “analyses” or “measurements” etc.?

Here we will add “measurements”.

Line 190: Unclear if “ ΔTA ” is given as an expression for the preceding text, then a comma separation is required, or intended to be included in the sentence but then more explanation is required for what is meant by the term “ CaCO_3 precipitation ΔTA ”

Here, a comma is needed before ΔTA

Line 208: plural “decreases” suggests multiple negative change events; there is insufficient sampling to distinguish multiple independent decreases

This was meant to be singular.

Line 290: “not measured” may be better phrased as “unmeasured”

Noted.

Line 299-331: Is this a single paragraph? Please restrict paragraphs to a single topic, it will benefit readers

This paragraph will be separated in 2 smaller ones.

Line 306: missing punctuation; should there be a period before "A"

Thanks for pointing this out. It will be addressed.

Line 307: sentence beginning "This in turn..."; the use of "when" suggests that a cause and effect relationship is being introduced but only active forms are used; if a cause and effect relationship is intended, clarify grammatically

The part "when increasing DIC and [CO₂]," will be removed.

Line 312: missing punctuation; should there be a period before "In contrast..."

Yes, noted.

Line 317: "exactly"; an absolutism and not technically accurate

Please see response to previous comment above.

Line 317: "Although a perfect match"; an absolutism and not technically accurate

Please see response to previous comment above.

Line 325: "...similar results. However,..."; these sentences are linked and should not be separated by a period

We will change to: "In the experiment with 1M Na₂CO₃ and quartz particles, both TA-based PIC estimates are similar. However, the measured PIC is about twice as low."

Line 328: "Finally"; this appears to be a new topic and could be a new paragraph?

We will start a new paragraph.

Line 357: "...this idea. Not yet dissolved..."; sentences are connected, join them with appropriate punctuation

We will change to: "The filtration of TA enriched seawater supports this idea since not yet dissolved..."

Line 401: Sentence beginning “In our experiments...” is not clearly structured

We will reformulate as: “In our experiments, a 1:1 dilution could seemingly stop CaCO₃ precipitation in seawater, even if performed only after one week for the +500 μmol kg⁻¹ TA addition.”

Line 406: The use of “however” and “but” both indicate contrast but the first half of the sentence appears to agree with the previous linked statement; please clarify

“However” will be removed.

Line 414: from context it is assumed this is a spelling error and “from” was intended?

Thanks for pointing out the typo.

Line 430: Is “mineral” intended to be singular?

We will change to plural as suggested.

Line 440: Why is “Ocean Alkalinity Enhancement” italicised?

We will remove Italic font.

Line 446: “as of potential” doesn’t make grammatical sense

We will change the sentence to: “This is probably also the case for other minerals with even lower lattice compatibility for CaCO₃, because in coastal settings, CaCO₃ could precipitate onto naturally present mineral phases, such as resuspended sediments.”

Line 447: Grammar of sentence beginning “Safely increasing...” is ambiguous

This sentence has been reworded. Please see our response to a previous comment.