Biogeosciences Discussions

Biogeosciences Discuss., community comment CC1

https://doi.org/10.5194/bg-2021-330-CC1, 2021

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Comment on bg-2021-330

A. Mucci (Referee)

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-RC1, 2021

In this paper, the authors determine 1) how much alkaline material (CaO or Ca(OH)2) can be dissolved without inducing CaCO3 precipitation in seawater, 2) what triggers CaCO3 precipitation, and 3) how it can be avoided by limiting the OEA, through dilution with natural seawater or by lowering the temperature of the solution.

The objectives of the study are laudable because avoidance of CaCO3 precipitation is one of the major challenges of OEA. As rudimentary as the experiments are, they do provide some insights but the choice of OEA substrates is less than ideal, given that they provide reactive surfaces (for heterogeneous precipitation) and carry a very large production carbon signature (calcination of limestone).

The descriptions of the methodologies are incomplete, the experiment during which the authors add Na2CO3 is not described. It would appear that it may have been omitted or erased and, consequently, some of the statements in section 2.2.2 are blatantly wrong.

Thank you for pointing this out. We agree that the Na_2CO_3 method description is indeed lacking some detailed explanations. We addressed this issue and made sure that these experiments are clearly described, understandable and repeatable for the reader.

The manuscript would greatly benefit from a more extensive review of the literature with respect to factors that control the spontaneous nucleation of calcite and aragonite from seawater. The authors are directed to a number of these in the specific comments that follow.

Finally, although the written English is acceptable, there are innumerable grammatical errors and the structure of several sentences is so awkward as to be incomprehensible.

Thanks for the additional references. The authors added information and double-checked grammar and structure.

Specific comments-

Lines 39-40: How much CaO or Ca(OH)2 would be required to mitigate anthropogenic CO2? Would it be physically feasible to produce or displace so much CaO or Ca(OH)2? What would the carbon signature of producing and/or transporting this much CaO or Ca(OH)2? Under the IPCC IS-92S "business as usual" scenario, more than 4000 Gt of CO2 will be emitted to the atmosphere by the end of this century. Hence, this OEA proposal would remove at most only 20% of the emitted carbon dioxide! The authors need to address the impact and feasibility of their proposed mitigation mechanism.

Currently, the global cement industry produces about 4.1 Gt of cement per year (https://www.statista.com/topics/8700/cement-industry-worldwide/). Depending on whether hydraulic ($CaO \cdot Al_2O_3 \cdot Fe_2O_3$) or non-hydraulic ($Ca(OH)_2$) is being produced, and assuming a Ca^{2+} to C sequestration potential for CO_2 of 1.6, between 2.7 and 3.9 Gt of atmospheric CO_2 could be captured per year. This is on the order of CDR required to be built-up in the next 30 years, based on the shared socioeconomic pathways RCP2.6 scenario that would keep global warming below the 2 °C target (Huppmann et al., 2018). Furthermore, it is unlikely that there will only be one negative emission technology approach. In the marine realm alone, there are several currently under consideration, such as increasing open ocean productivity or marine biomass-fuelled bioenergy with carbon capture and storage (Gattuso et al., 2021).

Line 46: Calcination requires a lot of energy (heating to 1200°C) and the process produces a lot of carbon dioxide. Hence, is the proposed OEA really a feasible option?

Different strategies have been proposed to capture CO_2 during calcination, which would negate CO_2 emissions. Furthermore, with the rise of renewables, such energy-demanding process could be carbon-neutral. Finally, limestone-based minerals have certain advantages over others as they are highly abundant and have relatively quick dissolution rates. A last important point would be that they do not require fine grinding, as for instance hard olivine.

Line 70: This is a challenge for most OAE strategies.

Noted

Lines 74-76: The critical threshold for the precipitation of aragonite is more relevant since this CaCO3 polymorph nucleates and precipitates first (due to Mg2+ inhibition - e.g., see Pan et al. (2021). Among many others publications on the spontaneous nucleation and precipitation of calcite and aragonite from seawater and seawater-like solutions, including Chave and Suess (1970; L&O 15:633); Rushdi et al. (1992; Geolog. Rundschaud. 81:571); Choudens-Sanchez and Gonzalez (2009; J. Sed. Res. 79:363); Ruiz-Agudo et al. (2011; GCA 75:284), Kontrec et al. (2021; Crystals 11:1075), and Pan et al. (2021).

The authors have reviewed these research articles and added more background knowledge on $CaCO_3$ nucleation pathways into this section (lines 78-95).

Lines 98-100: What was the salinity of the natural seawater? I could not find it reported in the text.

The seawater batches were collected at different times of the year. The salinities varied between 35.46 and 36.91. The authors added all salinity data to the appendix.

The first paragraph of section 2.2.2 is likely incomplete as either an experiment is not properly described or, as written, many statements are blatantly wrong. I can only presume that the authors carried out an experiment during which they added the 1M Na2CO3 solution to the natural seawater as results are presented in section 3.4.

This is correct. In these experiments, the authors used a 1M Na_2CO_3 solution as alkaline agent. However, it is clear that this section is incomplete. More details on the experiments with 1M Na_2CO_3 have been added (lines 137-152).

Lines 124-125; 127-128: Irrespective of the amount of Na2CO3 added, the saturation state of a Milli-Q solution with respect to CaCO3 minerals will remain null as it is devoid of calcium ions. One cannot use CO2SYS to calculate the saturation state of a Na2CO3 solution prepared in Milli-Q water with respect to CaCO3 minerals.

The Ω_{CaCO3} values were not calculated for the 1M Na_2CO_3 solution. Ω_{CaCO3} values were calculated for the seawater batch, to which the 1M Na_2CO_3 solution was added. Then, with the changes in TA and DIC, the associated changes in Ω_{CaCO3} were calculated. The authors have reviewed this section to make it clearer (lines 138-146).

Section 2.3: What is the precision and accuracy of the TA and DIC measurements?

The TA measurements were made in duplicates, and a standard deviation is reported, i.e., 0.8 µmol kg^{-1}. The DIC measurements were made in triplicates, and similarly, a standard deviation is reported, i.e., 0.6 µmol kg^{-1}. Using these measures of precisions and taking into account that they are referenced against a certified standard with very similar precision, the overall uncertainty for TA is 1.0 µmol kg^{-1}, and 0.8 µmol kg^{-1} for DIC (as calculated from an error propagation).

Line 158: Open-cell titrations?

This was changed to “open-cell titration protocols” (line 181).

Lines 167-168: What fraction of the filters and how were filters introduced in the elemental analyzer? Why was an IRMS used? As a detector, as no isotopic data are reported?

The whole filter was introduced in the elemental analyser. To do so, the filters were folded and wrapped into small tin capsules, that were pressed into round-shaped balls. The elemental analyser is connected to an IRMS as the detector in our lab, hence the reason it was mentioned. We clarified this in the text (line 190).

Line 180: What boron:salinity relationship did the author use in CO2SYS (Uppstrom (1974) or Lee et al. (2010))?

The authors used the boron to salinity relationship from Uppstorm 1974. This has been added (lines 203-204).

Line 188: Although CO2SYS will return values of the stoichiometric solubility of calcite and aragonite (K*) at the temperature and practical salinity of interest, values of TA and DIC are not required since K* values are independent of TA and DIC but are a function of t and SP (and P).

The reviewer is correct, and our formulation was vague. We calculated K_{sp} based on temperature and salinity (Mucci, 1983), and then used it with addition-corrected calcium concentrations, together with CO_2SYS-derived CO_3^{2-}, based on DIC and TA, to calculate Ω_{CaCO3}. We clarified this in the revised version of the manuscript (lines 210-214).

Line 191, Eqn. (3): Why use the Ca:chlorinity ratio rather than the Ca:SP ratio? Equation 3 would simplify to: [Ca2+] = (0.01028/35)*SP + ΔTA/2.

We agree, this is a much straight-forward approach, and it was changed it accordingly (line 215).

Lines 228-229: Unclear. "TA" does not precipitate, CaCO3 does.

This part was fully reformulated.

Lines 247-251 and 259-267: Why are the results of this duplicated experiment repeated? The authors should comment about their reproducibility in section 3.3 and focus of the results of the dilution experiments in this section.

These results were not duplicated, but a new batch of TA+500 µmol kg^{-1} was freshly prepared to be used in the dilutions experiments. For completeness, the undiluted treatment results were presented as well.

Lines 339-344: The threshold saturation value also determines the induction time, a variable that the authors did not investigate or refer to. Several studies have been conducted on the subject, including Morse and He (1993) and many others.

Following the research on $CaCO_3$ nucleation pathways, the authors mentioned the suggested paper.

Lines 344-347: It should theoretically precipitate until saturation is reached, but precipitation kinetics decrease rapidly as saturation is approached and is strongly inhibited by the presence of DOM and orthophosphate. As the authors used natural seawater, both solutes must have played a role. What was the DOC and soluble reactive phosphate (SRP) of the natural seawater?

Unfortunately, DOC was not measured. From left-over water, however, we did determine phosphate concentrations in one of the seawater bathes, which was 0.3 µmol L^{-1}. This information was added to a table in the appendix.

Lines 350-351: Would this not have been revealed by the SEM examination of the precipitates?

Unfortunately, the SEM analysis did not show any obvious aragonite formation around CaO or $Ca(OH)_2$ particles, as they were taken at the end of the experiments, after 14 days for the first dilution experiment, and up to 48 days in other experiments. At these stages, relatively small CaO or $Ca(OH)_2$ particles are likely to be completely covered in $CaCO_3$ overgrowth. Furthermore, with EDX analysis, it is difficult to differentiate between CaO/$Ca(OH)_2$ and $CaCO_3$ as the elemental composition is quite similar (note that there is always a carbon background from the polycarbonate filters). Hence, we could only speculate on the potential $CaCO_3$ precipitation on not yet dissolved particles. That was however different to the non-dissolving quartz particles, as their $CaCO_3$ overgrowth was clearly visible and distinguishable by element analysis with EDX.

Line 380: CO2 capture upon calcination of limestone would have to be 100% efficient. This brings us back to the issue I raised earlier on in my comments about the net carbon signature and feasibility of the proposed OAE process.

Please see reply above.

Lines 383-384: A mere 14% of projected emissions by the end of this century!

It is actually more than double, what would be required to stabilize global temperature below 2 °C increase until the end of the century (see reply above).

Lines 391-392: How is this possible (Ωar <1), unless calcite is precipitated. Yet, the authors have established and shown (Figure 5) that, in most cases, only aragonite precipitated from their experiments. In other cases, the authors believe that vaterite was precipitated.

In our model simulations, precipitation stopped at an Ω_{Ar} =2. The re-equilibration with the atmosphere and resulting ingassing of CO_2 increases DIC and further lowers Ω_{Ar}, i.e., in this case to be slightly below 1. This has been clarified (line 436).

Lines 430-433 and 445-447: The sentence structures are awkward and nearly incomprehensible.

These sentences were reviewed and reformulated, implementing both reviewers' comments.

Biogeosciences Discuss., community comment CC1

https://doi.org/10.5194/bg-2021-330-CC1, 2021

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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 µmol 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 µmol kg^{-1} of TA paint a coherent image of OAE related Ω thresholds, which is our main conclusion. Furthermore, two similar pre-experiments with the 500 µmol 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 $CaCO_3$ 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 $CaCO_3$ 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 have been re-written (see responses to the specific comments below). We apologize for the inconsistency in in-text citations and organised 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 added 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 made sure that all necessary details are 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 $CaCO_3$ comment, we added the following information to the text: "Such secondary precipitation constitutes the opposite of alkaline mineral dissolution and would decrease pH and Ω_{CaCO3}, simultaneously increasing seawater [CO_2]." (line 79).

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 µmol kg^{-1} at day 47 of the experiment with a TA increase of 500 µmol kg^{-1} with CaO, would be misleading, and we hence rounded to ~540 µmol kg^{-1} instead.

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

When it comes to the initial state before the dissolution, that is shown in Figure 4. Here, one can see that in the 1:7 dilution of the +2000 µmol kg^{-1} TA addition, where about 150 µmol 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 $CaCO_3$ 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 moved 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 corrected 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 have added 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 reformulated the sentence (lines 12-14).

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

We reformulated the sentence (lines 13-14).

Line 19: The author uses “so-called” here but later in the discussion at line 292 indicates that this is an established form of CaCO3 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 Ωar 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_{CaCO3} 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 has been discussed at lines 386-387. 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 reformulated “model considerations” to “OAE simulations” (line 25). Regarding the simulations in section 4, the following paragraph was added to the methods, lines 220-228:

“2.6 OAE simulations

CO_2SYS 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, temperature = 19 °C, using the same acid-base equilibrium constants as described in section 2.5. In the first scenario, for all three additions, no $CaCO_3$ precipitation was assumed, and the amount of CO_2 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 $CaCO_3$ precipitated as TA was added, and second, that $CaCO_3$ precipitated down to an Ω_{Ar} of ~2 as observed in our experiments. Again, after calculating full carbonate chemistry speciation in these various scenarios, the amount of CO_2 taken up after atmospheric re-equilibration was determined.

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 added the following information at line 26: "to atmospheric CO_2 levels, i.e., to a pCO_2 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 was reformulated as "ideally below +1.5 °C" (line 37).

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…"

We reformulated as "Among carbon dioxide removal approaches, OAE has a high carbon dioxide removal potential, with models suggesting that between 165 and 790 Gigatonnes (1 Gt = 1e15 g) of atmospheric CO_2 could be removed by 2100 on a global scale" (lines 40-42).

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 added 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. A recently described approach aims to increase alkalinity by 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 was reformulated to “Suitable candidates are magnesium-rich minerals such as brucite, periclase or forsterite, and calcium-rich minerals such as quick and hydrated lime.” (lines 46-47).

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

This was changed (line 47).

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 CO_2 capture during limestone calcination. We added the following information “Once heated to temperatures of ~1200 °C, each molecule of $CaCO_3$ breaks down into one molecule of CaO and one molecule of CO_2 (Ilyna et al., 2013; Kheshgi, 1995). Hence, for maximum OAE potential, carbon capture during calcination and subsequent and storage would be advisable (Bach et al., 2019; Renforth et al., 2013; Renforth and Kruger, 2013)“ (lines 50-52).

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 “The chemical reaction of CO_2 and $Ca(OH)_2$ dissolution can be written as follows, which includes the subsequent and rapid oceanic uptake of atmospheric CO_2, and ignores the non-linearities of the seawater carbonate system (i.e., changes in total alkalinity, TA, and dissolved inorganic carbon, DIC, are not 1:1):” (lines 55-57).

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 added the following explanation: “The dissolution of CaO and $Ca(OH)_2$ and the subsequent addition of TA increases seawater pH, while changing the carbonate chemistry speciation. DIC can be approximated by being the sum of HCO_3^- and CO_3^{2-} (ignoring the relatively small contribution by CO_2). Similarly, TA can be approximated as the sum of HCO_3^- and 2 CO_3^{2-} (ignoring the smaller contributions by boric and silicic acid, and other minor components). Combining both DIC and TA equations reveal that CO_3^{2-} concentrations can be expressed as $[CO_3^{2-}]$ = TA-DIC. Hence, increasing TA at constant DIC,

e.g., by dissolving CaO or $Ca(OH)_2$, increases [CO_3^{2-}], shifting carbonate chemistry speciation towards higher pH (Figure A 1) (Dickson et al., 2007; Wolf-Gladrow et al., 2007; Zeebe and Wolf-Gladrow, 2001)." (lines 61-66).

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, pCO_2 and [CO_2] are linearly correlated.

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

This has been removed.

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

The major constraint is to keep Ω_{CaCO3} below a threshold above which it $CaCO_3$ 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 has been 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 $CaCO_3$ shifts carbonate chemistry speciation towards a lower pH and higher CO_2 concentration, reducing ocean's uptake capacity. This was mentioned at lines 80-81.

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 CO_2SYS 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 clarified 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). For the latter, 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).” (lines 86-90).

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

ESI is the acronym of the company that provided the ablation unit. The complete name has been added (line 103).

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 added the following: “accurately weighed (in grams to 2 decimal places)” (line 116).

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 added the following to the Method section “calculated amounts of weighed-in alkaline compounds were added”. The unit, i.e., mg, has been mentioned in the following paragraph while explaining the alkalinity weighing and addition processes (line 120).

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 clarified with: “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.” (lines 122-123).

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 changed to “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 play a role in changing DIC and TA.” (lines 123-125).

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 clarified the issue by: “Following the previously described beaker setup, TA was added by sieving CaO and $Ca(OH)_2$ through a 63 µm mesh, avoiding the formation of larger CaO or $Ca(OH)_2$ aggregates.” (lines 129-130).

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 µmol 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 µmol kg^{-1}, leading to a redesign of the addition towards +250 and +500 µmol kg^{-1} over +500 and +1000 µmol 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 clarified this issue by adding the following: "Three further experiments assessed the role of mineral phases during $CaCO_3$ precipitation observed 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." (lines 138-140).

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

We added: "Ultrapure Na_2CO_3 was accurately weighed, i.e., in mg (with 2 decimal places), into a clean 100 mL Schott bottle and made up to 100 g with MilliQ (18.2 MΩ)". (lines 140-141).

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 clarified by: “The solution was then sonicated for 15 minutes, and gentle mixing every five minutes.” (lines 141-142).

Line 126: “almost twice the alkalinity increase” is vague; in the first, “almost” indicates a concentration less that 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_{CaCO3} increase smaller. All carbonate chemistry calculations were done in CO_2SYS (see below).” (lines 143-146).

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 added the following to the paragraph: “Quartz powder was chosen as it does not dissolve on the timescales relevant for this study (Montserrat et al., 2017)”. (lines 147-148).

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

We clarified by: “The mass of quartz particles added, recorded in mg, 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}.” (lines 149-151).

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 spheric.

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

We changed to “Finally, a third experiment was carried out in which all particles were removed by filtration, using $Ca(OH)_2$ as the alkaline compound and following the same setup as described above (section 2.2.1).” (lines 153-154).

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 reads: “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.” (lines 122-123).

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 added this piece of information in the respective methods sections (lines 162-164).

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 was 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 removed “as described in the following”.

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

We changed to “Calculated weighed-in masses of $Ca(OH)_2$ were added to the first bottle as described in section 2.2.1 using the 63 µm sieve, while the natural seawater in the second bottle was kept for subsequent dilutions.” (lines 164-166).

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 moved 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 added the following information: "Following the $Ca(OH)_2$ 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." (lines 167-169).

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 provided a reference here, i.e., Gafar and Schulz, 2018.

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

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

Line 174: Why was CaCO3 precipitation "suspected", this indicates to the reader that these there was insufficient evidence to support the conclusion

We added the following information: "In cases where TA and DIC decreases were detected, indicative of $CaCO_3$ precipitation, several 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 °C) GF/F filters and stored frozen until analysis" (lines 186-189).

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 changed to: “Measured DIC, TA, temperature and salinity were used to calculate the remaining carbonate chemistry parameters with CO_2SYS script for MATLAB® (MathWorks).” (lines 202-203).

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

In our case, the relevant calculated parameters were the pCO_2, pH, Ω_{Ca} and Ω_{Ar} values.

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

We changed “amount” to “concentration” (line 212).

Line 203: The author states that a “~250 µmol 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 CO2 mixing ratio of the introduced gas? How comparable is the CO2 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 pCO_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 was added to the sentence: "In contrast, DIC increased slowly, about 1 µmol kg^{-1} per day, reaching about +50 µmol kg^{-1} on day 47 of the experiment (Figure 1b)." (lines 237-238).

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 clarified the point with: "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 hours before slowly decreasing on day 3 (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 µmol kg^{-1}." (lines 240-242).

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 changed to: "relatively small" (line 243).

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

We changed to: "a much more significant". (line 244).

Line 211: The ΔDIC is given as approximately 465 µmol kg-1 but Fig. 1b indicates that this should be a negative value

Thanks for pointing out this typo, it now reads "about -465 µmol kg^{-1}".

Line 213: "rapidly" is vague and subjective

We changed to: "dropped quickly to 2.4".

Line 217: The sentence beginning "The DIC concentration…" indicates a constant rate of increase to a total of 70 µmol kg-1 but Fig 2b indicates a greater rate of change between the 6th and 9th sampling intervals; please clarify

This was clarified with: "The DIC concentration increased relatively quickly over the first 6 days after the TA addition before slowing down, reaching about +70 µmol kg^{-1} by the end of the experiment (Figure 2b)." (lines 251-253).

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

This was clarified with “This was followed by a relatively steady decrease by ~18 µmol kg^{-1} per day over the next 2 weeks, after which the decrease accelerated to ~28 µmol kg^{-1} per day until day 35, before levelling off at a ΔTA of about -420 µmol kg^{-1} towards the end of the experiment.” (lines 256-258).

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 µmol 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 $CaCO_3$ 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 moved 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 µmol 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 Na_2CO_3 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 shortened the description.

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

We changed to: "between day 5 and 12". (line 271).

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 was reformulated as "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 to ~3.9 between day 5 and day 12, before stabilizing around ~2.0 at the end of the experiment." (lines 273-275).

Line 239: further repetition of method

The repetition has been removed.

Line 241: What is the variable with concentration of 470 µmol 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 added the following to section 2.2.3: "All dilutions were performed 10 minutes, 1 hour, 1 day and 1 week after $Ca(OH)_2$ addition, leading to 2 TA-enriched and 8 diluted treatments." (lines 171-172).

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

Thanks for pointing out the typo. It now reads: "These changes in TA were followed by a decline to ~320 µmol kg^{-1} after 14 days, although the latter being a slightly slower decrease than previously (Figure 2a)." (lines 285-286)

Line 252: repetition of method

Any repetition was removed.

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

We clarified with: "Overall, in the 1 week dilution, ΔTA was slightly lower, i.e., ~205 µmol kg^{-1} instead of ~230 µmol kg^{-1} on average." (line 291).

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 ΔDIC 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 added a measured TA column to Table 1.

Line 262: sentence beginning "From then on…" is vague

We changed to: "Over the second week of experiment, TA appeared to stabilise before slightly increasing until day 21." (line 299).

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 162 and 168.

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 has been removed.

Line 273: repetition of lines 269-270

Any repetition has been removed.

Line 274: "slowly increased over time" is vague

This was changed to "DIC changes were similar to the TA changes, slowly increasing over time between 0.6 and 2.5 µmol 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)." (lines 308-310).

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 now reads "~5.0-5.1"

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

This sentence was 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 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)." (lines 310-312).

Line 275: "Ωar 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 359 to 367.

Line 280-281: Source of percentages unclear; reviewing Table 2 indicates a 14% and a 7% overestimation respectively in the 500 µmol kg-1 cases and 67% overestimation in the the 2000 µmol 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 are:

Experiment	ΔTA Theo	ΔTA Meas	% = (ΔTA Theo – ΔTA Meas)/ΔTA 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 were changed as: "Furthermore, PIC estimated from the theoretically maximum TA increase upon full mineral dissolution, ΔTA_{Theo}, was always higher than estimated PIC from ΔTA, by about 7 to 14% in the ~500 µmol kg^{-1} TA additions with $Ca(OH)_2$ and CaO, respectively, and up to 67% in the experiments with ~2000 µmol kg^{-1} TA additions." (lines 315-317).

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

This was changed to "In some of our experiments with at least 500 µmol kg^{-1} TA increase, secondary precipitation was detected via TA and DIC decreases, as well as PIC increases."

Line 285: "...TA additions equal to or higher than 500 µmol 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 µmol kg-1 had lower measured TA changes; please clarify

We clarified our point here and referred to the actual saturation state, ultimately governing precipitation, by changing to: "More specifically, at TA additions leading to an Ω_{Ar} higher than 7 (in the +500 and +1000 µmol kg^{-1} TA treatments), we observed "runaway $CaCO_3$ precipitation", 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." (lines 321-323).

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 clarified that we make a general point by changing to: "In a subsequent set of experiments, we simulated ocean mixing to test the required timescales to avoid and/or stop secondary $CaCO_3$ precipitation for applications that initially have TA additions above the critical threshold." (lines 324-326).

Line 290: Subsection 4.1 also addresses errors including CO2 invasion from the headspace beyond precipitation which are not indicated by the title

We changed 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 334 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 removed the reference to Equation 1.

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

We added the following reference: Zeebe and Wolf-Gladrow, 2001. (line 338).

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 reformulated as "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…" (lines 339-342).

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 CO2 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 was amended, and the following sentence was 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 allowed to overflow, corresponding to ~150 mL of seawater sampled per time-point (Dickson et al., 2007)." (lines 175-178).

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

ICPMS analysis is only picking up the elemental composition and not able to tell apart CaO from $Ca(OH)_2$. Also, EDX analysis can have problems. Hence, we are not aware of a method that would have distinguished CaO from $Ca(OH)_2$. 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 increased. 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 moved 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 352).

Line 314: repetition of results

We removed the repetition.

Line 315: "about -970 µmol kg-1" this value deviates from the -950 µmol kg-1 given in the results; please clarify which is the correct concentration

Thanks for pointing out this typo. We changed to 950:465 (line 353).

Line 317: "Although a perfect match"; an absolutism and not technically accurate; for CaO with a reported TA loss of -950 µmol kg-1 this would reflect a change in DIC loss of 475 µmol kg-1 rather than the reported 465 µmol kg-1; similarly, for the Ca(OH)2 this would be 430 µmol kg-1 rather than the reported 395 µmol kg-1; the absolute statements appear misleading

We changed to: "And indeed, measured DIC loss was very close to this 2:1 ratio in both CaO and $Ca(OH)_2$ experiments with a TA addition of 500 µmol kg^{-1} (950:465 and 860:395 for CaO and $Ca(OH)_2$, respectively)." (lines 352-354).

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 CO2 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 clarified this issue by adding this sentence before: "This suggests that TA was precipitated in the form of $CaCO_3$. The slight off-set can be explained by ingassing of CO_2 from the head space which would lower the TA:DIC ratio, becoming visible when precipitation ceases towards the end (Figure 1b). 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." (lines 354-357).

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 changed 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 365-367).

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 clarified the point by: "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. This is mostly evident in the +2000 µmol kg^{-1} TA addition (Figure 4), where DIC decreases due to $CaCO_3$ precipitation, yet TA increases due to higher $Ca(OH)_2$ dissolution rates. It also explains why estimated PIC calculated from measured TA changes are generally smaller than actually measured PIC

concentrations (Table 2). In the experiment with 1M Na_2CO_3 and quartz particles, the measured TA-based PIC estimates however, were larger than the measured PIC. This is difficult to explain, although we observed a white layer on the bottle walls, indicative of $CaCO_3$ precipitation. However, this was also observed during the other experiments with $CaCO_3$ precipitation, yet measured PIC concentrations were larger than when estimated from the TA decrease." (lines 356-364).

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 adopted the reviewer's suggestion and change to: "An important finding". (line 369).

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 as CaCO3 precipitates onto CaCO3 mineral phases at any saturation state above 1, and the initial precipitation at high saturation states provides new nucleation sites (Morse et al., 2007; Zhong and Mucci, 1989). The rate is directly proportional to Ω_{CaCO3}, decreasing exponentially until reaching zero at an Ω_{CaCO3} value of 1 (Figure A 4)." (lines 374-376).

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 added 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 $CaCO_3$ 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 clarified with: "In contrast, Lioliou et al (2007) did not report $CaCO_3$ precipitation onto quartz particles at an Ω_{Ar} lower than 3.5, and in order to trigger $CaCO_3$ precipitation onto quartz particles, Ω_{Ar} would need to be further increased." (lines 394-396).

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.

Please see comment above.

Line 355: "above an Ωar 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 changed to: "Here, we indeed observed $CaCO_3$ precipitation above an Ω_{Ar} of ~9.2 (Figure 3)." (line 396).

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 CaCO3 precipitation…"; Repetition. Early precipitation during dissolution was discussed at length in the previous subsection.

We removed this sentence.

Line 370: "When CaCO3 precipitates…" is repetition

We removed this sentence.

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

We clarified this point by: "During $CaCO_3$ precipitation, dissolved [CO_3^{2-}] and Ω_{CaCO3} are decreasing, and [CO_2] is increasing, which reduces the ocean's uptake capacity for atmospheric CO_2, hence impacting OAE potential." (lines 409-411).

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 CO2 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 CaCO3 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 CO2 sequestered per tonne of source material mined? If not, these estimates could be misleading

We clarified this point by only using the term "source material". (line 417).

Line 381-382: Please explain the source of these sequestration estimates. Caserini et al. (2021) only indicate the given annual discharge rate of Ca(OH)2 but estimate a CO2 uptake of 1.5-3.3 Gt a-1. What is the source of the 1.2-2.8 Gt a-1 CO2 given in the text? Please clarify the arrangement of the citation to indicate the correct sources of information

We clarified 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 $Ca(OH)_2$ per year (Caserini et al., 2021), between 1.2 and 2.8 Gt of CO_2 per year could be absorbed by the ocean." (lines 419-421).

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 clarified this issue by: "Including direct coastal TA discharge at a constant addition of $Ca(OH)_2$ at 10 Gt $year^{-1}$ (Feng et al., 2016), we could expect to absorb an additional 7 Gt of CO_2 per year." (lines 421-422).

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 CaCO3 precipitates as TA was added". In cases where precipitation occurred, "runaway CaCO3 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 CaCO3 precipitation" has been mentioned; please define in more detail what is meant by this term. 4) How relatable is the DIC uptake of restricted gas exchange experiments with open ocean implementations?

These are thought experiments. We clarified 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 represents a decrease by nearly 40% in OAE potential. Similarly, runaway $CaCO_3$ precipitation until an Ω_{Ar} of 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). Furthermore, secondary $CaCO_3$ precipitation higher than TA addition will lead to pH_T and Ω_{CaCO3} levels lower than initial ones. For instance, runaway 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 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 µmol 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).” (lines 428-437)

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 changed 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 (Caserini et al., 2021; Feng et al., 2017; Mongin et al., 2021).” (lines 444-446).

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

We removed “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 µmol kg-1 CaO or Ca(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 CaCO3, enhance further precipitation. When proceeding to the dilutions in 1L Schott bottles, CaCO3 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 reformulated 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." (lines 447-448).

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 Ca(OH)2 dilutions from 500 µmol kg-1 to comparing Na2CO3 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 $Ca(OH)_2$ 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 CO2 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 clarified 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.” (lines 459-461).

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

We clarified our point here by: “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, corresponding to a reduction by about 260 ppm (Feng et al., 2017). (lines 465-467).

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 clarified this by: “Finally, another option to increase atmospheric CO_2 uptake would be to not add minerals to seawater directly, but to keep the seawater equilibrated with air or CO_2 enriched flue gases, during minerals dissolution.” (lines 476-477).

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 CO_2 during mineral dissolution is a step that would need to be done on land, before pumping the water into the ocean. We also reformulated 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 occurs after instead of during the dissolution process. And secondly, when reaching an Ω_{Ar} 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 ~3 and ~6 between 30 and 5 °C).” (lines 477-481).

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 CO_2-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 changed to: “Ocean alkalinity enhancement is a negative emission technology with relatively large potential for atmospheric CO_2 removal.” (line 487).

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 also changed “safe upper limit” to “safe limit”. (line 493).

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 reformulated as: “Safely increasing the amount of TA that could be added to the ocean could be achieved by allowing for major mixing and dilution of enriched seawater by coastal tides or in the wake of ships, equilibrating the seawater to atmospheric CO_2 levels prior to the addition

during mineral dissolution, and/or targeting low rather than high temperature regions." (lines 495-498.

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 [CO_2] 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. Please see above for corrected paragraph.

Technical Corrections:

Line 16: In what way does the sentence beginning "However, …" contrast or oppose the preceding sentence?

We changed to: "However, while no $CaCO_3$ precipitation was found to occur at a saturation state (Ω_{Ar}) of about 5, $CaCO_3$ precipitated in the form of aragonite beyond a threshold of 7." (lines 17-18).

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 changed 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." (lines 21-22)

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

This comma has been removed.

Line 31: Capitalise "IPCC" in the given citation

This was corrected.

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

We removed 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 changed to: "OAE typically relies on the dissolution of alkaline minerals in seawater, releasing alkalinity similarly to natural rock weathering." (line 45).

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 put the explanation in parentheses: "The chemical reaction of CO_2 and $Ca(OH)_2$ dissolution can be written as follows, which includes the subsequent and rapid oceanic uptake of atmospheric CO_2, and ignores the non-linearities of the seawater carbonate system (i.e., changes in total alkalinity, TA, and dissolved inorganic carbon, DIC, are not 1:1):" (lines 55-57)

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 also used the verb forms as suggested.

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

We changed to: "The shift in DIC speciation leads to a decrease in [CO_2], reducing the partial pressure of CO_2 (pCO_2) in seawater and increasing its atmospheric CO_2 uptake potential." (lines 67-68).

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 has been 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 consolidated 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)." (lines 86-89).

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

Thanks for pointing this out, we added 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 addressed 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 in mg.” (lines 130-131).

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

Thanks for pointing this out, the second CAS number has been removed.

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

Here we changed to “similar”.

Line 142: There is a mixture of singular and plural in the statement beginning “Ca(OH)2 was added”; “final alkalinity enrichments” in the plural should be used

We changed to: “$Ca(OH)_2$ 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 added “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 “CaCO3 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 was separated in 2 smaller ones.

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

Thanks for pointing this out. It has been 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],” was 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 changed to: “In the experiment with 1M Na_2CO_3 and quartz particles, the measured TA-based PIC estimates however, were larger than the measured PIC.” (lines 360-361).

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

The paragraph has been rewritten.

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

We changed to: “The filtration of TA enriched seawater supports this idea since not yet dissolved mineral phases that could facilitate early nucleation are removed, preventing runaway $CaCO_3$ precipitation (Figure 3)”. (lines 399-400).

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

We reformulated as: “In our experiments, a 1:1 dilution could seemingly stop $CaCO_3$ precipitation in seawater, even if performed only after one week for the +500 µmol kg^{-1} TA addition.” (lines 446-447).

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” was 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 changed to plural as suggested.

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

We removed Italic font.

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

We changed the sentence to: “This is probably also the case for other minerals with even lower lattice compatibility for $CaCO_3$, because in coastal settings, $CaCO_3$ could precipitate onto naturally present mineral phases, such as resuspended sediments.” (lines 493-495).

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

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

Biogeosciences Discuss., community comment CC1

https://doi.org/10.5194/bg-2021-330-CC1, 2021

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Comment on bg-2021-330

Eyal Wurgaft

Community 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-CC1, 2021

Dear Mr. Moras and co-authors,

Means to counter the anthropogenic increase in atmospheric CO2 and its effects on the global climate and on the ocean chemistry, are urgently needed. The ocean, being the largest CO2 reservoir that is in direct contact with the atmosphere, has the potential to absorb the excess-CO2, and later counter it by increased weathering of carbonate and silicate rocks. The problem, is that these processes occur on time-scales of 10,000 – 100,000 years, while the threats posed by atmospheric CO2 increase are immediate. Consequently, several mechanisms for accelerating the natural processes have been suggested in the past two decades. As mentioned in the introduction to your manuscript, Ocean Alkalinity Enhancement (OAE) has been pointed as one of the more promising mechanisms. Nevertheless, there is a surprisingly small number of published studies that tested OAE and associated processes in laboratory experiments. In particular, the problem of “runaway CaCO3”, which can dramatically reduce the CO2-removal efficiency of OAE, has never (to the best of our knowledge) been properly addressed in controlled laboratory experiments. Given all that, we found your manuscript, entitled “Ocean Alkalinity Enhancement – Avoiding runaway CaCO3 precipitation during quick and hydrated lime dissolution” very important. We found the manuscript well-organized, and we enjoyed reading it.

Below, we list several questions and suggestions that came up during the reading of the manuscript. We hope that you will find them useful.

Sincerely,

Eyal Wurgaft and Noga Moran

The Open University of Israel

Comments, questions, and suggestions:

Line 52: It is somewhat unclear to what processes do you refer. We assume that you refer to the small fraction of the acidity created by the added CO2, that would be countered by proton acceptors other than CO32-. For example, borate: CO2 + B(OH)4-→B(OH)3 + HCO3-. For which, ΔTA = 0 and ΔDIC = +1. Whether we are correct or not, we believe that a more explicit description of the processes you had in mind would make this part clearer.

The chemical reaction we refer do not suggest that CO_2 is added to the system. In fact, the molecules of CaO (and $Ca(OH)_2$) reacts with the dissolve CO_2 that is already naturally present in the seawater.

Lines 65-66: since the increase in [CO32-] results from the increase in pH, we suggest rephrasing this sentence to: "Furthermore, dissolving…and raising the calcium carbonate saturation state by increasing [Ca2+].

Thank you for pointing this out. Following your comment, we decided to re-write the section to add more information and make it more understandable.

Line 106: "calculated" or "weighed" amounts?

It was meant to be "weighed" amounts.

Line 114: What is the rationale for sieving the CaO and Ca(OH)2? Why 63 µm?

Thank you for pointing this out. In preliminary experiments, we realised that CaO and $Ca(OH)_2$ particles tended to aggregate if not sieved directly above the seawater. Therefore, we used a thin mesh to avoid this. We have added this information in the revised version of the manuscript.

Lines 154-163: While the variations in DIC and TA you measured are very large, mentioning the analytical precision and accuracy of these parameters would make the methods section more complete. Were the experiments conducted in duplicate bottles? We found no mention of that.

Thank you for pointing this out. In the revised version, we mention that the TA measurements were made in duplicate, while the DIC measurements were made in triplicates.

Line 194: Morse et al., (1997) should also be cited here.

Thank you for pointing this out, we added the mentioned citation.

Line 335: Ωaragonite~2 as a lower threshold for heterogeneous precipitation was also reported by Morse et al., 2003, for the Great Bahama Banks seawater and sediment (see Fig. 5 in their paper).

We have reviewed the paper and cited it in our revised discussion section.

Line 355: We suggest re-writing to "…$CaCO_3$ precipitation on quartz particles did occur (Figure 3).", for better clarity.

We have reformulated this part of the discussion in the revised version of the manuscript.

Lines 378-384: During the production of CaO, CO_2 is produced both by the breaking of $CaCO_3$, and by the production of energy required to heat the $CaCO_3$ to 1200 °C. Do these estimations take into account this accompanied CO_2 production?

Thank you for pointing this important step of calcination. These numbers assume an efficient carbon capture during calcination. This piece of information has been added to the revised version of the manuscript.