

Reply No 2 to Comments on bg-2022-126 for the revised MS

"Stability of alkalinity in Ocean Alkalinity Enhancement (OAE) approaches – consequences for durability of CO₂ storage" by Jens Hartmann et al., Biogeosciences Discuss., <https://doi.org/10.5194/bg-2022-126-RC1>, 2022

We thank the editor and the reviewers for the comments. Please find our reply to the comments based on the revised manuscript

With best greetings, Jens Hartmann et al.

RC1: 'Comment on bg-2022-126', Olivier Sulpis, 26 Jun 2022

The manuscript presents results from a set of experiments assessing the fate of alkalinity added under various forms to natural seawater. Predicting alkalinity stability is key to quantify the potential of OAE to neutralize atmospheric CO₂. Hence, this study is particularly timely.

The particularity of this study is that it is composed of many different experiments, providing a vast quantity of results, all quite convincing, and numerous take-home messages. The authors seem to have designed their series of experiments incrementally, guided by the preliminary results obtained along the way. As a result, they went very far into the search for answers to their initial research questions, and the diversity and quality of results they produced is impressive. The discussion section nicely summarizes and explains the key findings, analyzes them in the context of preexisting literature, and offers guidance for implementing OAE techniques. This study is overall a pleasure to read, and it will certainly have broad implications. That said, the fact that numerous experiments were carried on leads to some lack of clarity in the methods. A proper statistical treatment on the collected data is also missing. Finally, the absence of analyses on the recovered precipitates is frustrating, as knowing what these precipitates are and how they form would be capital to better understand how to deal with them.

REPLY: Thank you very much for your detailed and constructive evaluation. Following your suggestions, we implemented CO₂sys_v2.5. A comprehensive description of used constants was given in L197-198, uncertainties and their resulting errors were provided in the attached data table. If feasible, uncertainties (/error bars) were added to each plot. The error bars are often so small that they are not visible due the precision of the measurement and the large range of plotted parameters. As inquired by both reviewers analyses of several precipitated materials were conducted using SEM/EDX. Information about the findings were added to the manuscript. For detailed replies, please see below.

General comments:

It is clear from the water chemistry data that carbonate minerals are precipitating. In abiotic experiment II, the authors observed immediate precipitation of centimetric needle shaped precipitates floating at the center of the bottles, suggesting spontaneous nucleation of aragonite. After 1 day, they observed precipitates on the walls of the reactors. They also observed these precipitates on the walls in experiment III. In all other cases, it seems that precipitation happened on preexisting particles, such as natural particles smaller than 55 microns, or minerals added as a TA source. In all those cases, precipitation occurred presumably without the need to nucleate in the first place, as growth on preexisting nuclei. What is precipitating exactly is unknown, but the results shown on Fig. 7 suggest that it may be a phase more soluble than aragonite.

REPLY: "Fig. 7 suggest that it may be a phase more soluble than aragonite" Yes this is correct, as the Omega for aragonite is larger 4. A discussion about ACC can be found in section 4.2.

The majority of CaCO₃ precipitates observed by Moras et al. (under review) were aragonite, and a little of vaterite. It would be enlightening to provide visuals of what the precipitates observed in the present study look like, and analyses of their mineralogy, as other similar studies have done using a combination of scanning electron microscope or energy dispersive X-Rays (Moras et al., under review; Fuhr et al., 2022). At minimum, it is needed to discuss the hypothesis of ACC precipitates in comparison with observations from the Moras et al. study.

REPLY: As suggested, SEM images of the precipitates for experiment IIa were prepared, including EDX measurements. Information will be provided.

There is a lack of proper statistical treatment. Results should be given with an associated uncertainty that should reflect uncertainties arising from (i) the experiments, from (ii) the instruments/analyses and from (iii) the computations (errors on thermodynamic constants, uncertainty propagation, etc.). (i) it seems that only experiment V was conducted in replicates, but any resulting uncertainty quantification is absent in Fig. 7. (ii) in the measurements section, no precision is provided for the instruments used, and even though it is stated that some samples were taken and measured in duplicates, the resulting uncertainties are not provided in the text or shown in figures (apart from Fig.4). (iii) the authors should use the new CO₂SYS versions recently published, available in excel (Orr et al., 2018), that allow to include and propagate all uncertainties including those from the thermodynamic constants.

REPLY: As proposed, CO₂sys_v2.5 was implemented, constants: K₁/K₂ from Lueker et al. 2000; KHSO₄ Dickson 1990; K_HF Dickson and Riley 1979, pH scale Total scale; [B]TValue Uppstrom 1974 were used. Like recommended uncertainties were calculated in CO₂sys, based on following input conditions: Uncertainties for Salinity were constantly set to 0.1 and 0.020 units for pH, both based on the provided uncertainties of the used calibration standards. Depended on the experimental measuring series the input for TA and DIC uncertainties were individually calculated by the average deviations from the measured Dickson standards for each experiment. The resulting uncertainty outputs of CO₂sys_v2.5 for each parameter (TA, DIC, pH, pCO₂, Ω(ar), Ω(cal) and Salinity) were provided in the attached data tables.

uncertainty quantification is absent in Fig. 7:

REPLY: Was provided and implemented in Fig. 7.

some samples were taken and measured in duplicates, the resulting uncertainties are not provided:

REPLY: Double measurements for experiment I+II (only abiotic) are available for TA measurements and were provided in the attached data tables. Comment: the average deviation is about +/-2.0 $\mu\text{mol/kgw}$, just two pairs of measurements reached deviations of +/- 7.5 – which is basically not plottable by using error bars. For experiment V triplicates exist and statistics will be implemented. For all other experiments there are no duplicates or multiple measurements due the nature of the conducted experiment. However, we gain robustness in the interpretation using concentration gradients in the experimental design and by the coherent results. In general, the uncertainties in TA/DIC exist, but are of minor importance and almost neglectable. Using pH probes, as the ones used here, always produces uncertainties which are quite high with around +/- 0.02 units. However, we got constantly relative robust and reproducible measurements.

Reading through the methods section was challenging, due to the large number of experiments and to the lack of details provided, see list of specific comments. In particular, the motivations for the experimental design are not well explained. It would be helpful that the paper reflects the same succession of thoughts and actions that the authors went through when designing their study.

REPLY: Methods, experimental design and introduction section were adjusted in various ways to improve clarity, please see other comments.

Specific comments:

L19: precise which minerals and that it does not apply for the deep ocean

REPLY: Changed to “Seawater close to the surface is already supersaturated with respect to calcite and aragonite ...”

L26: precise that the carbonates mentioned are carbonate *minerals*

REPLY: “... due to carbonate formation if added total alkalinity (ΔTA)...” was changed to “ ... due to carbonate mineral formation if added ...”

L28: precise what kind of slurry

REPLY: The term slurry was changed to “slurries with alkaline solids”.

L31-32: “unless alkalinity addition shifts the system beyond critical supersaturation levels”: this portion of the sentence is unclear, please rephrase

REPLY: Rephrased: “...unless alkalinity addition via solutions shifts the system beyond critical supersaturation levels.”

L45: field experiments are lacking but not laboratory studies, although more are needed, please precise that and add relevant references

REPLY: We rephrased the sentence: “This is due to the lack of laboratory and field experiments targeting OAE, while laboratory experiments focusing on seawater carbonate chemistry in general exist in large quantity, with limited implication for OAE application. Consequences of application and its techniques for optimal deployment need therefore to be determined to develop sustainable ways of OAE.”

L48: modeling studies have also focused on the OAE applied specifically in coastal environments and in oceanic regions of high CO₂ outgassing, e.g., Fakhraee et al., under review, please precise that

REPLY: The suggested reference is still a preprint and not reviewed. Therefore, we are uncertain to cite it. This is located on a server not known to us. We included the reference however in the text but delete it if there is uncertainty.

L52: here and after, please precise carbonate *minerals*

REPLY: In the first public reply letter we wrote that this will be adjusted. However, going back to literature on carbonate mineral formation in water we realized that phase is the more correct term instead of minerals, as amorphous phases form in general first, which are strictly speaking no minerals. Therefore, the modern literature uses dominantly the term carbonate phase formation. Some proportion becomes minerals, but not all. As it is unknown how much of the lost alkalinity goes into minerals and how into metastable phases which may redissolve with time (one experiment suggested that here), we prefer the term carbonate phase.

L54: adding one sentence here on nucleation itself being the greatest energy barrier to encompass before crystal growth can continue would be insightful, possibly referring to Sun et al. 2016.

REPLY: Thank you for this comment. We added one sentence citing Sun et al., 2015 (I think 2016 was a typo).

L60: please precise that the optimal conditions refer to natural, typical sea surface environments

REPLY: We changed to: "Even under optimal natural conditions for air-sea gas exchange, in a typical sea surface environment, CO₂ equilibration..."

Methods: there are a lot of experiments and variables, and the methods section describing them is sometimes hard to follow. Table 1 really helps. In addition, in the methods, it would be helpful to explain which research questions enumerated in the introduction relates to which experiment, to guide the reader and explain why all these different experiments were needed.

REPLY: The research questions raised in the introduction are now linked to the conducted experiments listed in table 1, last column.

Table 1: precisizing the type of seawater used (North Sea or Gran Canaria) in this table would be useful. In addition, please provide elsewhere eventual details on dissolved silica and phosphate concentrations for both seawaters, as well as the TA and S for the North Sea seawater.

REPLY: A new column for the type of used seawater was added to table 1. There are no available data for DSi and phosphate for the Gran Canaria seawater. Same applies for phosphate in the North Sea water. DSi for North Sea water was added in L115.

L101: please provide further details, e.g., how much of NaHCO₃ and Na₂CO₃²⁻ were added, what was the pCO₂ of the solution and of the air?

REPLY: Added amount NaHCO₃ and Na₂CO₃ for each treatment was calculated separately for each treatment (adjusted to the target TA level and the volume of water in every reactor). Detailed information were provided in the attached data tables. For the equilibrated experiments 420 ppm were set (added to L121-122).

L110: is there a reason for not using the same Dickson bottles for all experiments?

REPLY: Yes, limited resources during the field work as the experiment was developed there adhoc (not enough bottles to conduct two experiments simultaneously – biotic/abiotic at the same time) and the volume of Dickson bottles is too small for the additional sampling during the experiment for biotic measurements.

L114: please precise why should airspace be avoided in the case of Ib, since this experiment is in principle equilibrated

REPLY: To prevent gas exchange, as organisms might impact the carbonate system due ongoing life processes. We are not sure here what to precise.

L115: why not keeping the same alkalinity addition steps than for the abiotic experiments?

REPLY: In parallel other research questions were studied by the biologists during these shared biotic experiments, benefiting from smaller TA steps of 150 $\mu\text{mol/kgw}$.

L119: replace "gained" by "retrieved" or "collected"

REPLY: Replaced gained by retrieved.

L119: at this stage we have no information on what those precipitated carbonates are. What are the mineralogy, grain size, composition?

REPLY: We now studied the collected precipitates with SEM/EDX. The composition is a Ca dominated carbonate, from the shape likely aragonite. Information on size distribution and the measurements are added into the text. Results confirm the 2:1 TA:DIC loss trends.

L120: that the experiment took place in the harbor introduces temperature as a new and potentially important variable: what was the temperature and its difference between day and night, and how were the effects of temperature kept track of when interpreting the results and comparing them to experiments carried out in temperature-controlled environments?

REPLY: Experiment III tested the general concept of inducing precipitation, there was no tracking of temperature or any comparison to lab experiments. The average temperature range in the harbor area during the experiment was between 20-23°C. We added this information.

L121: how much liquid was sampled?

REPLY: In general, 150 ml each sampling day (day 0-10), 40 ml day 46 and 90. We added this information (L143+145)

L121: replace “the 10 days of processing” by “10 days of experiment,”

REPLY: Done.

L138: was only the liquid sampled or some solid with it?

REPLY: Just liquid. We added this information.

L142: how many Erlenmeyer-flasks were there and why?

REPLY: Three flasks per timestep (triplicates) plus one control flask – 12 timesteps => 48 flasks. This information was given in L167-168.

L142: it is a different type of seawater than for the previous experiments. What was the composition of that seawater? What was the temperature for those experiments?

REPLY: The composition ($T_{\text{initial}} \approx 2297 \mu\text{mol/kgw}$, $S \approx 32.9$, $\text{pH} \approx 8.05$, $\text{DSi} 16 \mu\text{mol/L}$) was added in L115 and temperature ($23 \text{ }^\circ\text{C}$ - constant lab conditions) in L166

L143: do “timesteps” here correspond to sampling times? Please clarify, and precise how much liquid was sampled each time.

REPLY: The timesteps describe the time material was in contact with water, so the duration between adding the mineral powder to the flasks and filtering it out again. Out of 300 g of seawater per flask roughly 200 ml were saved, stored and used for measurements. We added this information.

L145: please precise why the need for a shaking table and why 125 rpm.

REPLY: 120 rpm, is the maximum frequency without risk of splashing. The idea was to simulate favorable conditions for gas exchange as possible. This information was added.

L145: delete “value”

REPLY: Done.

L149: how many different solid masses were investigated? How much solid was added in each? Were the experiments conducted in triplicates?

REPLY: 15 masses + 1 control, per 300 g of seawater following masses [g] of Mg(OH)₂ were added 0, 0.001, 0.005, 0.01, 0.02, 0.03, 0.05, 0.125, 0.2, 0.500, 0.800, 1.000, 1.500, 1.750, 2.000 and 4.000 g. No triplicates, just one flask per treatment. Weights and a short overview about the experimental setup were given in the attached data table.

L152: replace “as” by “than”

REPLY: Replaced: “The same bottles (500 ml PC flasks) and experimental setup (shaking table) than in experiment V was used.”

L155: please provide more details on how airtight filtrations were done

REPLY: For experiment I, II, V and VI Nalgene filtration bottles were used (0.2 µm filter). Immediately after the end of each experiment the whole water volume was carefully purred on top the filter in the filtration vessel. For experiment III and IV a peristaltic pump and an attached 0.2 µm syringe filter was used. In general, unnecessary contact to the atmosphere of non-CO₂-equilibrated samples have been avoided as much as possible. This information was added to L181 + L182-83.

L157: were dissolved silica and phosphate not measured in the two types of natural seawater used? If not, how were their contributions to total alkalinity removed in CO₂SYs?

REPLY: DSi and phosphate were not measured during the Gran Canaria experiments. Other working groups on Gran Canaria measured Silica and phosphate in the water of the Mesocosms placed in the harbor of Taliarte, but these data are not available for us. North Sea water was measured for DSi (16 µmol/L) in another project conducted with the same batch of water. Neither DSi nor phosphate were included in the CO₂sys calculations.

L165: what scale was the pH expressed on and how was this conversion made?

REPLY: We used the seawater pH scale in CO₂SYs (information added to L198).

L183: the term “carbonate chemistry remained stable” is unclear. In fact, it seems that this last sentence does not bring anything new relative to what was said earlier in that paragraph and could be removed.

REPLY: Sentence was removed.

Fig.3 I suggest adding dashed lines in the background showing the 2:1 ratio, as a reference for the reader to assess the decline in TA:DIC ratio observed in the experiments

REPLY: We provided a grey “2:1” arrow for that purpose in Fig. 3 and 6.

Fig.3: is “added TA” similar to “ Δ TA”? If so, precise or update to Δ TA for consistency with the text and the other figures

REPLY: Following the scheme of $\Delta TA_{\text{net}} = TA_{\text{final}} - TA_{\text{initial}} = \Delta TA_{\text{added}} + \Delta TA_{\text{loss}}$ all related terms in the text and figures were adjusted

L243: were floating precipitates, as described in experiment II, also observed here?

REPLY: In comparison to experiment II (non-CO₂ equilibrated) experiment III is CO₂-equilibrated, accordingly $\Omega_{\text{aragonite}}$ values are much lower and, in this case, even below the critical threshold for precipitation. As described, precipitation was only observed at the walls after considerable time.

L246: “due to other surfaces abundant”: this portion of the sentence is unclear, please rephrase

REPLY: Rephrased: “... due to other surfaces abundant like naturally occurring particles.”

Fig.5: are the black/grey, and light blue/dark blue lines replicates? This is not indicated. If so, it would be clearer and make more sense to combine them and use the spread between them as a measure of uncertainty (which should also include and reflect the other uncertainty sources).

REPLY: No, each line represents an independent treatment. Description of Fig. 5 was adjusted to clarify: L320 (day 0 – black/grey), 1 day (red) and 4 days after (blue); abiotic treatments – black, red and dark blue graphs, biotic – grey and light blue graphs

L255: can more information on the dissolution rate of brucite be provided, e.g., approximatively how much was left after 4 days?

REPLY: No additional data are available. Further experiments might be able to answer this question.

L260: the use of “aspired” seems odd, perhaps change to “targeted”

REPLY: “aspired ΔTA_{added} ” was replaced by “target ΔTA_{added} .”

L273: what did the aggregates look like, and couldn't they be disaggregated with gently shaking the bottles?

REPLY: Aggregates looked like flakes in a snow globe (mm to cm sized) and could not be disaggregated, even with intense persistent shaking.

L299: the title of section 3.7 mentions CO₂ equilibration, but Table 1 says the opposite. If I understand correctly, there is an ambiguity here because Ca(OH)₂ dissolving induces a disequilibrium with the atmosphere which is then compensated by CO₂ uptake from the air due to the open flasks. Here and in general, it would be good to distinguish more clearly between “CO₂-equilibrated” as in preparing a solution with amounts of TA and DIC targeted to produce a certain pCO₂ that would match that of the air and “CO₂-equilibrated” as in actual exchanges between air and seawater until both are at equilibrium.

REPLY: The title was changed to “Alkalinity recovery after mineral precipitation due CO₂ equilibration with time” to avoid this confusion.

L327: please rephrase “wave line”

REPLY: Replaced by “directly below the sea surface”

L342-343: “The reason is that the carbonate system (based on W of the bulk solution) stayed within boundaries to avoid mineral precipitation” and L345-346: “The reason is that, for the same DTA, perturbations of the carbonate system that affect mineral precipitation are much stronger in this non-equilibrated scenario”: because it is a very important issue for anyone implementing OAE to understand, I believe those two sentences should be explained in more details

REPLY: Additional explanation was provided focusing on the chemical difference in applying an equilibrated and non-equilibrated approach using either precalculated ratios of HCO₃⁻ and CO₃²⁻ to form a water being in equilibrium with the atmosphere or pure alkalinity in the form of OH⁻.

L360: the threshold observed by Morse and He is for nucleation, which is more specific than spontaneous carbonate formation. It should be made clear here and in the intro that nucleation and growth are two different things with different energy barriers

REPLY: The difference is now made clearer in the text adding the suggested difference to the text.

L367: “between adding carbonate precipitates and not” this portion of the sentence is understandable but could be better phrased

REPLY: This was rephrased.

Data availability: the data should be made available at the time of submission for reviewers to be able to see it

REPLY: All generated data were plotted. A supplement xls-file was provided with the upload of the revised manuscript (Supplement_Stab_Alk_File_1_2022_11_12.xlsx)

References:

Fakhraee et al., under review, <https://doi.org/10.21203/rs.3.rs-1475007/v1>

Fuhr et al., 2022, <https://doi.org/10.3389/fclim.2022.831587>

Moras et al., under review, <https://doi.org/10.5194/bg-2021-330>

Orr et al., 2018, <https://doi.org/10.1016/j.marchem.2018.10.006>

Sun et al., 2016, <https://doi.org/10.1073/pnas.1423898112>

RC2: 'Comment on bg-2022-126', Scott C. Doney, 09 Jul 2022

RC3: 'Reply on RC2', Scott C. Doney, 10 Jul 2022

Overall this is an important study presenting a series of small-scale experiments regarding the potential for mineral precipitation during ocean alkalinity addition, with the possibility of mineral formation significantly counteracting the intended net change in total alkalinity. The authors do a good job framing the experimental results of the study in terms of the efficiency or efficacy of ocean alkalinity enhancement approaches. The study highlights a number of key nuances in terms of the amount and character of the added alkaline solutions or alkaline solid phases. I did not identify any significant conceptual issues with the study or with the main data analysis approaches and results presentations. The 6 sets of experiments involve a wide range of conditions, source waters, materials added, time durations, and underlying scientific questions. Interpreting these different experiments, therefore, requires some effort, and most of my comments below involve possible clarifications to the text that may help improve the readability of the study.

REPLY: Thank you very much for your supportive comments, which help to improve comprehensibility a lot. Especially the misleading use of "Delta TA" will be adjusted. As inquired by both reviewers' analyses of several precipitated materials were conducted using SEM/EDX. For detailed replies, please see below.

Abstract

Line 25-27:

"The application of CO₂-equilibrated alkaline solution bears the lowest risk of losing alkalinity due to carbonate formation if added total alkalinity (Delta TA) is less than 2,400 micromol/kgw. The addition of reactive alkaline solids can cause a net loss of alkalinity if Delta TA > 600 μmol/kgw (e.g., for Mg(OH)₂)."

If I am interpreting the text correctly, the notation "Delta TA" is used in three different, and somewhat confusing, ways:

- 1) initial amount of total alkalinity added to the seawater solution prior to mineral precipitation (e.g., Delta TA₁₂₀₀, etc.
- 2) net change in total alkalinity reflecting both the amount of alkalinity added as well as the loss of alkalinity due to mineral precipitation (e.g., Delta TA in Figure 8).
- 3) loss of alkalinity due to mineral precipitation following alkalinity addition (e.g., Figure 4)

The addition of an equation along the following lines may be useful:

net TA change = TA_{final} - (TA_{initial} + TA_{added} + TA_{loss})

[RC3: 'Reply on RC2', Scott C. Doney, 10 Jul 2022] rephrased:

Delta_{net} TA = TA_{final} - TA_{initial} = Delta_{add} TA + Delta_{loss} TA

It would be very helpful to avoid multiple usages for Delta TA and be more specific about the quantity being presented.

REPLY: Thank you for this suggestion. We added the indices and definitions accordingly to:

$$\Delta TA_{\text{net}} = TA_{\text{final}} - TA_{\text{initial}} = \Delta TA_{\text{added}} + \Delta TA_{\text{loss}}$$

ΔTA_{net} : net change of TA

TA_{final} : absolute reached TA after TA addition (measured)

TA_{initial} : initial TA of used seawater (measured)

ΔTA_{added} : amount of increased TA by alkalinity addition

ΔTA_{loss} : amount of TA decline during the experiment (negative sign)

Also, as a general comment it would be helpful to clearly state at each use of the term what is meant by "loss of alkalinity". In some extreme cases in the experiments "loss" refers to a "net loss" relative to the natural background concentration. In other situations, "loss" appears to refer loss of alkalinity relative to the expected increase in alkalinity following the addition of alkaline solutions or solids.

REPLY: This was rephrased as described above and we were careful replacing the new abbreviations in an understandable way.

Line 43

"(NAS,2021)" (also Line 655 in references)

Please update the citation and reference to "NASEM, 2022" for the final report:

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

REPLY: This was updated.

Line 49:

"negative TA could be a consequence"

I think this should read: "negative net change in TA could be a consequence"

REPLY: This was adjusted.

Line 70:

The authors present a well-formulated set of research questions. Very helpful.

REPLY: Thank you.

Lines 74 to 85 and Table 1:

The study used quite a number of different experiments with different conditions for filtering, material added, storage, etc. The list of the six main experiments in the text and in Table 1 provide a reasonable description, but the details perhaps could be amplified. In particular, a better link early in the Methods section to how the experiments address the science questions at the end of Section 1 (Line ~70) would be helpful. This is done well for filtering in Line 88-93 but could be done for other conditions within the experiment introduction section.

REPLY: The research questions raised in the introduction are now linked to the conducted experiments listed in table 1, last column in brackets. Thank you for this comment.

Line 96

For CO2SYS, a brief description should be added of any choices made in equilibrium coefficients, carbonate saturation coefficients, etc.

REPLY: A description of all used equilibrium constants was added in L197-198. (as also requested by [RC1: 'Comment on bg-2022-126', Olivier Sulpis, 26 Jun 2022]) version 2.5 has been implemented, including uncertainties for each constant

Line 99-109

It may be beneficial for readers who are not seawater carbonate chemists to add a sentence or two on the difference chemically between "equilibrated" (Ia) and "non-equilibrated" (IIa) experiments using NaHCO₃/Na₂CO₃ versus NaOH. While perhaps obvious to chemists, the distinction may not be immediately obvious to the full range of potential readers or why the added alkaline solution is clearly equilibrated with the atmosphere CO₂.

REPLY: For clarification the concept of "equilibrated" and "non-equilibrated" was extended in the introduction before the equation with alkalinity abbreviations.

Line 134

From the text, it appears that the particle experiments incorporated mixing only for 5 minutes at the beginning of the experiment. Some comment is needed on the affect of no mixing over several days in the tubes for particle dissolution kinetics and particle boundary layer dynamics relative to what would happen to particles added to the real ocean. I am not sure the kinetics are actually that comparable to ship disposal as mentioned in line 139 where most schemes assume a turbulent dispersion component during discharge plus natural background turbulence in the water column.

REPLY: We added a comment four lines later: "The mixing at the beginning should simulate turbulence during application, assuming further low to no turbulence. Given the further still water a scenario is simulated, which lowers the particle boundary layer dynamics. This can be seen as a baseline scenario, where more turbulence might cause higher dissolution rates."

Line 141

"This experiment focused on redissolution of alkalinity"

Perhaps consider an alternate phrasing:

"This experiment focused on addition of alkalinity due to the redissolution of alkaline precipitates"

REPLY: We changed the sentence to: "This experiment focused on the addition of alkalinity due redissolution of instable alkaline phases formed after $\text{Ca}(\text{OH})_2$ application causing an initial net loss of TA."

Line 148-149:

"The experiment was set up to check if potential threshold values for TA loss/gain after 24 hours exist in case larger amounts of solids are dissolved than in the previous experiments, resulting in the loss of TA."

Perhaps add clarification "for net TA loss/gain with the combined effects of alkaline material addition plus mineral precipitation ..."

REPLY: We added the recommended text.

Line 154:

Are the particles captured on the filters for each experiment analyzed for the amount and character of the material? In particular, was anything done to analyze precipitates?

REPLY: Filters exist for experiment IIa (day 0, 1 and 4) and experiment V. SEM-images have been taken now (including EDX-analyses). The description was added to L199.

Line 169:

which coefficients are used for carbonate saturation state?

REPLY: A description of all constants was added in L197-198

Line 172-175:

Perhaps worth noting that the notation Delta TA_2400 (or Delta TA_1200) is only approximate as the the actual increases are not exactly 2400 or 1200 but are close, for example 2400 is actually 4750 - 2411 = 2339.

REPLY: Delta TA 2400 is a label to characterize the target change. The simplification of choosing the target TA level is supposed to make treatments of different experiments comparable. We added for clarification: "Achieved additions vary slightly from the targeted additions."

Line 178-179:

"Neither in the abiotic (0.2 micrometer filtered) nor in the biotic (55 micrometer filtered) treatment, including living planktonic organisms, a detectable loss in TA could be observed after 1 and 4 days."

Perhaps reorganize this sentence as:

"No decidable loss in TA was observed after 1 and 4 days following the initial TA addition at time 0 for either the abiotic (0.2 micrometer filtered) or in the biotic (55 micrometer filtered) treatment, including living planktonic organisms."

Also, this sentence helps better understand some of the earlier text in the Abstract and the Methods regarding the meaning of "alkalinity loss". Perhaps a sentence or two could be added along the lines of:

"The seawater TA was monitored after the initial alkalinity addition to determine if any alkalinity was lost subsequently do to mineral precipitation processes."

REPLY: We changed the first sentence here as recommended. And the second sentence was added.

“Perhaps a sentence or two could be added along the lines of”:

Line 180

"while carbonate chemistry remained stable in all TA treatments [after the initial alkalinity addition]."

REPLY: This sentence was deleted due replicating information as suggested by reviewer 1.

From Figure 1 there does appear to be a noticeable, if relatively small, decline in pH and aragonite saturation state in the abiotic-equilibrated experiments. This should be mentioned briefly in the text.

REPLY: The small decline is now mentioned in L216-217.

Line 185, figure 1

The change in seawater carbonate system in the experimental treatments is over-determined with the measurements of 3 variables of the seawater carbonate system (pH, alkalinity, and DIC). Would be good to clarify for plots what is measured versus what is calculated from CO2SYS (only saturation state?) and if the measurement and CO2SYS calculated values are consistent.

REPLY: There was no over-determination: for Exp. Ia TA and pH, for Ib TA and DIC were used to calculate the other third parameters of the carbonate system. This was clarified in the text.

Minor point but in all of the captions it would be good to add the number and name of the experimental treatment to connect back to the notation on Table 1. So add Ia and Ib in the bolded text in the caption.

REPLY: Captions were adjusted as proposed.

Line 221-226:

"Consequently, while precipitation was absent in the abiotic and biotic set-up in the equilibrated treatment, strong alkalinity loss through precipitation occurred in the non-equilibrated experiment ... The loss ratio in TA:DIC was about 2:1 (Fig. 3b, d) in all treatments, indicating the loss of alkalinity due to the precipitation of carbonates."

This is a good line and perhaps something like this would be helpful in the Abstract.

REPLY: We added the following sentences to the abstract, also we analysed in addition the precipitates now: "Analysis of precipitates indicates formation of Ca-dominated mineral phases. However, instable carbonate phases formed can to some part redissolve, indicating that net-loss of a fraction of alkalinity must not be permanent for a given time, which has important implications for real world OAE application."

Line 250, Figure 4:

"development of alkalinity loss (Delta TA) over time"

Here is a third different usage of "Delta TA", here the "loss" due to mineral precipitation.

REPLY: The abbreviations were changed as described above.

Line 330, Figure 8

A point about notation. Here Delta TA label on y-axis of both sub-panels indicates the net change in alkalinity rather than the use of the notation Delta TA in some previous figures for TA initially added via solution or solids. Perhaps change label to "net Delta TA".

REPLY: The label was corrected.

Line 335

Section 4.1 General discussion

This is a well written summary of the many of the key results.

REPLY: Thank you very much.

Line 377-378:

"Not only particle surface processes on added solid alkaline particles are to be considered."

Perhaps rephrase as, "In addition, particle surface processes ..."

REPLY: **Rephrased.**

Line 385:

"... partly be released again. Here probably facilitated ..."

I think these should be a single sentence (second sentence may be a sentence fragment), so

"... partly be released again, here probably facilitated ..."

REPLY: **Rephrased as suggested.**

Line 408:

"... lead not to a positive TA ..."

perhaps change to

"... did not lead to a positive change in TA ..."

REPLY: **Adjusted.**

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[RC3: 'Reply on RC2', Scott C. Doney, 10 Jul 2022], included into the text above:

" I noticed an error in my post near the beginning. The base equation should be:

$\Delta_{\text{net TA}} = \text{TA}_{\text{final}} - \text{TA}_{\text{initial}} = \Delta_{\text{add TA}} + \Delta_{\text{loss TA}}$ "

See reply above. We adjusted the abbreviations and homogenized them.