

Biogeosciences Discuss., referee comment RC1
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Comment on bg-2022-126

olivier sulphis (Referee)

Referee comment on "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

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.

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. The majority of CaCO_3 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.

- 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.

- 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.

Specific comments:

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

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

L28: precise what kind of slurry

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

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

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

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

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.

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

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.

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.

L101: please provide further details, e.g., how much of NaHCO_3 and $\text{Na}_2\text{CO}_3^{2-}$ were added, what was the pCO_2 of the solution and of the air?

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

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

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

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

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

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?

L121: how much liquid was sampled?

L121: replace "the 10 days of processing" by "10 days of experiment,"

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

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

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?

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

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

L145: delete "value"

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

L152: replace "as" by "than"

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

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?

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

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.

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

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

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

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

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).

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

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

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

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.

L327: please rephrase "wave line"

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

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

L367: "between adding carbonate precipitates and not" this portion of the sentence is

understandable but could be better phrased

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

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>