

Biogeosciences Discuss., referee comment RC2
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Comment on bg-2022-126

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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-RC2>, 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.

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:

$$\text{net TA change} = \text{TA}_{\text{final}} - (\text{TA}_{\text{initial}} + \text{TA}_{\text{added}} + \text{TA}_{\text{loss}})$$

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

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.

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>

Line 49:

"negative TA could be a consequence"

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

Line 70:

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

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.

Line 96

For CO₂SY_S, a brief description should be added of any choices made in equilibrium coefficients, carbonate saturation coefficients, etc.

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.

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.

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"

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 ..."

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?

Line 169:

which coefficients are used for carbonate saturation state?

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 $4750 - 2411 = 2339$.

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."

Line 180

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

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.

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.

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.

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.

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.

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".

Line 335

Section 4.1 General discussion

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

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 ..."

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 ..."

partly be released again. Here probably facilitated

Line 408:

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

perhaps change to

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