Dear Dr. Bach:

Thank you for submitting this stimulating work to Biogeosciences. Four referees have evaluated your work and agree that a revised version will be publishable. I concur with their evaluations. Moreover, your rebuttal indicates that you will address most of the issues identified. I therefore invite you to submit a revised version.

One of the referees commented on the citation to one of Olaf Schuilings' papers that did not go from the discussion to final stage. Perhaps you could alternatively cite the below reference which covers similar material.

Schuiling, R. D., & de Boer, R. L. (2010). Coastal spreading of olivine to control atmospheric CO2 concentrations: A critical analysis of viability. Comment: Nature and laboratory models are different. International Journal of Greenhouse Gas Control, 4(5), 855-856.

With best regards,

Jack Middelburg, Associate Editor

Dear Dr. Middelburg

Thank you for your encouraging and kind words. Please find below my responses to the Reviewers' comments.

Thank you also for pointing me towards the alternative Schuiling and de Boer reference, which I included in the revised version (and replaced the previous version, which had not gone through peer-review).

I submitted both a tracked_changes and a cleaned up version of the revised manuscript.

Thank you very much for the time and effort you put into editing this manuscript and the excellent reviewers you recruited.

Kind regards,
Lennart

Reviewer #1 (Matt Eisaman)

Comment 1
Ocean Alkalinity Enhancement (OAE) is a promising approach to carbon dioxide removal (CDR) that is being investigated by many research labs and companies worldwide. To realize OAE's full potential for CDR, careful measurement, reporting, and verification (MRV) must be employed to accurately determine the net CO_2 removed. "The additionality problem of Ocean Alkalinity Enhancement" by L. Bach presents a well designed experimental study that, for the first time, quantifies an important response of the natural alkalinity cycle to OAE interventions. This work will be crucial to the accurate quantification of the net CO_2 removed as the result of a given OAE intervention. My comments are included as comments in the attached pdf.

REPLY: I thank Matt Eisaman for the kind words and his constructive review.

Comment 2:
I feel like "problem" implies that these considerations make OAE untenable, but really, you are just pointing out an important detail in properly accounting for additionality, which will certainly be a consideration in where OAE is deployed. Maybe a slightly different title like "Shifting baselines: The importance of indirect responses in assessing the additionality of OAE" or something like that..

REPLY: Thank you. I think the word "problem" does not imply OAE being untenable but rather that this is an issue that needs to be solved and addressed in a process of developing and potentially applying OAE. If we take Fig. 8 seriously, this "additionality problem" may be more than an important detail for OAE. My current thinking is, the additionality problem is possibly a substantial issue that requires more research to constrain its relevance. Therefore, I would like to keep the title as is to create awareness and hopefully inspire follow-up research.

Comment 3:
Line 10:For clarity, it should be defined as how much it increases CO2 sequestration, not "carbon" as written

REPLY: Agreed. Changed to CO2.

Comment 4:
Abstract equation: I would reword/rewrite slightly and be very clear about what each term means. For example, maybe something like "A_OAE = (C_Direct + C_Indirect) - C_baseline, where for all terms a positive value indicates sequestration of CO2 from the air and negative values indicate emission of CO2 into the air, C_Direct represents the CO2 sequestered from the air directly as a result of the pCO2 disequilibrium induced by an OAE intervention, C_Indirect represents changes in the net CO2 sequestration from the air other than that due to the pCO2 seawater disequilibrium resulting from the OAE intervention, and C_baseline represents the CO2 sequestration in the baseline counterfactual case where the OAE intervention did not occur.

REPLY: Thank you. The term "additionality" is more thoroughly introduced in the introduction section. Further distinguishing fluxes into direct and indirect ones in the C_OAE scenario may be distracting (in particular in the abstract) as it is not the direction the study is heading. Also, I think it is generally perhaps not particularly useful in the additionality context because air-sea CO2 flux that needs to happen in the C_OAE scenario is just one of several steps that need to work. So, I don't think it needs specific mentioning in the context of the paper.

Comment 5:
I like this framing of the natural and anthropogenic alkalinity cycles

REPLY: Thank you.

Comment 6:
I suggest that you point out that this is what you (originally) encapsulated into the term C_OAE (or what I include as C_Direct in my comments)

REPLY: As mentioned in response to comment 4, I see no reason why air-sea CO2 influx (one of several important steps for "additional" OAE) should be outsourced as a specific item in the additionality equation. The equation encapsulates this step implicitly already as the step is one essential component of marine CDR.

Comment 7:
Si not SI as written

REPLY: Thank you! Changed.

Comment 8:
I suggest that you replace "water is split..." with "water dissociation into H+ and OH- is catalyzed in bipolar membranes, and these ions are then separated using electrical energy and ion-selective membranes", which is more technically correct. Water "splitting" is electrolysis and is not what we are doing and requires a higher voltage.

REPLY: Excellent, thank you! Changed as suggested.

Comment 9:
See my comments in the abstract about how I suggest rewriting this equation to be more explicit and clear.

REPLY: I provided a more comprehensive introduction on the term "additionality" here but left the equation as is due to reasons outlined in my replies to comments 4 and 6.

Comment 10:
Can you call eta_CO2 in equation (9) eta_CO2^equil and eta_CO2 in equation (10) eta_CO2^exp? You use the same variable for two different expressions

REPLY: Thank you, good point. Eta_CO2 is still conceptually the same but calculated in different ways depending on the Experiment. I Specified better that eta always means the same but can be calculated differently (depending on the case) in the revised version.

Comment 10:
Colon should be division sign?

REPLY: I will change to /

Comment 11:
What about plotting eta_CO2 for experiment 2?

REPLY: eta_CO2 for Experiment 2 is plotted in Fig 8.

Comment 12:
Can you plot one of pH_T or omega along the top horizontal axis and label the data points with the other? Either on this plot or in a supplemental table, pH and Omega for each data point should be described.

REPLY: Omega/ pH cannot be plotted in a meaningful way here because the unequilibrated NaOH treatment has different Omega/pH values than in baseline (sand-only) treatment. I added initial and

final Omega/pH values alongside ΔAlkalinity values to the supplement as requested (Table S3). Furthermore, all data generated and used for this study (measured and calculated alongside all R-scripts) are available for download at zenodo.org under the doi:10.5281/zenodo.8191516.

Comment 13:
True, but you might want to point out that practically speaking, in the case of NaOH as an alkalinity source, adding NaOH that has been "pre-equilibrated" to the carbonate state before addition to the ocean will likely have been performed by contacting the NaOH with air, in which case the same amount of CO_2 is removed from the air and stored in the ocean as bicarbonate per mol of Alk generated, it's just that a significant amount of that CO_2 removal occured on land prior to dispersal in the ocean.

REPLY: I agree, in a pre-equilibrated application, the "additionality problem" may be mitigated. I added this to the new "Suggestions for practitioners" Box 1".

Comment 14:
Quickly

REPLY: Thanks, changed to "quickly".

Comment 15:
Fewer

REPLY: Thanks, changed to "fewer".

Comment 16:
It would be very helpful to explain to what environments these experiments correspond. What water depth/distance from shore corresponds to the case in your experiments? As one moves further offshore, you must transition from the case studied in your experiments to a case with no sediments? What experimental baseline measurements could be performed to baseline a site prior to an OAE deployment such that the data could be used to determine a "discount" factor for the expected DeltaAlk_Indirect? What would those measurements be? Particle concentration, particle size distribution, elemental analysis? Using these results to give a practical (even if imperfect) guide for estimating the expected decrease in the Del_DIC/Del_Alk ratio would be very valuable.

REPLY: Thanks, the case for which these experiments apply is discussed in section 4.3. The driving factors on the magnitude of the "additionality problem" are also discussed there but remain speculative until further research has been done. I agree that "suggestions for practitioners" are very useful and I added Box 1 to outline my suggestions.

Comment 17:
The magnitude of the effect cannot be explained by higher omega resulting in lower alk release from sand with no precipitation of $CaCO_3$, correct? The magnitude of the effect implied omega must have triggered $CaCO_3$ precip? At least in experiment 1. In Exp.2 under low pH conditions, does the primary effect of increased omega and pH due to OAE become reducing natural alk release from the sand?

REPLY: A couple of questions were asked here
- Yes, correct. The reduction of release of alkalinity due to NaOH/slag would have been unlikely to reduce ΔAlkalinity relative to the No-sand scenario. Secondary precipitation is one problem of OAE, but the "additionality problem" is another one (as emphasized in section 4.2.2.).
- Rather than the magnitude, it is the direction of change in comparison to the No-Sand treatment that is indicative. Secondary precipitation is likely because ΔAlkalinity is lower when sand is present than in incubations with NaOH/slag without sand.

- Yes, I think in such scenarios the "additionality problem" would be more severe than the "secondary precipitation problem", although this is only my impression and future research will need to provide more evidence to support/dismiss this.

Comment 18:
Did you do any "no sand" experiments, for example the seawater but with only NaOH and no sand? Would you see no precip of CaCO3 under conditions that would show precip with sand? If so, is most of the effect you are describing in this paper, the effect of suspended particles, i.e. nucleation sites, on runaway precipitation?

REPLY: Yes, such "No Sand" experiments were done with all alkalinity sources (see Fig. 4, first column on the left) and these indicated no (or less) secondary precipitation (I can only confirm "no" secondary precipitation for NaOH as the alkalinity at the beginning of the experiment was (after NaOH addition) very close to the alkalinity measured at the end of the experiment). Thus, in agreement with the Reviewer, nucleation sites provided by Sand made the crucial difference for CaCO3 precipitation. I adjusted the text in section 4.2.1. to clarify.

Comment 19:
There seems to be a phase transition for NaOH in eta (panel B) at about 200umol/kg DIC. Do you understand why? No such transition for slag and olivine: why not? That transition seems like it is giving you information about the natural alk release system.

REPLY: Unfortunately, I have no particularly convincing explanation for this observation. It may have to do with the onset of undersaturation (Omega becomes <1 around this turning point, see Table S3), but this does not explain why this is not observable in e.g. the slag treatment. I avoid speculations in the text as I have no plausible explanation for this.

Comment 20:
There seem to be two strong outlier data points for NaOH panel B at 0 and 150 DIC. Any idea what is going on there?

REPLY: I can only speculate here. The origin of this is in the carbonate chemistry measurements. It may just be analytical uncertainty, but it is also possible that above-average respiration was going on (e.g. via a small animal in the sand, see section 4.2.2.). I cannot find a plausible explanation but have high confidence these are outliers and not a trend that is worth discussing.

Comment 21:
For Fig. 7, same comment as earlier: Can you plot one of pH_T or omega along the top horizontal axis and label the data points with the other? Either on this plot or in a supplemental table, pH and Omega for each data point should be described.

REPLY: Thanks, added the requested data to Table S3.

Comment 22:
Explain why data points in B and C but not A and D. Because A and D are calculated quantities?

REPLY: This is because I subtracted the data fits (not the individual datapoints) from each other. This was necessary because the amount of added DIC different among treatment and baseline and thus data points differ on the x-axis.

Comment 23:
I thought "unequilibrated" was adding NaOH directly (and then it will equilibrate with atmospheric CO2 over time as it remains in the surface ocean) and equilibrated was reacting NaOH with atmospheric CO2 to the carbonate state and then adding it to the ocean? Why not plot "NaOH

unequlibrated" as the value it would have if all the added alk equilibrated with atmospheric CO2 *at that assumed atmospheric CO2 concentration*, assuming no downwelling?

REPLY: Thank you, I agree the "equilibrated/unequilibrated" scenario needed further clarification for what they stand. I added a clarification in the revised version (section 3.3). From a logical stand-point it does not make sense to calculate eta_CO2 (and thus DIC_OAE) for the unequilibrated treatment because these calculations require the assumption of subsequent air-sea CO2 equilibration. The unequilibrated scenario would then be turned into an equilibrated scenario, for which I already have a specific scenario.

Comment 24:
Is there an optimum alk addition level given that once you add alk, you prevent the release of some (smaller amount) of natural alk? But if natural alk release is relatively small compared to the OAE alk amount you can add before triggering runaway precip, is the sweet spot (optimum) the alk level that avoids runaway precip but is sufficiently larger than the natural alk release suppression that it is worth taking the efficiency "hit" of reducing the natural alk release?

REPLY: Thank you, this is one of the questions, which I think should be addressed in upcoming research. My study has not varied alkalinity additions and has therefore limited capacity to answer your question. However, my expectation is that such an optimum dosing of alkalinity would be dependent on the environment. For example, the additionality problem may be particularly severe in organic rich sediments (see section 4.3.), while lower Omega in such environments may reduce secondary precipitation.

Comment 25
Can your experiments suggest practical guidelines? For example: if the ratio of alk addition to dilution rate is less than x, then the "additionality problem" becomes negligible? This case will be especially true for any field tests and deployments over the next few years where the amount of alk released is relatively small.

REPLY: Thank you, great suggestion! I added a "Suggestions for practitioners Box 1" where these thoughts are considered. While I am not be able to provide specific advice on how much alkalinity can be considered "unproblematic", I can point towards critical considerations to be made by the practitioners (as you suggest in Comment 26).

Comment 26:
Instead of just saying "future work is needed", it would make the paper much more impactful if you were to provide a section of practical recommendations of steps that OAE/CDR should take, based on these results, to account for this phenomenon. For example, these results imply that this effect needs to be considered when: (1) choosing a site for OAE; (2) designing MRV for OAE etc. Suggesting a path forward would be appreciated by the community, I think. From reading the paper, it seems that OAE still has enormous potential to contribute to CDR goals, but that this effect must be taken into consideration, and so pointing the community in the right direction is critical, I think.

REPLY: Thank you, this is an excellent recommendation and I have added such suggestions in the revised version (see REPLY to comment 25).

Reviewer #2

Comment 1:
The manuscript by L. Bach 'The additionality problem of Ocean Alkalinity Enhancement' deals with the question of how much of the natural marine benthic alkalinity release might be reduced due to the addition of alkaline minerals as carbon dioxide removal (CDR) measure. L. Bach found in an experimental investigation, that the natural alkalinity release might be significantly reduced due to the increase in the calcium carbonate saturation state.

The findings by Bach highlight an important aspect concerning the CDR measure of ocean alkalinity enhancement (OAE), which- to the best of my knowledge- has not been discussed in such detail to date. The experiments are thoroughly conducted and serve well to answer the research question. In general, I strongly support the publication of this study, though I have some points, where I would like to see a bit more detail in the discussion.

REPLY: Thank you for your encouraging and constructive comments.

Comment 2:

My biggest concern is the extremely short mention of the effect of 'natural mineral grinding', which is one of the largest arguments at the moment for beach applications in the context of OAE. This effect is only discussed in two sentences, in lines 546-550. I wonder, how much of the observed alkalinity increase is caused by this grinding effect and the continuous provision of reactive surfaces and how much by the changes in the carbonate saturation states. It would have been nice to conduct experiments without the shaking effect of the plankton wheel to study and quantify this grinding effect caused by the constant moving in. However, I am aware that such a comment in a review is not helpful when an experimental series is completed, but it might be worth to at least mention and suggest this additional kind of experiment.

REPLY: Great comment, thank you. Ironically, this project started with the motivation to address exactly the question raised by the Reviewer here but during the study I changed directions because I think the "additionality problem" is more multi-facetted and ultimately more critical for OAE in general. A student has continued to study the abovementioned question and we will publish results as soon as possible. Most importantly, (Flipkens et al., 2023) recently published findings on this specific research question, which I reference in the revised version. Due to these reasons, I would prefer to not speculate more on the topic here. Especially, because the experiments presented here have no control treatment (i.e., without movement) and thus only very limited capacity to provide answers beyond recent findings by (Flipkens et al., 2023).

Comment 3

Secondly, I am not a big fan of introducing another technical term to a topic where a lot of abbreviations and terms are already used and confused. I wonder, is it really necessary to call the observed effect 'additionality', when the term 'net sequestration effect' describes it perfectly. Same goes for 'anthropogenic alkalinity', whereby the latter is a bit more self-explanatory. I'm happy to wait and see if this term is accepted and used by the community, though I would urge the author to reconsider if it is really necessary to introduce this new term here!

REPLY: Thank you, I agree the term "additionality" needs better introduction (also based on comments by Reviewers Adam Subhas and Matt Eisaman). Additionality is not a term introduced here but widely used in carbon accounting, with the possibly the first prominent appearance in the Clean Development Mechanism under the 1997 Kyoto Protocol (Havukainen et al., 2022; Michaelowa et al., 2019). Additionality is the necessary term in this study because based on its definition additionality is assessed based on the comparison of an implementation and a hypothetical

counterfactual (a "business-as-usual scenario"). "Net sequestration" is more ambiguous. It could mean the same as additionality but could also just be used to account for the sum of carbon fluxes in an implementation scenario.

The term "anthropogenic alkalinity" is useful because it increases readability (the clunky alternative would be "alkalinity derived from olivine/NaOH/slag") and the distinction to natural alkalinity is important in the "additionality" framework of the study. This framing was seen positively by Reviewer Matt Eisaman (see his comment 5).

Comment 4

Further I wonder, how much the precipitation of secondary carbonates affects OAE in beach environments due to the quick dilution with seawater movement. This topic is shortly discussed in lines 680ff, were it is also pointed out that the batch experiments represent an extreme case which is likely not directly transferable to the open ocean environments. Here I'm missing a discussion and comparison with the beach transect results. Two beaches (Goats and Clifton North) show no difference between the swash zone and sampling stations with increasing distance to the beach. Also interesting is the difference between Clifton North and South, is there a difference between carbonate contents or is Clifton South a more sheltered environment with less extreme seawater movement and thus a higher chance of alkalinity accumulation? These environmental factors might be good to sum up as a sort of guidance for the site choice of OAE deployments as also highlighted in the conclusions.

REPLY: Thank you, this comment (asking for more specific guidance for the choice of OAE deployments) is consistent with the key comment by Reviewer Matt Eisaman. To account for it, I added "Suggestions for practitioners" (Box 1 in the revised version). With regards to differences between beaches: Thank you, good point and this is now pointed out in the revised version that alkalinity (and silicate) deviations measured in the swash zone become indistinguishable very quickly when moving offshore. The exact reason for the differences in profiles between beach locations is unclear. I note that CaCO3 and organic content varies within meters (see table S2 for Clifton Beach) but I have no data on dilution rates, so I cannot provide an informed discussion here.

Minor points:

Comment 5

Line 84: The official mineralogical abbreviation for aragonite is 'Arg'. Please change throughout the manuscript.

REPLY: Excellent, thank you. Changed throughout.

Comment 6:

Line 99-102: I would recommend to state more clearly, that carbonate dissolution as a natural alkalinity source was likely not considered in the context of CDR yet, but it is in general a well-known natural process (e.g. Torres et al., 2020 *Earth-Science Reviews*; Wallmann et al., 2022 *Frontiers in Marine Sciences*).

REPLY: Thank you. I restructured this paragraph slightly and added the suggested references and three other ones to make absolutely clear that dissolution is a well-known natural process.

Comment 7:

Line 103: Please give an amount or range and add a reference. Same for organic matter.

REPLY: This is a difficult request due to the heterogeneity in PIC and POC content of sandy beaches. I found no global compilation but case studies which for example reported carbonate contents along the US east coast of 0.3 – 45.7% CaCO3 content (Pilkey et al., 1967). Likewise, organic matter content varies greatly within sand sediments as can be seen in papers referenced after these first two sentences (Liu et al., 2021; Perkins et al., 2022; Reckhardt et al., 2015). As such, I am nervous about giving a range here as it will not be widely applicable. I changed the sentence structure to not give a quantitative estimate (changed "sandy beaches are often…" to "sandy beaches can be…").

Comment 8:

Line 131-134: I would suggest to start with the aim and then continue with the sampling details. Further I would recommend to move figure S1 to the main text, as it gives a nice impression of the setting. If possible, it might be good to indicate a transect in figureS1 C as an example of the sampling locations from the beach to off-shore in order to give this picture a bit more content.

REPLY: Agreed. I restructured this paragraph as suggested. Figure S1 was moved to the main text and is now Fig. 1. A transect was added to the photograph.

Comment 9:

Line 164: Grams as a unit for seawater? Further, 'S' for salinity was not introduced as abbreviation.

REPLY: Yes, this was measured in grams. I changed S to salinity, thanks for spotting this.

Comment 10:

Line 262ff: There are several places of small grammar/spelling issues, for example line262: alkalinity needs a capital 'A'; line 283: 'a values'; citation styles; line 338: 'we', not 'I'?; line 499: 'carbonate sources'. Please check carefully throughout the manuscript.

REPLY: Thanks for spotting these. I corrected accordingly. With regards to the "we": this meant to include the reader (the reader and I assume this together as we go through this thought experiment). I think "we" is ok here.

Comment 11:

Line 281: Strictly speaking, silicate is a solid, in solution it's silicic acid.

REPLY: Good point. I defined "dissolved silicate" as $Si(OH)_4$ in the revised version.

Figure 7: in panel B, there is a large difference between the first and further data points for the sand only experiments. Is this correct or a calculation error? Any explanation for this difference?

REPLY: Good questions. η_{CO2} was calculated based on ΔAlkalinity and ΔDIC, where ΔDIC was derived from alkalinity and pH measurements. In the treatments with lower DIC addition, very little dissolution occurred and so that Δ-values were very small and sometimes within the measurement uncertainty. As such, this is most likely a "noise" issue and not real. I added a remark to the caption.

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Reviewer #3

Comment 1

Ln 26: isnt it more useful to introduce alkalinity in are where low alkalinity is released until now?

REPLY: Yes absolutely, this is what the sentence aimed to suggest. Thank you, I can see that it the sentence could have been misread and clarified accordingly.

Comment 2

Ln 69: the acid can also be used to acidify seawater and convert DIC to CO2 which is captured for storage.

REPLY: This is correct. However, the process you are referring to here is called "direct ocean capture", which differs from OAE in that alkalinity remains stable (the acid is neutralized with base after purging the CO2) and the CO2 extracted from seawater is sequestered elsewhere, e.g. in geological reservoirs. Therefore, I did not refer to this process here.

Comment 3
Ln 107: At first CO2 is released into the surface water and reacts with acid-base system. Release into atmosphere is to my understanding rather minor except for the escape in gaseous forms (e.g. from oversaturation or vents)

REPLY: I agree with your statement, but part of the CO2 may ultimately be released into the atmosphere. This is what the referenced studies have shown, and I think the sentence correctly cites these studies. Nevertheless, to acknowledge that not necessarily all CO2 released that way is sequestered changed this to "can sequester".

Comment 4
Ln 133: I respect you paddle skills, but sampling surface water for sedimentary alkalinity fluxes is subject to variety of errors (residence time of the water, submarine groundwater discharge etc.), hence benthic flux chamber would have been a good accomplishment for better comparison of the different systems.

REPLY: Thank you :-D . I agree with you, benthic flux chambers are a necessary next step. We are planning to get them to provide better insights on the additionality problem. For this study, however, I had no such tools at hand.

Comment 5

Ln 110-112: OAE is supposed to happen in the water column or sediment surface, whereas microbial respiration is mainly performed in the sediments. As soon as Alkalinity is lost to pore water and irrigation is not able to flush these sediments over saturation is occurring, with OAE source material or not. I think you should be more precise on how OAE is implemented and where natural processes and OAE application is supposed to react.

REPLY: I am a bit unclear about what the Reviewer means here. Wouldn't reduced flushing of sediments lead to less flushing of respired CO2 and thus, lower saturation state? In general, OAE is implementable in a huge variety of pathways. These have been summarized by (Eisaman et al., 2023).

It is highly likely that anthropogenic alkalinity would interact with hotspots of alkalinity cycling (e.g. pore waters or marine aggregates). For example, looking at current tests by Ebb Carbon or Planetary Technologies, anthropogenic alkalinity is released in shallow environments or even partially dissolving on/within sediments. Likewise, Project Vesta found that olivine is integrating into sand and not necessarily remaining on top of sediments. As there are so many possible pathways, I cannot account for all of them here but only refer to (Eisaman et al., 2023) who have done a great job in summarizing them.

Comment 6

Ln 206: What about the anthropogenic CO2 that is sequesterd by natural TA emissions to the coastal waters such as in North Sea?

REPLY: Line 206 describes results from the dissolution assays under different pH levels. Assuming you refer to line 106: Yes, the described feedback also works for neutralization of anthropogenic CO2. This applies for the North Sea as for other areas as well. To be more general here, I removed "respiratory" and added the reference by (Archer et al., 1998) describing anthropogenic CO2 neutralization due to carbonate sediment dissolution.

Comment 7

Ln115: Would over saturation at first place be beneficial for the ocean to buffer ocean acidification and further CaCO3 producers under the circumstances of ocean acidification and haven an impact on the biological carbon pump? Shouldn't this be integrated into OAE research and efficiency discussion?

REPLY: Yes, these biogeochemical feedbacks are already quite widely considered, see for example (Bach et al., 2019) and (Gately et al., 2023).

Comment 8

Ln 262: Alkalinity

REPLY: Thanks for spotting, changed.

Comment 9

Ln: 283 a value, or value...

REPLY: thanks for spotting, changed to "a value".

Comment 10

285 experiments when slag was incubated: not 100 % clear to me how you have assumed these values, consider some measured values/data for supplementary section

REPLY: Based on a related study with the same olivine and steel slag material that is currently under review in Biogeosciences. I will add the reference (the review for this paper is relatively far advanced so should be available soon). https://egusphere.copernicus.org/preprints/2023/egusphere-2023-2120/

Comment 11

Ln: 430: How does this Experiment design help to understand the increase in Alkalinity under low-high DIC conditions?

REPLY: I am a bit unclear what the Reviewer means here. The increasing DIC reduces the saturation states and leads to higher alkalinity release, but I am sure the Reviewer knows this. The gradient from low to high DIC was set up to test for interactions between anthropogenic and natural alkalinity release along the gradient. This has been outlined at the beginning of section 3.3.

Comment 12

Ln 432: Can you also add pH_T plots to it. I assume that sudden DIC increase will lower the pH and causes acidification where as A_T production and neutralization will react on different speeds (e.g. olivine lowest)

REPLY: I cannot add such plots as I have only measured pH at the beginning and end of the incubation period. Such dynamics are therefore not resolvable in this study, unfortunately.

Comment 13

Ln 527: Could you prove that? This is an important aspect for "Leakage" in OAE and in your system precipitation could be investigated/monitored under controlled conditions (SEM or Ca concentrations). As for slag and olivine it wont make sense, since nuklides can be formed as well but did you test the nuclide hypothesis in your experiments by having NaOH + seawater only? Therefore interactions between alkalinity and dissolved ions can be investigated.

REPLY: I have no further measurements to prove this conclusion. The conclusion is based on the observation that Δalkalinity was significantly higher when no sand was present for the NaOH treatment (see Fig 4A). I acknowledge that the evidence for this conclusion is limited, but I don't find it overly speculative as this exact process has been shown multiple times and could arguably be considered "OAE mainstream knowledge" (as evidence by the multiple references provided to support this conclusion). Nevertheless, I toned this down and provided some additional context to better explain this conclusion.

Comment 14

Ln 547: Or movements of the sediment caused abrasion of smaller particles and edges, which might have dissolved a faster than more resistant material that remained afterwards. There is a new paper coming by Gunter et al 2023 (accepted for publication)

REPLY: Yes exactly that, thanks for pointing towards (Flipkens et al., 2023) which I added as an excellent reference for this.

Comment 15

Ln 596: *Hangx, Suzanne J. T., and Christopher J. Spiers. 2009. "Coastal Spreading of Olivine to Control Atmospheric CO2 Concentrations: A Critical Analysis of Viability." International Journal of Greenhouse Gas Control 3 (6): 757–67.*

REPLY: Thank you, added the reference here.

Comment 16

Ln 699: In your Conclusion and Outlook you could give some recommendations of how we can tackle the additionality problem. Do we either look for areas in which low alkalinity turn-over is present and try to make them more productive or do we increase productivity of high productive system. What is the benefit of this paper to the discussion and where do you want it to guide us?

REPLY: Thank you for this excellent suggestion, which is consistent with the major feedback by Reviewer Matt Eisaman. I added a Box with suggestions how to possibly deal with the additionality problem.

References

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Reviewer #4 (Adam Subhas)

Comment 1:

This review is for the manuscript submitted to Biogeosciences entitles "The additionality problem of Ocean Alkalinity Enhancement" by L.T. Bach. The manuscript describes incubation experiments conducted using beach sand collected from Tasmania, spiked with three different alkalinity sources. It then goes on to describe the results from these experiments in the context of the concept of additionality in CDR.

The manuscript as written provides much food for thought for scientists working on OAE, and how anthropogenic alkalinity will interact with natural alkalinity (and ultimately carbon) cycling. However, there are several places where more care could be taken in the framing of the problem, the description of the experiments, and the discussion of results. My largest question to the author is in the definition of "baseline" and whether ocean acidification (OA) and its modification of the ocean's carbonate system should be included. Sedimentary $CaCO_3$ dissolution will play a large role in neutralizing fossil fuel CO_2 over the next ~10,000 years, with several indications that OA-induced dissolution is already occurring. Should this current scenario really be our baseline if it is already changing the natural alkalinity cycle? Does preventing OA-induced dissolution "count" in the author's baseline framework? Or, do we reference the OAE "baseline" to a preindustrial state? These are larger questions that I am not sure can be answered with this manuscript and may need a much lengthier discussion, with a potentially completely new way to think about additionality for OAE.

REPLY: I thank Dr. Subhas for the thorough and constructive review and for the kind words.

- The Reviewer's largest question is for: "the definition of "baseline" and whether ocean acidification (OA) and its modification of the ocean's carbonate system should be included." The definition of the baseline is part of the definition of additionality, which has been elaborated by UNFCCC, for example within the Kyoto Protocol as part of the Clean Development Mechanism: Any mitigation activity that is considered for a market-based mechanism to demonstrate that the corresponding [CDR] would not have happened in the absence of the support from the market-based mechanism (Michaelowa et al., 2019). In other words, the baseline accounts for all natural/anthropogenic processes except for the one considered for implementation (here OAE). As such, this and the follow-up questions raised by the reviewer below have already been answered as part of defining additionality as a climate policy concept and accounting framework.

Reviewer: "Should this current scenario really be our baseline if it is already changing the natural alkalinity cycle?"

REPLY: The baseline includes ocean acidification as the baseline is the "business-as-usual scenario" that considers all but the climate mitigation option under consideration (here OAE). This is implicit in the definition of additionality as used by UNFCCC.

Reviewer: "Does preventing OA-induced dissolution "count" in the author's baseline framework?"

REPLY: OA is part of the baseline scenario and as such preventing OA-induced dissolution via OAE reduces OAE efficiency. As such, OAE may compete with "natural" CO2 neutralization, an issue I called "chronic" additionality problem in the revised version (see REPLY to Comment 72)

Reviewer: "Or, do we reference the OAE "baseline" to a preindustrial state?"

REPLY: No, the baseline is by definition the "business-as-usual" scenario in the absence of the mitigation tool (here OAE).

Reviewer: "These are larger questions that I am not sure can be answered with this manuscript and may need a much lengthier discussion, with a potentially completely new way to think about additionality for OAE."

REPLY: The definition of additionality is well established under UNFCCC and I don't think the mCDR or OAE community needs to re-invent the wheel, but rather utilize this established concept. In my opinion additionality is THE most relevant metric to asses any CDR deployment.

To account for the reviewer's comment, I added a more thorough introduction of additionality as a concept (and accounting framework) of climate policy in the introduction.

Comment 2:

In terms of the framing, a more precise description of additionality would be helpful to the reader, and the chemical equations presented could reflect this reference frame. In terms of the experiments, more detail could be given in several places (see specific comments below). In terms of the discussion, issues of kinetics and thermodynamics are at times conflated, with implications for how these experiments directly inform OAE deployments and/or carbon accounting. Please see the detailed comments below, and I hope these comments help to clarify and improve the manuscript on this important and emerging topic.

REPLY: A more thorough introduction of additionality was added to the revised version. With regards to the other points raised here please see my replies to specific comments.

Comment 3:

11-12: Is there also a climatic benefit in preventing ocean acidification (OA)-induced sedimentary CaCO3 dissolution?

REPLY: If climatic benefit means a generation of alkalinity (and thus more capacity to store seawater CO2) then there should be no such benefit by preventing neutralization of anthropogenic CO2 by CaCO3 sediment dissolution.

Comment 4

14-17: I am not sure I understand this equation as written. Shouldn't the left hand side be in units of carbon (moles) or DIC concentration? Is C(OAE) in units of carbon, if so, why is it referred to as alkalinity enhancement (units of alkalinity?) What is dC(baseline), and why is it a delta here? Why is it subtracted from C(OAE)? I worry that this description of additionality is too stripped down to be useful for the community at this stage, and raises the question of who the audience is for this manuscript.

REPLY: Good point, as written now alkalinity and C sequestration are not clearly distinguished. I changed this sentence to: "So far, feasibility studies on OAE have mainly focussed on enhancing alkalinity in the oceans to stimulate CO_2 sequestration (C_{OAE}) but not primarily how such anthropogenic alkalinity would modify the natural alkalinity cycle and associated baseline CO_2 sequestration ($\Delta C_{baseline}$)".

Comment 5

47: On its face, I am not clear on how Eq. 2 describes the uptake of atmospheric CO2 into seawater and the resulting increase in DIC.

REPLY: Eq. 2 is just to introduce DIC, but I agree that this is a bit unclear from the current sentence structure. I changed to: "This transfer (retention) of atmospheric CO_2 into the ocean leads to an increase of the dissolved inorganic carbon (DIC) concentration in seawater, with DIC defined as:"

Comment 6

53: Perhaps "accomplished" instead of "generated"?

REPLY: Thank you, changed to accomplished.

Comment 7

55-73: I found this section confusing because it conflates OAE and CDR in a single equation, whereas I think the point of the manuscript is to separate these two out and analyze the interaction of OAE with the natural alkalinity cycle, and the net effect on CDR. Could the author think about a way to write these alkalinity generating "half-reactions" and include the CDR component separately?

REPLY: Thanks, I deleted these equations as they are not picked up later and thus not really needed here.

Comment 8

75: As written, Eq. (3) produces DIC and Alk in a 1:1 ratio, which will actually increase seawater pCO2 (most of the surface ocean has TA:DIC>1). By definition, this reaction can also not proceed if Omega > 1, so it cannot increase saturation states to drive excess precipitation.

REPLY: Equation was deleted.

Comment 9

84-85: The author should be careful when describing thermodynamic propensities to precipitate/dissolve in relation to kinetic effects. It is well-established that most of the surface ocean is supersaturated and does not precipitate CaCO3 spontaneously (with maybe a few exceptions…). This is brought up later in the context of previous OAE work, and could be considered and fleshed out here in the introduction.

REPLY: I changed the sentence to account for the Reviewer's comment: Aragonite (Arg) and Calcite (Cal) precipitation is thermodynamically favoured when Ω_{Arg} and Ω_{Cal} are ≥ 1, although significant rates of precipitation generally only occur at $\Omega \gg 1$ (Adkins et al., 2020).

Comment 10

93: Kinetic thresholds play a role here, too, not just thermodynamics.

REPLY: Agreed. This aspect, while not specifically mentioned, is covered in the references cited here but I also added (Adkins et al., 2020) for further reading on the topic. Importantly, while kinetics are largely driven by Ω especially in the open ocean, rates can also be high when sufficient particle surface is available as is stressed in the (Zhong & Mucci, 1989) reference. So, for the context of the paper, I avoid stressing too much that rates of precipitation are often only detectable above certain Ω thresholds as this would be overly restrictive to an open ocean context.

Comment 11

100-101: As a rule, I try to avoid statements of primacy. This is new work, and everyone will recognize it as such!

REPLY: Deleted.

Comment 12

108-111: Replacing CaCO3 dissolution with OAE through e.g. reactions 4-6 will not have a 1:1 impact on CDR. This is raised later on in the discussion, but could be introduced here to tee the reader up for this insight.

REPLY: Thanks, equations were deleted not referred to anymore. That way any indication for quantitative implications of the effect is avoided as this is indeed a key outcome of the study. Thus, the key information needed at this point is provided with the relevant explanations provided in the discussion with sufficient detail.

Comment 13

117: I am not sure that simplicity is warranted given the complexity of this topic. As stated above, this definition of additionality could use some more detail here, and be consistently applied throughout the text.

REPLY: Thank you, I added more background on additionality and its established definition. With regards to "consistency": I assume the Reviewer means the use of the concept to describe the additionality in alkalinity and the additionality in DIC increase (more broadly CO2 sequestration). This distinction was made to develop some of the key messages of the

dataset, for example that the "additionality of alkalinity increase" is not proportional to the "additionality of potential DIC uptake" (e.g. Fig. 8) as it depends on the alkalinity source. This distinction was articulated when necessary in the text, so I think the concept is used consistently.

Comment 14

122: Mixed "three" and "3" in one sentence

REPLY: Thanks, adjusted.

Comment 15

131: What is the swash zone? It is used multiple times but never defined.

REPLY: The swash zone is the zone where wave bores run up the beach. I added this definition upon first use of swash zone.

Comment 16

133: "The goal of these transects…"

REPLY: Sentence was deleted.

Comment 17

152: Terminology for the alkaline feedstocks could be tightened up throughout the text. At times these are referred to as "weathering minerals", "alkaline minerals", "alkaline rocks or alkaline industrial products"…

REPLY: Thank you, good point. I cleaned this up and now mostly speak about "alkaline materials" (since NaOH is not a mineral), unless a clear distinction is needed.

Comment 18

159: Based on my calculations, this amount of NaOH should increase alkalinity by ~428 umol/kg. The targeted alkalinity enhancement would be useful to state here as a reference for later figures and results.

REPLY: Yes, and the measured increase was 434.6 µmol/kg. I added the target in brackets in the revised version.

Comment 19

182: Are these HDPE bottles stable for DIC over the experiment duration? Polyethylene bottles typically have quite a high permeability to CO_2 regardless of their density. This is especially relevant for interpreting the DIC enrichment experiments and the pH trends for all experiments.

REPLY: Thank you, to understand if there is no issue, I did a small test where I incubated CO_2-enriched seawater in the same HDPE bottles for 14 days (N=3) at 15°C. The pH was initially 6.93 in the beaker where I enriched the seawater. The seawater was then poured into HDPE bottles (I did not measure pH and after handling it, unfortunately). After 14 days, pH was 7.02, 7.014, and 7.03. Hence there was a ~0.09 pH increase over 14 days (twice as long as the experiment lasted), which may be due to handling (see above) and permeation. I admit that not measuring after the handling was a silly mistake but I think the test is good enough to clarify that permeability does not explain the results observed here (noting that the test was twice as long, testing the most pronounced pCO_2 gradient, and that pCO_2 gradients are quickly reduced in the actual experiments due to buffering by $CaCO_3$)

Comment 20

191: How was this CO_2-saturated water stored, and how was the DIC/CO_2 saturation monitored?

REPLY: The CO_2-enriched water was not stored and it was just enriched, not necessarily CO_2-saturated (please note that I wrote "enriched" in the text). Basically, I took a small amount of seawater and bubbled it with CO_2. Then, small increments of this enriched water were immediately added to the main seawater batch used to fill incubation bottles and pH was recorded simultaneously.

Comment 21

196-197: "Filled with an increasing CO_2 concentration" is unclear to me. What I think happened is that sequentially more volume of CO_2-saturated seawater was mixed with natural seawater to create an array of DIC enrichment. However I don't quite get that from this description.

REPLY: You understood this correctly :-) . I tried to improve the description in the revised version.

Comment 22

215: Too many sig figs for the reported pH uncertainty of 0.015?

REPLY: Thanks, adjusted.

238: So, the grain size for the olivine and slag was 150-250 um?

Comment 23

240: What temperature did you dry the grains at?

REPLY: 60 degrees Celsius. Information added to the text.

Comment 24

255: How was the pH determination modified for beach samples in the field?

REPLY: All measurements (lab and field) were done the same way with a pH probe as described here.

Comment 25

262: "Total alkalinity was determined…" What size of sample did you measure?

REPLY: Approximately 60g per sample. I added this information.

Comment 26

297: I am confident that this calculation goes back much further, no? To maybe a Humphries paper, or even earlier to other papers describing buffer factors? As described in this study, no component of mixing, advection, or isolation from the atmosphere is considered, which means that the calculation is not exactly analogous to the approach of Tyka et al., 2022.

REPLY: (Humphreys et al., 2018) defined the isocapnic quotient (Q) as $\Delta TA/\Delta DIC$, so basically eta as defined in (Tyka et al., 2022) is $1/Q$. (I could not find an equivalent to it in earlier studies, based on the summary of buffer factors in (Middelburg et al., 2020). Since eta is buffer concept specifically defined for OAE, I think it is ok to cite Tyka et al here, although $1/Q$ is probably a concept that deserves to be developed specifically (e.g. by implementation in carbonate chemistry software).

Comment 27

313-314: I am not clear on this calculation. Can't the buffer factor be calculated explicitly as an instantaneous change, using the latest CO2SYS packages?

REPLY: They do not calculate eta, although PyCO2sys and maybe CO2SYS can calculate Q (and thus it would be simple to calculate $1/Q$ manually; see previous comment). I used seacarb for R (Gattuso et al., 2021) which currently does not include the relevant calculations. However, I reached out to Jean-Pierre Gattuso to create awareness for this and am pretty confident these calculations will be implemented in the future. I will leave this calculation in the paper as this is how I did it in the end.

Comment 28

322: I'm not sure I follow how eq. 10 is arrived at from eq. 9. Could you explain the individual terms, and how they relate to the terms in eq. 9?

REPLY: Thank you for pointing this out. There was confusion because η_{CO_2} as calculated in equation 6 (formerly 9) is not calculated in the same way as η_{CO_2} in equation 7 (formerly 10). I therefore tried to better denote for what cases η_{CO_2} is calculated in what way.

Comment 29

329: Based on the discussion of these experiments, it does not appear that you can rule out CaCo3 precipitation in the olivine experiments, just that physical abrasion may have increased the dissolution rate of the olivine. Can you justify this assumption in another way?

REPLY: I cannot rule out CaCO3 precipitation but it would have reduced ΔAlkalinity, and hence I find it a stretch to speculate about CaCO3 precipitation when the trend indicates the opposite. It would have been precipitation with some other alkalinity enhancing (maybe abrasion) overcompensating for it. Or it would have to be precipitation in the control without sand, counteracting alkalinity release from olivine. But this is highly speculative and I don't see how such speculation would improve the text. The conclusion I consider most likely is that sand-induced abrasion explains slightly higher ΔAlkalinity in the sand+olivine treatment (relative to olivine only). This conclusion is supported by recent findings (published after this study was submitted) by (Flipkens et al., 2023) and I updated the text in the discussion accordingly.

Comment 30

330: Based on Table S2, these sands are only partially CaCO3. Couldn't some other phase be dissolving to produce alkalinity, in which case some of the alkalinity change would be Alk(non-carbonate)?

REPLY: Yes in theory I cannot fully exclude that but since the ΔAlkalinity:ΔDIC release ratio was close to 2:1 mol:mol when alkalinity was generated it seems very likely that this is predominantly a Alk_carbonate source. I justified my assumption accordingly in the revised version.

Comment 31

332-334: I think this is a restatement of lines 330-331, for expt. 2. The DIC calculations (based on, I assume, TA and pH data) in these experiments is not presented in the main text or the supplemental, and could be useful as a figure to bolster this claim, especially given the low CaCO3 content of these sands.

REPLY: Thank you, I clarified in the revised version that the assumption for η_{CO2} in Experiment 1 being 0.36 in the sand only treatment based on the 2:1 ΔAlkalinity:ΔDIC release ratio observed in Experiment 2 where there was substantial dissolution occurring to be more reliably detectable with the methods used here (note that DIC was calculated from pH/alkalinity). As such, I linked this assumption better to the observation made in Experiment 2. I also added ΔAlkalinity and ΔDIC data to a new Table S3 in the supplement.

Comment 32

341: I am not sure what operation the colon in this equation is performing.

REPLY: changed to /

Comment 33

343: and then delta-Alk(non-carbonate) makes up the difference? So, d(TA) = d(TA_carbonate) + d(TA_non-carbonate)? This would be helpful to state explicitly.

REPLY: This is correct. I explicitly state that in the revised version as requested by the Reviewer.

Comment 34

349: I'm not following this equation, or how it results from the previous equations 9-11.

REPLY: Equation 9 (formerly 12) does not build upon the previous equations. When η_{CO_2} is $\Delta DIC/\Delta TA$, then ΔDIC can be calculated as in this equation simply by solving for ΔDIC. I added the mathematical definition of η_{CO_2} to make this more obvious.

Comment 35

358-360: Tenses changed from passive to active. Check for consistency throughout.

REPLY: Thanks, adjusted.

Comment 36

366-369: What is the purpose of fitting the data with quadratics? Is there a specific functional relationship that is described by a quadratic? It's unclear how these fits are used, if at all, in the results and discussion, making it difficult to understand the choice of the function and its use in the interpretation. Perhaps the raw data could be used to evaluate trends, instead?

REPLY: This is an empirical equation that fitted the data well (There is no mechanistic underpinning for the equation). I changed the text to improve clarity. Using raw data to subtract baseline (sand-only) from the various treatments (NaOH, slag, olivine) is not possible because the amounts of DIC added differed across scenarios.

Comment 37

375: Is there a figure/table limit for biogeosciences? With only 2 additional tables and some consolidation of the supplemental figures, the author could consider eliminating the supplemental entirely, making for a smoother reading experience.

REPLY: Good point, thank you. Biogeosciences adds the appendix at the bottom of the main manuscript pdf file so that, luckily, this will not be an issue.

Comment 38

375-381: Could some of these alkalinity variations be explained by salinity-normalizing the data?

REPLY: Yes, possibly but I did not measure salinity in every sample and did not trust the salinity data of the beach transects as I did not make measurements in a temperature-controlled room and temperature instability caused large fluctuations in the field. In the end I used a value of 35 for all beach transects, but note that this has no relevance for the data presented here.

Comment 39

407: How does the change in alkalinity match up with the amount of NaOH you added? How about comparing to the amounts of olivine/slag and their stoichiometries, are you close to the maximum? Or, how much alkalinity yield was there over the 6.8 day period?

REPLY: The measured increase of alkalinity due to NaOH additions (434.6 µmol/kg) was close to the planned addition of ~428 µmol/kg. For slag and olivine it is unclear what fraction of the alkalinity potential (i.e. alkalinity in theoretically in the solid phase) was released. While I agree that this is in principle an interesting question, it is not of relevance for the present study and its conclusions so that I will not discuss it here.

Comment 40

418-420: this claim could be confirmed by assessing the d(pH) data and CO2SYS calculations, assuming no CO2 gain/loss through the HDPE bottles.

REPLY: This sentence has been deleted.

Comment 41

439: Isn't the increase quadratic, as described by your model, not exponential? What is the role of the quadratic model in fitting this data?

REPLY: This is an empirical fit that was chosen as the equation is reasonably simple but fits the data well. There is no mechanistic underpinning to this equation at this point (see also reply to comment 36).

Comment 42

449: "The d(Alkalinity) increase in the unequilibrated treatment weakened along…"

REPLY: Thank you, added this.

Comment 43

461: How was the x-axis on this plot generated? I assume through measurements of TA and pH in the experimental bottles at time-zero of the experiment? It would help to clarify this point in the Methods section, and potentially here in the caption as well.

REPLY: Thank you, carbonate chemistry calculations are based on measured alkalinity and pH, which is described in the methods (section 2.5). Yes, I plotted against initial DIC and good point to mention this in the caption. I added this information here and also repeat that DIC was calculated from alkalinity and pH.

Comment 44

470: The manipulation of the carbonate chemistry in this fashion implies that the dependency could also be driven by pCO2, or total DIC, not necessarily pH.

REPLY: Good point, changed to "carbonate chemistry dependency" and also added: "but note that pH was used for plotting the data but other carbonate chemistry parameters could also be the driver of the response".

Comment 45

471: How does fig. 4 demonstrate this two-way ANOVA result?

REPLY: Thank you, this is mentioned in the caption and I added "($p<0.05$)"

Comment 46

473-475: The second number in the range is the final pH in each experiment? I inferred this from the previous sentence, but would be good to state explicitly.

REPLY: Thank you, changed.

Comment 47

494-505: As discussed above, the other issue with carbonates is that they can only add alkalinity if the initial solution is undersaturated with respect to the mineral. This requires either respiration, or offline mixing of carbonates and a CO_2 source.

REPLY: Yes, I fully agree. Seawater has to be sufficiently corrosive for carbonate dissolution to occur at a relevant rate. This prerequisite for carbonate-based OAE is neither questioned here nor in the papers referenced here, which discuss the use of carbonates for OAE and the need for undersaturation. (Please also note that one of the paper referenced here discusses the use of ikaite for OAE, for which seawater would generally be corrosive).

Comment 48

519: Eq. 8 describes a change in the baseline, but nothing explicitly about the baseline state of the counterfactual. This is another example where some nuance in this framework would be useful further up front in the manuscript.

REPLY: See REPLY to Comment 1.

Comment 49

526-527: in the absence of CO_2 gain/loss through the HDPE bottles, this hypothesis could be verified with your d(pH) measurements.

REPLY: Yes good point, checking if Δalkalinity/ΔDIC molar ratio is 2:1 is a possible test for this hypothesis in the case for the NaOH experiment. However, this is not an option for the slag experiment because alkalinity is generated over the course of the study and not instantaneously available (necessary to calculate Δalkalinity) as in the case of NaOH. I tried this calculation and it yields 2:1 molar ratios in a few bottles but then is quite off in many others (ratio ranging between -5 to 18). This is likely because ΔDIC is generally associated with quite some error due to it being calculated from two pH and alkalinity measurements and ΔDIC values too low (i.e. unfavourable signal-to-noise ratio). Thus, I am afraid, I cannot

confirm this statement with this approach and it will have to remain a hypothesis, although a very plausible one.

Comment 50

528-529: This statement is unclear. Are you referring to particles other than the slag itself? If so, where did these particles come from?

REPLY: This sentence has been deleted.

Comment 51

536-537: Could you also include the T and S conditions of these experiments? Or perhaps the saturation state, to be consistent with the following discussion?

REPLY: Thank you, added their Omega_Arg value

Comment 52

537: "This suggests…"

REPLY: Thanks, corrected.

Comment 53

540-542: Was the measured decrease in pH large enough to drive undersaturation for, e.g., aragonite? In general, this raises the question of how biological activity was controlled or monitored in these experiments.

REPLY: Thank you, I added Omega values for clarification. Biology and geochemistry were only monitored via alkalinity and pH measurements, as described in the methods. Occasionally, biological activity was an important factor, for example in the sand flea bottle as explained in section 4.2.2.

Comment 54

548-550: In my opinion, it is not appropriate to cite work that has not made it through peer review. I defer to the editor on this point.

REPLY: I think Schuiling and de Boer's text deserves recognition as it induced significant research and basically the entire Project Vesta is based on this hypothesis. The original text (and revised version) is fairly clear that they provide a hypothesis but no proof for it. In the revised version I added that (Flipkens et al., 2023) have recently confirmed their hypothesis.

Comment 55

551-562: These experiments mix kinetic effects (dissolution rates) with thermodynamic drivers of CaCO3 precipitation. The dissolution rates of slag and olivine are different,

whereas NaOH is essentially instantaneously added. These factors are important to consider when interpreting these results, as well as the effects of temperature, grain size, mixing/advection/diffusion in sediments…all of these complicate a purely thermodynamic interpretation of the results as is done in this paragraph.

REPLY: I am not quite with the reviewer here. This paragraph merely argues that secondary precipitation would likely have progressed in the relevant treatments if the experiments had been longer than 6.8 days. It then explores to which degree secondary precipitation would have progressed based on findings by (Moras et al., 2022). Two independent studies have shown the instability of alkalinity when Omega is beyond a certain threshold for long enough time, resulting in runaway precipitation until precipitation declines at a lower Omega_Arg (here ~2) (Hartmann et al., 2023; Moras et al., 2022). The interpretation provided here builds on these results.

Comment 56

557-558: Could the author provide a plot? Would it look similar to Fig. 6?

REPLY: This was a back-of-the-envelope calculation. I clarified in the revised version.

Comment 57

569-570: Could the increase in alkalinity also be due to the respiration of organic carbon and production of nitrate from fixed nitrogen, or the production of organic alkalinity? The sand does appear to have measurable POC. You could check the stoichiometry of dDIC:dTA and compare to, e.g., the stoichiometry for respiration of representative organic matter (i.e. C:N of 106:16).

REPLY: I can generally not exclude that alkalinity is also produced/consumed by other pathways than carbonate dissolution/precipitation. However, the pH was substantially lower in only the one replicate where a relatively big arthropod (~5 mm) was present and alive during the experiment. As such, it makes sense to emphasize the most plausible explanation rather than discussing alternative pathways that seem much more unlikely. On a more general note, biological activity and redox processes may have occurred in the incubations and they may have modified the net production/consumption of alkalinity. However, there is abundant evidence that the major driver of change is dissolution/precipitation of carbonates. Thus, I don't think adding more speculation about other pathways makes the paper better, but rather just more complicated and harder to read with limited gain. We are already doing follow-up research where we will dive deeper.

Comment 58

582: Why just lines in 7A, but points in 7B? Could you not just show the data points instead of the fits?

REPLY: This is because the data points on the X-axis can differ for treatment and baseline.

Comment 59

590: subscript "non-carbonate"

REPLY: Good spotting, thank you!

Comment 60

593: The author could bring up the units (mol:mol) earlier in the manuscript when this term is introduced, and leave them off later on.

REPLY: Good point, thank you. Adjusted.

Comment 61

599: Do you mean high enough, not low enough? If, not, then this statement is confusing to me and could use some clarification.

REPLY: Thank you, yes you are right: "high enough" is correct. Changed accordingly.

Comment 62

605: Where does the respiratory CO2 come from? I'm not sure this sentence is necessary, or this effect could be described in a different way.

REPLY: Thank you, the DIC I added was meant to simulate respiratory CO2 that is abundant in beach sediments. But I can see why this sentence was confusing and therefore changed it for better clarity.

Comment 63

608: The DIC_OAE calculation could use a reference to the appropriate equation as well as the figure.

REPLY: Thank you, I added a reference to the equation.

Comment 64

613: As defined, additionality is only about carbon and not explicitly about alkalinity at all. Thus, DIC_OAE is THE important parameter!

REPLY: I agree, and emphasize this in lines 683. For developing the paper it is nevertheless critical to apply the conceptual framework of "additionality" also to alkalinity itself because it allows me to carve out how different sources of alkalinity have different impacts in its CDR efficiency. Furthermore, even sophisticated MRV schemes currently use alkalinity (not DIC_OAE) as the first parameter against which the success of the OAE deployment is measured (see for example, https://www.planetarytech.com/science/planetarys-oae/planetarys-mrv/; but note that the available protocol by Planetary does also consider air-sea CO2 influx).

Comment 65

615-617: So, there is no additionality issue for slag or NaOH? But maybe one for olivine, although the expt. 1 results suggest a complicated story with respect to olivine dissolution, abrasion, and protection…?

REPLY: There is still a potential additionality problem for NaOH and slag but at least in this experimental setup, additionality (of DIC_OAE) does not change along the gradient of DIC concentrations investigated here. In the real-world, one would very likely not be able to determine whether the DIC that is measured as DIC_OAE came from dissolving sediment CaCO3 or from atmospheric CO2. As such the "additionality problem" in this case is that the DIC_OAE may be indirectly accounted for as a result of an OAE deployment.

Comment 66

620-623: This is an important point, and one that I believe people have made before, if not in the literature. I am glad it's being made here.

REPLY: Thanks.

Comment 67

626: Calculating DIC of the unequilibrated treatment using TA and pH data could help to assess ingassing/outgassing of CO2 through the HDPE bottles over the course of the experiment.

REPLY: See REPLY to Comment 19 with regards to the permeability of the bottles.

Comment 68

643: Are your mixing conditions on the plankton wheel comparable to the mixing conditions of a high energy wave impact zone?

REPLY: I changed to "…inspired by conditions observed in a high energy wave impact zone."

Comment 69

647-648: not to mention the open ocean?

REPLY: The open ocean case is addressed in more detail in the next paragraph.

Comment 70

657: "were predicted to protect…" I am not sure this paper includes observations that directly verify the proposed hypothesis via the modeling results.

REPLY: The study by (Sulpis et al., 2022) made a convincing case that one buffer system (dissolving Aragonite) protects another carbonate (Calcite) from dissolving. This is very similar to the observations made here that one anthropogenic "buffer systems" can protect natural alkalinity dissolution. I find drawing the analogy to (Sulpis et al., 2022) very plausible

and do not see a reason to exclude their paper as analogous evidence for the observations made here.

Comment 71

675-679: Organic alkalinity and sulfur (and other redox element) cycling complicates this as well.

REPLY: Thank you and agreed. Now mention other redox processes and organic alkalinity here.

Comment 72

683-684: These experiments take a snapshot along a kinetic curve, and how these dissolution/preicpitation kinetics play out in time will also be important to assess and verify.

REPLY: Yes, I agree. Many questions do remain and acknowledge the limitations of my study. My hope is that the study will stimulate follow-up research, as emphasized in the text. In particular, there are many interesting aspects with regards to time-dependency. One thought that I found worth adding (thanks for stimulating this via your comment!) is pointing out the difference between an "acute" and a "chronic" additionality problem. I added the following text: "Another interesting aspect to consider is the time and scale-dependency of the additionality problem. A detectable slow-down of natural alkalinity formation may occur in the environment where anthropogenic alkalinity was added (as observed in the experiments presented here). Such an "acute" additionality problem may be comparatively easy to associate with the responsible OAE deployment and there may be straight-forward ways to mitigate it. (see section 4.4 and Box 1). However, the problem could turn from "acute" to "chronic" over much longer timescales should OAE be up-scaled to climate-relevance and cause a significant increase of Ω throughout the ocean. In the chronic scenario, anthropogenic alkalinity may partially replace the "natural" alkalinity release enforced by fossil fuel CO_2 neutralization via carbonate dissolution (Archer et al., 1998). A chronic additionality problem would unlikely be attributable to individual OAE deployments and suggested mitigation measures described in section 4.4. and Box 1 would not work. Indeed, similar chronic problems for CDR imposed by Earth system feedbacks have already been described, for example the possible weakening of natural terrestrial and marine CO_2 sinks due to CDR implementation (Keller et al., 2018). However, assessing whether the hypothesis of a chronic additionality problem is valid remains to be seen and will require more targeted follow-up research."

696: But, as shown for equilibrated NaOH and slag, if that alkalinity release does not affect the total C uptake via OAE, then it doesn't matter, correct?

REPLY: See REPLY to Comment 65.

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