

Response to Anonymous Reviewer #1 Comments on “Assessing technical aspects of ocean alkalinity enhancement approaches”

We thank the referee for their careful review of the manuscript and for their constructive comments. All comments are addressed point by point below.

1. **Reviewer Comment:** “The authors should indicate that ocean-CDR/OAE has the potential to compensate for CO₂ degassing associated with large-scale removal of CO₂ from the atmosphere. This makes oceanCDR one of the only pathways that delivers CO₂ removal with no CO₂ release consequences ensuring that it is one of the most (the most?) resource efficient means for large scale CDR.”

Response: Excellent point. The following text has now been added at lines 967-968 in the Conclusions section: “OAE’s unique potential among CDR approaches to compensate for CO₂ degassing from the ocean resulting from large-scale atmospheric CO₂ removal makes it an especially valuable approach worthy of continued pursuit.”

2. **Reviewer Comment:** “The figure number needs to be corrected: “The two primary electrochemical processes used to generate alkalinity from brine are electrolysis (O'Brien, Bommaraju, and Hine, 2005, pp.31-34) and electrodialysis (Strathmann, 2011, pp.163-167), as shown in Fig. 3.3.” ***Figure 3”

Response: Thank you, this has been corrected to read: “The two primary electrochemical processes used to generate alkalinity from brine are electrolysis (O'Brien, Bommaraju, and Hine, 2005, pp.31-34) and electrodialysis (Strathmann, 2011, pp.163-167), as shown in Fig. 3.”

3. **Reviewer Comment:** “Regarding Figure 3: It is not always necessary to have pretreatment, and to segregate the brine into divalent-rich, and -poor streams. The process flow could be shown more generally, and it could be indicated that many possible configurations exist.”

Response: Good point, thank you for catching this. The figure has been revised to show pretreatment and divalent separation as optional and the following text has been added to the caption of Fig. 3: “Both pretreatment and the separation of brine into divalent rich and divalent lean streams is optional and is not performed in all processes.”

4. **Reviewer Comment:** “The authors may wish to consider the following two publications which are relevant to one particular approach for ocean-based CDR, but which contain commentary of relevance to many ocean-based CDR approaches:
 - a. <https://pubs.acs.org/doi/full/10.1021/acssuschemeng.0c08561>
 - b. <https://pubs.acs.org/doi/full/10.1021/acsestengg.3c00004>

Response: La Plante et al, 2021 was already cited in the original manuscript. Thank you for pointing us to the recent La Plante et al., 2023 paper. Both are now cited. An additional sentence was added (lines 253 – 255) that reads: “A third version of this approach relies primarily on the precipitation of $\text{Mg}(\text{OH})_2$, in addition to the precipitation of some CaCO_3 , and prevents release of CO_2 in the process of CaCO_3 precipitation by generating alkalinity at a sufficiently high rate to keep the pH at a constant target value (La Plante et al. 2021; La Plante et al., 2023).”

5. **Reviewer Comment:** “The authors are correct in that CO_2 is released in a static seawater system wherein CaCO_3 's precipitation is induced. However, when CaCO_3 precipitates under conditions of constant alkalinity generation (i.e., in the presence of a constant pH pump as proposed via the La Plante et al. process), as noted in the second reference above – no CO_2 is released. Furthermore, the process of La Plante et al. is not based only on CaCO_3 precipitation. Rather, CaCO_3 precipitation is the secondary contributor to CDR, the primary contributor being $\text{Mg}(\text{OH})_2$ derived alkalinity. As such, the second sentence is inaccurate and should be corrected for content, and for its indication regarding efficiency which is not assessed herein. “In a second version of this approach, the $\text{NaOH}(\text{aq})$ is added to seawater to remove CO_2 as $\text{CaCO}_3(\text{s})$, with additional $\text{NaOH}(\text{aq})$ then added to restore this lost alkalinity and draw CO_2 from the air to replace the removed CO_2 (de Lannoy et al. 2018; Eisaman et al. 2018; La Plante et al. 2021). The precipitation of $\text{CaCO}_3(\text{s})$ releases CO_2 , making this second version relatively inefficient from a CO_2 -removal perspective, but may be pursued if other considerations such as ease of verification outweigh this inefficiency.””

Response: Thanks for this clarification. The existing sentence was kept as is, but the La Plante et al, 2021 reference was removed from that sentence. An additional sentence was added (lines 253 – 255) after the sentence in question that reads: “A third version of this approach relies primarily on the precipitation of $\text{Mg}(\text{OH})_2$, in addition to the precipitation of some CaCO_3 , and prevents release of CO_2 in the process of CaCO_3 precipitation by generating alkalinity at a sufficiently high rate to keep the pH at a constant target value (La Plante et al. 2021; La Plante et al., 2023).”

6. **Reviewer Comment:** “Line 259: reactions at anode and cathode are interchanged. H_2 is produced at the cathode and Cl_2/O_2 at the anode”

Response: Thanks for catching this error. It has been corrected.

7. **Reviewer Comment:** “Line 263: LaPlante (2023) discusses the approach described here to neutralize the acidic efflux of an electrolyzer using the acid-neutralization capacity of different solutes. It would be appropriate to cite this work.”

Response: Agreed, thanks. La Plante et al., 2023 is now cited at line 277 as: “Such acids (including the hydrochloric acid described in the previous section) can be reacted with alkaline minerals to produce more neutral metal salts and water (La Plante et al., 2023).”

- Reviewer Comment:** “It is worth mentioning that the development of efficient and durable oxygen selective electrodes would be an important direction to make seawater electrolysis more feasible – Page 2 because otherwise the large-scale production and handling of gaseous chlorine (in addition to acid) could make standard electrolysis processes difficult to scale.”

Response: Agreed. A sentence was added at line 165 that reads: “The development of efficient and durable oxygen selective electrodes is critical to making seawater electrolysis more feasible (La Plante et al., 2023).”

- Reviewer Comment:** “Many figure numbers are written as 3.x. These should be updated/corrected.”

Response: Thank you. All figure references have been corrected.

Response to Prof. Justin Ries Comments on “Assessing technical aspects of ocean alkalinity enhancement approaches”

We thank the referee for their careful review of the manuscript and for their constructive comments. All comments are addressed point by point below.

- Reviewer Comment:** “Although highly informative, the manuscript is quite long and, at times, somewhat redundant. For example, the issue of trace element release is brought up in numerous sections, sometimes providing little additional information relative to the prior section. One way to shorten the length of the manuscript and increase its concision would be to combine all the sections on trace element release into a single section at the end (or the beginning), and then reference that section for the various sections addressing different methods of OAE. The same could be done with ecological impacts.”

Response: Thank you for the comment. Trace metals are considered in four sections electrochemical approaches, AWL, pelagic and benthic addition. While there is some similarity in these various descriptions, the causes and implications of metal release from these approaches varies and it would not be appropriate to combine them into a generic section, and may not shorten the text significantly. Ecological impacts also vary for each of these approaches.

- Reviewer Comment:** “would also encourage the authors to take this opportunity to clarify the matter around reprecipitation of carbonates following net alkalinity addition reducing the efficiency of OAE...”

Response: Thank you, this is addressed in comments 14 and 15 below.

3. **Reviewer Comment:** Line 22: 'and' instead of 'or'

Response: Changed as suggested.

4. **Reviewer Comment:** "63: 'pCO₂'

Response: Added partial pressure of CO₂

5. **Reviewer Comment:** 65: this would work with oxides (e.g., CaO, MgO), as well, no?

Response: Notionally, alkaline materials added and example hydrated lime now included.

6. **Reviewer Comment:** "Line 259: reactions at anode and cathode are interchanged. H₂ is produced at the cathode and Cl₂/O₂ at the anode"

Response: Thanks for catching this error. It has been corrected.

7. **Reviewer Comment:** "The statement that 'For these approaches to be meaningful for CDR, the concentrated CO₂ used in the process must come from the atmosphere' is too stringent... The concept of marine CDR should be expanded from 'direct removal of CO₂ from the atmosphere' to include the 'transfer of CO₂ in the atmosphere and/or seawater into stable carbonate or bicarbonate ions in seawater', as both processes (i.e., removal of CO₂ from atmosphere and/or seawater) will result in the eventual drawdown of CO₂ from the atmosphere once equilibrium wrt pCO₂ is re-established between these coupled systems.."

Response: Good point, 'or the surface ocean' added

8. **Reviewer Comment:** "Likewise, CO₂ removal from the atmosphere alone is not sufficient for CDR, as increasing the pCO₂ of the atmosphere through increased CO₂ emissions also drives the flux of CO₂ from the atmosphere to the ocean, but surely this should not constitute marine CDR. Perhaps a more useful framing for CDR is the transfer of C from shorter residence time reservoirs (atmospheric CO₂, seawater CO₂, terrestrial biomass, marine biomass in mixed layer etc.) to longer residence time reservoirs (bicarbonate ion reservoir, carbonate ion reservoir, terrestrial and marine biomass transported to deep ocean and/or into marine sediments below mixed layer, etc.) (c.f., Prentice, I. C., 2001,

Response: There is a range of framing to consider CDR, each with its own limitations. The removal of CO₂ from the quick bio cycle to the geo cycle, while reasonable for what we are suggesting here, would exclude approaches that increase stocks of biomass.

9. **Reviewer Comment:** 70: It seems that the authors should more explicitly address the fact that calcination of CaCO₃ to produce Ca(OH)₂ releases CO₂, which offsets more

than half of the CO₂ sequestration potential associated with using the produced Ca(OH)₂ for OAE. They mention storing or reusing the CO₂, but at Gt scale this would probably not be practical. It should also be highlighted that Mg(OH)₂ is unique in this regard bc, unlike Ca(OH)₂, it is naturally occurring and can be mined, and thus does not require calcination in its production.

Response: We address this later in the chapter when we consider ocean liming, and it would be better to explain in detail later than include too many clauses in the summary statements here. Mg-hydroxide, while naturally occurring, does not exist abundantly in pure deposits and would need to be 'extracted/purified' from host rock.

10. **Reviewer Comment:** 101: delete 'which'

Response: replaced "which" with "that"

11. **Reviewer Comment:** 115: But the technologies shown between TRL 4 and 7 in the accompanying figure are being explored by both researchers and companies, so, although the general TRL discussion is informative, not sure how relevant the 'valley of death' discussion is here.

Response: Indeed, this is being explored by researchers and companies, yet it remains a risk for developing OAE approaches. The valley of death concept refers to the gap between research and translation and applies to TRL level, whether that research is being pursued in academia or industry.

12. **Reviewer Comment:** 131: Consider removing the informal reference to research being conducted at H-W University: Finally, the production and application of hydrated carbonate minerals such as ikaite has a TRL of 1, currently under investigation at the bench-scale at Heriot-Watt university examining aspects such as air stability and seawater dissolution kinetics.' If a citable reference exists for this research, then the reference can be included and discussed. Otherwise, its more of an informal communication that is probably not suited for the present contribution.

Response: Agreed. Text removed, and reference is now included.

13. **Reviewer Comment:** 236: Since alkalinity is defined as the sum of all proton-neutralizing ions minus the sum of protons in a solution, it could also be argued that removing HCl (and thus protons) from seawater via 'direct ocean capture' is indeed a form of ocean alkalinity enhancement because it is removing CO₂ from the atmosphere by enhancing (increasing) the alkalinity of seawater.

Response: Direct ocean capture, while it might use acids and bases to facilitate the removal of CO₂ gas, does not result in a net change of alkalinity. For example, direct ocean capture that strips CO₂ as a gas from seawater first generates equal parts H⁺ and OH⁻ from the water in seawater, resulting in no net alkalinity change. The acid is then added to seawater to shift all DIC to the form of dissolved CO₂ gas, reducing alkalinity. Because the equilibrium partial pressure of 2.4 mmol DIC converted to CO₂ gas is approximately 0.08 atm (i.e., less than 1 atm), this CO₂ must be vacuum stripped from seawater. The alkalinity is now restored to the acidified and decarbonized seawater by adding the OH⁻ generated in the first step. This simply return the alkalinity to the starting point. The restored alkalinity results in the absorption an equal amount of CO₂ from the air into the seawater, restoring the CO₂ that was stripped from solution. In this way, direct ocean capture results in no net increase in alkalinity, but uses acid and base to cycle alkalinity in a way that uses the ocean to “pump” CO₂ from the air.

14. **Reviewer Comment:** 244: ‘The precipitation of CaCO₃(s) releases CO₂’; this is a bit misleading as presently written. If the precipitation of CaCO₃ is caused by the net addition of alkalinity to a solution (such as in applied OAE using metal hydroxides, or the like), it will not result in the net release of CO₂. This is because the H⁺ generated from the calcification process are effectively neutralized by the added alkalinity. CO₂ is only released on a net basis by CaCO₃ precipitation when the CaCO₃ precipitation is driven by an elevation in the pH and saturation state in the absence of a net increase in alkalinity, such as that driven by CO₂ drawdown via photosynthesis. The idea that CaCO₃ precipitation following net alkalinity addition is a net emitter of CO₂ is a widely misunderstood aspect of the seawater carbonate chemistry system that I would suggest clarifying here because it is is creating confusion in the field of OAE and applied CDR

CaCO₃ precipitation without net alkalinity addition: $\text{Ca}^{2+} + \text{HCO}_3^- \rightarrow \text{CaCO}_3 + \text{H}^+$ (net acid and thus net CO₂ release)

[and]

15. **Reviewer Comment:** That said, precipitating CaCO₃ after OAE does reduce the efficiency of CDR via OAE because it only removes 1 mole of CO₂ for every 2 moles of alkalinity (CaCO₃ contains 1 mole DIC per 2 moles alkalinity), while conventional OAE is believed to remove approximately 1.4 to 1.6 moles CO₂ for every 2 moles of alkalinity. So the efficiency of OAE decreases by about 1/3 if the CO₂ and alkalinity reprecipitate out as CaCO₃, rather than staying balanced in a dissolved state.

Response: Agreed, we have tightened the language to state that carbonate precipitation reduces alkalinity resulting in a lower efficiency of removal or CO₂ release in the case of OAE. The new text reads: “The precipitation of CaCO_{3(s)} reduces alkalinity (resulting in either in lower efficiency of CO₂ removal per unit of added alkalinity in the case of OAE, or a release of CO₂ in cases where the precipitation occurs in the absence of an alkalinity addition)...” We appreciate the wider comment regarding the precipitation of CaCO₃ and the impact on the carbonate system in seawater. However, this chapter considers the

technical aspects of OAE and there are chapters dedicated to describing the implications of OAE on carbonate geochemistry (see Schulz et al.,).

16. **Reviewer Comment:** 338: should there be an 'and' between 'calcium' and 'bicarbonate'?
Response: Agreed, we have changed this as suggested.

17. **Reviewer Comment:** 438: consider elaborating on the 'flue gas' that is mentioned—is this the source of the CO₂ that is being sequestered and used to drive the dissolution of the limestone?
Response: Added 'This study explored the dissolution of limestone in seawater driven by high CO₂ from a point source of emissions rather than concentrated from the atmosphere, which may not have the same impurities.'

18. **Reviewer Comment:** 560-566: this is very useful information wrt liming via Ca(OH)₂ addition. Since several workers are also investigating OAE via Mg(OH)₂ addition, is it possible to report similar recommendations for Mg(OH)₂, which has the benefit of being a naturally occurring metal hydroxide that therefore, unlike Ca(OH)₂, does not require calcination (assuming the Mg(OH)₂ is mined, not calcined from MgCO₃)?
Response: Pure Mg(OH)₂ deposits are not sufficiently abundant that they can be mined and used for OL. It is found in reasonable concentrations (5-10%) in ultrabasic rock, but its extraction and purification from this for OAE has not been explored.

19. **Reviewer Comment:** 625: I would recommend including aragonite, high-Mg calcite, and even dolomite in Table 1 (only pure calcite is presently included) because these forms of CaCO₃ are globally abundant, some have existing mining industries built around them (dolomite), and are generally more soluble than pure calcite and, thus, potentially advantageous for OAE, ALW, etc
Response: The intention of including calcite in table 1 is for comparison of Gibbs free energies to hydrated phases, not for its specific use for OAE. There would be no additional benefit in including additional anhydrous phases.

20. **Reviewer Comment:** 685: consider clarifying 'upper water column' (thus in contact with the atmosphere to allow for equilibration wrt pCO₂)
Response: The "upper water column" refers to the mixed layer depth, which is influenced by atmospheric processes and therefore allows for equilibration with CO₂. We clarified this in the text.

21. **Reviewer Comment:** 692: and dolostone (or dolomite)
Response: We added this to the sentence.

22. **Reviewer Comment:** 702: again, reprecipitation of CaCO₃ after non-carbonate alkalinity addition (e.g., Mg(OH)₂) does not completely negate the CO₂ sequestration associated with the net alkalinity addition, it only reduces its efficiency by about 1/3 (see line 244 above).

Response: We agree and have added a clarification to the text.

23. **Reviewer Comment:** 858: the risk of secondary precipitation of carbonates in benthic environments outside of the tropics is relatively low; most deep-sea benthic environments are of course relatively undersaturated wrt CaCO₃, and even shallow shelf sediments experience net CaCO₃ dissolution in temperate latitudes and higher due to undersaturation at the sediment-water interface, in part owing to respiration of CO₂ from organic matter.

Response: We agree that organic matter degradation and the related drop in pH is a process causing carbonate dissolution and is contrary to the carbonate precipitation risk, discussed in this section. However, in coastal benthic environments microbial reactions can also induce carbonate precipitation by e.g. alkalinity increase during AOM or in conjunction with silicate dissolution, buffering the pH drop by OM degradation and by this, inhibiting carbonate dissolution. We clarified this part in lines 874-875.

24. **Reviewer Comment:** 892: May want to clarify that high rates of siliciclastic sedimentation should result in lower rates of organic matter degradation (ie., higher rates of organic matter preservation). The text here seems to suggest the opposite. It is a bit unclear whether the author is referring to rates of deposition of organic matter ('POC sedimentation'), or to rates of siliciclastic sedimentation ('detrital minerals', 'OAE minerals'). It may be worth parsing out this discussion to address different types of sedimentation separately in order to improve clarity of this section.

Response: Thank you for pointing this out. This section and the distinction between POC and detrital mineral precipitation rates was revised in lines 902-907.

25. **Reviewer Comment:** 920: should 'favourable' be 'favoured'; this sentence is a bit unclear as written.

Response: The sentence was re-written to increase clarity.

26. **Reviewer Comment:** 921: isotope tracers are not the only way to quantify secondary precipitation; direct measurement of secondary precipitates in sediment samples may be a more straightforward and accessible method worth mentioning. This section seems to be overstating the difficulty of characterizing secondary precipitation within benthic sediments.

Response: Thank you for highlighting this bias towards isotope tracers. We fully agree that more methods are available to identify secondary precipitates and we revised the section accordingly.