

## Review of Bice et al.

### General comments

Bice et al have used a 1D reactive transport model to assess the impact of carbonate addition to benthic acidification and alkalinity release in a system broadly comparable to Yaquina Bay, OR (USA). To better constrain their mineral dissolution data, they used laboratory measurements of bio-calcite and bio-aragonite dissolution. The work in itself is interesting and deserves in my opinion to be published. As the authors also state, relatively little work has been done on mineral addition to sediments as a way of OAE, so that a study focussing on this topic would surely benefit the community. However, the manuscript itself needs a major revision, especially in the introduction and in the motivation for this study.

My biggest issue with the title, abstract and introduction is that they focus a lot on ocean acidification (OA), while the manuscript itself mostly focuses on sediment biogeochemistry. As the authors acknowledge and also show themselves in Fig 5, OM mineralization is by far the biggest source of acidity in sediments. And what they achieve by adding carbonate minerals is to counteract the acidity produced by OM mineralization, not by OA. If the authors really wanted to investigate how the effect of OA in coastal sediments is countered by carbonate mineral addition, as the title states, their baseline simulation before mineral addition should be compared to a) a simulation with only OA (i.e. lower overlying water pH due to higher DIC) and no mineral addition and b) a simulation with OA and mineral addition (shown in Figure 5, but not compared to both of the above scenarios). And then perhaps vary with the extent of OA. But this is not done. In my opinion, the manuscript is much better framed solely in the context of OAE alone, and the links with OA only make it very confusing.

Besides this, there are some places in the introduction where the literature isn't properly cited, specifically on OAE; sediment buffering is determined without quantifying buffering factors / sensitivities, which are easy to calculate from the model results; and the budget construction is very difficult to understand without the supplementary information, so I suggest to move this part of the supplementary information to the main manuscript. I will elaborate on all of the above points in the detailed comments.

### Detailed comments

L. 13: "which can further lower both pH and the carbonate saturation state" → only in oxic conditions, else pH is increased due to TA generation

L. 13-14: This sentence, equal to the title, is one of the major issues I have with this work. Sediments are naturally lower in pH than the overlying water, due to the natural process of OM mineralization. Why is this framed as if this natural process is a bad thing? OA only leads to a slightly lower pH due to higher DIC in the bottom water, the majority still comes from OM mineralization and the impact of eutrophication (i.e. enhanced OM input) would be much higher. I feel the motivation that is presented here is not correct, and that it should be the potential of sediments to increase TA efflux to the overlying water and thus CO<sub>2</sub> uptake (as the authors themselves also write in L. 24-25, but which should come out much more strongly in the abstract).

L. 22: which "buffering effect"? The authors do not present any buffer factors / sensitivities

L. 30-31: "The effect of CO<sub>2</sub> additions depends on the buffering capacity of the water. This is quantified by its alkalinity" → this is incorrect and not stated by these authors. Alkalinity plays a major role in buffering, but the buffering capacity is quantified by buffer factors (or rather their inverses, sensitivities). Please rephrase.

L. 49-61: I have many issues with this paragraph. First, it feels very disjointed from the previous and following paragraph, as if it's put in at a later stage. But mostly, even after reading multiple times, I really miss the purpose of it in the motivation for this study. Yes, benthos impact the overlying water (L.60-61), but how does the overlying water impact benthos? The line of reasoning in L.54-61 states that benthos live under lower pH conditions than in the overlying water, and this lower pH is not due to OA. My suggestion would be to strongly shorten this paragraph and only keep the essential information in, without trying to find a motivation for this study.

L. 65: "OAE is mainly studied for its effect on ocean - atmosphere CO<sub>2</sub> exchange" Renforth and Henderson (2017) actually looked at the biological side too, and provided a motivation to study the biological response to OAE.

L. 65-68: This statement does not properly cite the literature. Taylor et al (2016) didn't investigate OAE, but enhanced weathering on land. While this ultimately also affects oceans through enhanced TA input, they did not investigate OAE.

L. 68-70: The work by Montserrat et al (2017) was also done in the context of coastal applications, so this citation does not match the statement.

L. 71-72: Also Ferderer et al (BG, 2022) had a coastal focus, and recently Fuhr et al (Front Clim, 2024) was published.

L. 77-78: Rather than assessing the extent and duration of buffering indirectly, why not simply calculate buffer factors or rather sensitivities as per Middelburg et al (2020)? With the data generated by the

model, it should be easily possible to compute one or more of these terms, which actually shows how a system change its sensitivity to acidification following mineral addition

L. 79: "Building on the previous work by Krumins et al. (2013) and Rassman et al. (2016)" → Rassman et al (2016) did not use an RTM, I would suggest to remove this citation here.

L. 97: Figure S2 does not show a correlation coefficient ( $r$ ) but a coefficient of determination ( $R^2$ ).

Table 1: on which scale is pH presented here? Which equilibrium constants used for this calculation (and the RTM in general)? The same as in L. 132-133?

Table 2: Are all these parameters based on Yaquina Bay, like  $R_{c0}$ ? If yes, would be good to explicitly add to the start of section 2.3 that the RTM is meant to describe this site.

L. 188-190: This statement initially confused me, because alkalinity does not only include carbonate alkalinity, but also sulfide and ammonia alkalinity. Perhaps, for clarity, the equation of L.180 should include only the acid-base species that were considered in the modelling, or L.188-190 should explicitly state which acid-base systems were included.

Table 3: I suggest to not only show  $dTA/dR$  but also  $dDIC/dR$  in this table. That will make part of the results and discussion easier to write because you can simply refer to this table when discussing the DIC/TA ratio (e.g. in L. 265 where you now refer to Thamdrup and Canfield (2000)).

L. 200-201: I miss a discussion in the manuscript (not per se here) on how this mineral addition would or could be done in practice. It now remains ambiguous how hypothetical this modelling exercise is.

L. 201-203: This is not clear without presenting the impact of environmental factors first. I suggest to move it to after discussing the sensitivity to environmental parameters.

L. 205-208: Why would minerals only dilute the organic matter and not the other solid phases in the sediment?

L. 209-217: I think this information is better presented in a table. The information that also the minerals themselves were changes to aragonite, and that mineral dose is varied and also bottom-water pH is varied, is missing here. Finally, it should be made clear that the low OW pH scenario (term in Figure 5) is an OA scenario because TA is kept constant in the calculation, so DIC is increased.

L. 219-230: I could not properly understand the method without the supplementary information, so I suggest to move here in a slightly shortened way, and at least include Figure S4.

L. 266-267: this pH effect is also shown by the work of Soetaert et al (2007) and Hoffman et al. (2010) which are logical to cite.

L. 270-274: I'm not sure how to interpret this statement. So if you had used another  $k$ -value for sulfide oxidation, you would have obtained very different results? How (un)certain and sensitive was this parameter value in your model? Also, Brenner et al (2016) did not use an RTM or a kinetic approach, so that may also explain the difference.

L. 282-284: I think this is a nice result because if this is sustained and the FeS is long-term removed, it is a net TA source on the system scale, as shown by e.g. Hu and Cai (2011) and Brenner et al (2016).

L. 292-294: In my opinion, this should come out much more clearly in the abstract, instead of the link with OA

L. 305: "lower  $dTA/DIC$  ratios" lower than what?

L. 311-313: I'm not sure if I entirely follow this statement, because also in this system the majority of  $NH_4$  is produced by sulfate reduction. Maybe paraphrasing would help.

L. 315: Figure 3 doesn't show the depth of the oxic layer, as it shows depth-integrated fluxes

L. 317-318: "added mineral dissolved at depth" → how deep? Or is it simply meant as opposed to at the top of the sediment?

L. 325-326: Why depth-averaged over 10 cm? The mixing depth is 4 cm (only 10 cm in Figure 5), and Figure 2 doesn't give a clear incentive for this choice since the conditions are still very different at the 0-10 cm depth range. I can imagine that choosing a different depth interval for the averaging would have yielded quite different results, have the authors checked this? And why not just make a 2D plot of depth versus time?

L. 326: "because the surficial sediment is most relevant for juvenile bivalves impacted by ocean acidification". I still don't follow, because the pH and saturation state are much lower in the top part of the sediment anyway, and not due to OA.

L. 346-347: "Burial of minerals" do you mean below 10 cm here?

L. 353: I am a bit critical when manuscripts talk about a "buffering response" without quantifying any buffer factors or better sensitivities. The authors have all parameters to compute many of the sensitivities in Table 1 of Middelburg et al. (2020). Perhaps in this case the Egleston et al. (2010) factor that looks at the response of  $CO_3^{2-}$  (and thus saturation state) to TA change ( $\omega_{TA-1}$ ) would make the most sense, or a general  $dpH/dTA$ . If you don't plan to include it, then maybe just better call this section a sensitivity analyses.

L. 362-365: These results (and those of Figure 5d) so nicely show that OM mineralization is by far the dominating factor governing sedimentary carbonate system dynamics, and not OA. It boils down to my major comment.

L. 365: "pH was buffered the most and increased the fastest in the aragonite implementation" that is a contradiction: stronger buffering means a smaller pH increase. Or am I misunderstanding this sentence?

L. 367: "as buffering developed" so this is typically something you would like to see with sensitivity factors.

L. 380-382: perhaps nice to show some of the key process results related to Figure 5 (like this once) in the supplementary information.

L. 394-396: I would still argue that the absolute changes are more important than the relative changes in pathways, but where can we see this? Perhaps also add to the supplementary information.

L. 399-400: It's written as if this is a problem. But is it?

L. 403-404: I would like to see these results as well, because Figure 3 seems to suggest that the impact of mineral addition is relatively minor compared to e.g. sulfate reduction.

L. 407-408: The work by Cyronak et al. and Yamamoto et al. is on coral reefs. How relevant is that in the context of your system?

L. 407-409: I miss eutrophication / low-oxygen conditions in this list. See work by Cai et al (2011) or Hagens et al (2015). Perhaps it falls under anthropogenic impacts, but that is very broad.

L. 414-415: Rather than being lost, this movement of minerals may actually also stimulate dissolution and thus shorten the time of reach steady state again. See e.g. Meysman and Montserrat (2017).

L. 426-431: I suggest to put all numbers in a figure (similar to Figure S4) or table for clarity.

L. 431-434: Does this upscaling from an annual flux consider full mineral dissolution?

L. 441-442: Also driven by primary production and aerobic respiration?

L. 447-448: Maybe you can speculate what this would mean for multiple applications. What would be the ideal timeframe for a second application?

L. 451-253: Is this simply because supersaturation would lead to mineral precipitation and these minerals would then dissolve again at a later stage? I'm not sure that I've read that somewhere explicitly.

Supplement L.77-78: And what about calcification? Is that assumed to be net zero in the water column?

Supplement L.83-85: This sentence does not read well, but do I understand correctly that RDIC, RTA and pH are all kept constant? Can you support that assumption?

Supplement L.92-94: This doesn't make much sense to present this way, because, pH is a logarithmic unit and so this value will change depending on the pH range you use. Better express in terms of [H<sup>+</sup>] change or add the pH range that is used.

#### Minor and technical comments

General comment: "Alk" and "TA" are both used throughout. Please choose one of both for consistency.

L. 20: "total alkalinity"

L. 21: change "significant" to "substantial", no statistics done

L. 32: "aerobic respiration"

L. 32-34: this is a complex sentence, better split it in the impacts of primary production & aerobic respiration on the one hand, and calcium carbonate dissolution / precipitation on the other hand

L. 36: "the decrease in pH" → change to "the OA-driven decrease in pH" for clarity

L. 38-39: remove "against ocean acidification", because the buffering capacity against any acidifying process is affected

L. 45: I'd remove "in particular" because TA generation is very minor under oxic conditions, and TA is even consumed if nitrification follows OM mineralization

L. 46: there are better references for this statement than Gimenez et al (2018). E.g. Chen & Wang (1999) for a first suggestion or Hu and Cai (2011) for a global estimate

L. 65: in other parts of the manuscript you use mCDR, instead of CDR. I would define therefore mCDR here and stick to that abbreviation.

L. 97-99: Add a reference to Figure S2 at the end of the sentence.

Table 2: typos in Van Cappellen.

L. 183: "The OM mineralization rate" add that this is Rc0 for clarity

L. 184: "the resulting Rc0 value"

Table 3: the term  $\gamma_{OM}$  is nowhere in the manuscript defined (or I missed it)

Table 4: I would say that Rc0 is calibrated to match experimental TA data, but the parameter itself is not experimentally derived.

L. 235-236: Rephrase to "The results are in line with other results used to setup the RTM" or equivalent. The relationship is not an outcome of the cited RTMs.

Figure 1: please show the equations, correlation coefficient and p-values of the fits. Use different symbols for both colours for clarity.

L. 281: Rassman et al (2018) is not a modelling study, so I would remove the citation here

L. 286-288: This sentence is not very clearly written, please rephrase.

Figure 2: please put the depth in positive values, instead of negative values. And add in the caption how much calcite was added

L. 303: "Our results are in line"

L. 303: "calcite mineral dissolution"

L. 309: "in the marine environment"

Fig 3: The orange colour represents either dissolution or precipitation, depending on the sign of the DIC/TA response. So the legend needs to be altered here.

L. 333-334: This cannot be clearly seen in the figure. Maybe add the baseline values as horizontal lines to the plots.

L. 343-344: also this is difficult to see in the figure. Adding vertical lines might help here, and/or a different figure design (2D plots as suggested earlier). Or the important times can be put in a table.

L. 346-347: "Burial of carbonate minerals"

L. 357: "the conditions" → which conditions?

L. 358: "with a low  $R_{CO}$  scenario"

L. 360: "the deep bioturbation scenario" → i.e. with a deep mixed layer? Try to be consistent with terminology

L. 361-370: References to subfigures are missing here.

L. 366: "than the baseline and high  $FeO_x$  flux scenarios"

L. 368-369: This is very difficult to see in the figure. I suggest a second y-axis for the low  $RCO$  scenario.

L. 374: Add that lower overlying water is the OA scenario as TA is kept constant

L. 382-384: This sentence does not read very well.

L. 390-392: Add that this is the OA scenario.

L. 396: "the low rate of aerobic mineralization" (because in the context of  $H^+$  production)

L. 439: "the Alk:DIC ratio"

L. 441: "which is drive by tidal exchange"

L. 450-451: True, but sulfate reduction is way more important then  $CaCO_3$  dissolution. Maybe paraphrase to show that.

L. 459-460: "higher dissolution rates"

Supplement L. 68: add that  $F_{aDIC}$  is atmospheric  $CO_2$  uptake and that negative values indicate outgassing.