

Please see below for our responses (in italics) to the detailed comments by the reviewers (normal font), outlining the changes we will make in our revisions. We appreciate their feedback which helped us to significantly improve our manuscript.

Reviewer 2:

Bice et al present a 1D reactive transport sediment diagenesis model, in which they test the effect of adding CaCO₃ to sediments on a) porewater alkalinity and other relevant species, and b) the resulting net production (i.e., sediment flux) of alkalinity and DIC. They also describe lab-based CaCO₃ dissolution experiments from which they derive the dissolution rate parameters employed in the model. While the porewater chemistry and related flux results are the primary focus of the study, they also use a box model to extend their modeled flux data to calculate the potential “marine CO₂ uptake”. At the porewater scale of analysis, they find that CaCO₃ addition to sediment results in little change in species affected by redox reactions, but pH and omega are increased significantly 2 years after mineral addition. They also conclude (via a CDR = 1/2 Alk flux relationship) that the CaCO₃ application can result in significant atmospheric CO₂ uptake.

This topic is timely and interesting, and I think the model study contributes meaningfully to the conversation. However, I find three major issues with the paper that need to be addressed before consideration for publication: 1) Unclear justification and aim (amelioration of benthic acidification seems to be the main point, but it’s not justified well; and mCDR via OAE is also discussed significantly); 2) the mCDR projections are coarse, misleading, and don’t fit well with the rest of the data; and 3) the kinetic parameterization used for CaCO₃ dissolution needs to be improved or better justified (modeling CaCO₃ dissolution is the meat of the paper, but the parameterization is quite simple, and doesn’t consider more thorough published data). Furthermore, the overall readability of the paper needs to be improved. A major issue on this point is that the lab methods are incompletely described, but reference an unpublished thesis. Despite these concerns, I think the topic is interesting enough that the study is valuable if these issues are addressed in a revised manuscript.

We thank the reviewer for the valuable feedback which helped us to improve the manuscript. As outlined in our responses below, we have made numerous revisions aimed at clarifying our work. In line with our response to feedback from reviewer 1, we more clearly delineate the effect of sediment mineralization from that of OA and improve the framing of our work, we better justify the use of our dissolution rate constants and clarify the value and limitations of the rough mCDR estimates.

Major issues:

Unclear aim: I found the aim of the paper unclear. Specifically, the focus on both mitigating the effects of OA on sediments, and mCDR (i.e., atmospheric CO₂ uptake via OAE) is confusing. These are different enough topics to merit dedicated conversations and scales of analyses, yet neither are sufficiently explored. The jump between a porewater model and atmospheric CO₂ uptake requires many intermediate assumptions, yet the assumptions made to calculate atmospheric CO₂ uptake are coarse and inaccurate (described in subsequent point). I think this paper could be

more valuable if it focused more on the sediment model, and limited discussion of atmospheric CO₂ uptake. Second, the justification that sediment acidification (due to OA) is a problem, is not well established in the introduction. References to benthic organisms are scattered throughout the paper, and the Introduction does not convincingly establish that buffering porewater pH is indeed an important objective for improving the health of benthic organisms. (Indeed, I imagine many benthic organisms are evolved to tolerate low pH conditions.) Related to this, I found the paper poorly grounded in OA, OAE (specifically accelerated weathering of limestone and coastal enhanced weathering), and CaCO₃ dissolution research, with foundational citations missing, or others mis-referenced (e.g., L 70: Montserrat et al, 2017, is not about open ocean CDR). Reframing the discussion, with better references, could help here.

We appreciate the reviewer's suggestion. As detailed below, and in part in our response to reviewer 1, we addressed the above points by focusing our work on sediment biogeochemistry and removing most of the discussion of OA. We present CO₂ uptake as a simple extension to our sediment model, so we tried to make it clear that it is not the main focus of this study, but only a rough estimate of the impact of altered benthic DIC and TA exchange fluxes following the addition of carbonate minerals. As suggested, we shortened details about calcifying organisms but focused on sediment biogeochemistry. We also reference some additional recent publications.

CaCO₃ dissolution kinetics: The rate parameters used for CaCO₃ dissolution, based on four experimental data points, need to be better justified. First, they use a linear dependency with omega, and assume a rate order of 1. Much existing research exists on this topic, and some of the most comprehensive studies (using both biotic and abiotic CaCO₃) have shown non-linear trends (due to dissolution mechanism transitioning from step-edge retreat to etch pit formation), and reaction rate orders not equal to 1. See, for example, Adkins et al, 2021 (Annual Reviews in Marine Science); Subhas et al, 2018 (Marine Chemistry)). While the simplified dissolution rates used in this paper may be adequate as rough approximations for the RTM, I find it strange that these other papers aren't considered, either using their published rate equations, or at least citing them. Second, aragonite dissolution has been shown to be slower than calcite dissolution (see same sources), but is comparable in the rate equations presented here. Furthermore, what are the dissolution constants used? They are not in Table 4, and only alluded to in Section 3.1.

We appreciate relevant articles suggested and by no means intended to minimize the vast existing literature on carbonate dissolution kinetics. However, this modeling study was carried out in part to inform a field study carried out in Yaquina Bay. Hence, we wanted to use dissolution kinetics directly measured on material that is being applied. The rate laws we used are commonly used approximation in early diagenetic models, and both rate constant and exponent derived from our data are in line with other reports. Thus, while we do not argue with the fundamental argument made by the reviewer, well documented by the literature they cite, we feel that our modeling approach is substantiated by both our data and has support in the existing literature.

However, we now discuss this in more detail. Specifically we now cite the suggested papers, and we state that the rate order is subject to debate and may change over time. We now also mention that this has implications for the long-term pattern for the buffering effect, and hence is identified as an important factor to consider with making predictions over the course of several years. Added the following after the Sensitivity analyses part where we talk about the limitations of our approach:

'We also acknowledge that changing the dissolution rate order would potentially lead to different outcomes which need to be explored in further studies. '

And as suggested, we added dissolution constants from 'Results' to Table 4.

CDR estimates: The authors calculate atmospheric CO₂ uptake as equivalent to ½ the sediment alkalinity flux resulting from CaCO₃ dissolution. This is not accurate for several reasons, first, the overlying water will be different from porewater (e.g., temperature, pH, etc.), requiring further thermodynamic considerations to assess CO₂ concentration in the water column. Second, a decrease in water column CO₂ does not necessarily translate to a 1:1 decrease in atmospheric CO₂, given air-sea flux time and potential subduction of water masses prior to equilibration. This is difficult to model. Third, the dependence on “unpublished data” to calculate CO₂ uptake (L 222) is problematic. If these data are available from the author team, why not include them in the paper or supplement? Furthermore, there are no uncertainties or temporal variability given, making any extrapolation dubious. While the presented estimate is a nice back of the envelope calculation, it is insufficient to present as a significant part of the paper's discussion, and should include many more caveats. Because of the public and commercial interest in CDR, studies like these should be particularly thoughtful and careful about making claims of CO₂ capture rates.

We accept that the model provides coarse estimates and demonstrate the potential link between sediment alkalinization and CO₂ uptake. The simplicity of our approach was based on previous work (Brenner et al., 2016). With regard to the specific issues raised: 1) We consider differences in thermodynamics (different sediment vs overlying water temperatures) however, and we also stress that the tidal exchange would dominate over these small changes. 2) We agree that CO₂ exchange is complex and not instantaneous. However, we also note that this is a shallow well-mixed shallow water environment. 3) We only use the unpublished data to estimate a reasonable system state for our rough flux estimates. We agree that more accurate estimates need to be supported by more extensive data.

In our revisions, we are clarifying these points, but we feel that establishing the link between benthic exchange and the fate of carbon fluxes is still a valuable point to make.

Other model concerns: the initial sediment conditions are not fully presented. Is there any initial CaCO₃ in the sediment? Or CaCO₃ deposition? Even a small amount of CaCO₃ can have a significant buffering effect, and adding CaCO₃ may not necessarily change alkalinity generation linearly. If Yaquina Bay sediments are 0% carbonate, that should be explained. Furthermore, seasonal variability is not considered. I imagine that changes in temperature / OM dissolution rates are important if considering year+ trends, but these are not considered or discussed.

Upper boundary conditions are presented in Table 1. In our model, we consider zero deposition flux of carbonate minerals to the sediment. This potentially does not reflect Yaquina conditions directly. However, considering average annual conditions we think the heterogenous presence of CaCO₃ would still be small compared to the relatively large mineral addition we are implementing. Seasonal dependencies and other factors that might impact our model results were included as limitations of the model in lines 405-425.

Readability: I found it difficult to follow both the study's motivation and methods, given some writing issues. The paper needs some significant editing, in overall structure, sentence structure, and word choice. I recommend having the revised manuscript reviewed by someone with scientific editing skills.

Clarified the manuscript in the light of comments.

Significant issues / clarifications needed:

The combination of existing data from an unpublished thesis (Myers, 2022) and the new sediment model is confusing as presented. The conclusion starts with "Our study successfully combines lab experiments and modeling". However, the lab data consist of only 4 data points (used to parameterize CaCO₃ dissolution rates), which were not particularly critical to the model, given the availability of published equations for dissolution kinetics (e.g., Adkins et al, 2021). As written, the paper takes a middle ground where much of the methods from Myers, 2022, are presented as new, but important details are also skipped over with a reference (which made it seem as if Myers, 2022, was a published study). Specific examples:

Description of the mineral dissolution kinetic experiments (L 85 to 106).

We appreciate this valid point that the paper is model dominated and there is not much experimental focus. Therefore, our approach uses minimal field/experimental data (such as dissolution and TA flux data that are consistent with previous work) to anchor a computational model where computational experiments were used to answer research questions.

L 183: boundary condition for TA flux. This is a very important value, and is mentioned casually without much explanation.

the alkalinity flux value mentioned here is the measured alkalinity flux from lab experiments. (see lines ~195)

L 184: Why is the remineralization rate altered to match the TA flux? What about mineral precipitation/dissolution, and oxidation of reduced species? Also, need to explain what the rates / rate ranges are, instead of just saying they're comparable to other studies. (E.g., Krumins 2013 provides values for both shallow banks/bays, and also deeper coastal sediments; why are you only comparing to the deeper sediments here?)

We use literature values to parameterize our model. However, to anchor our model to the site, we used measured alkalinity fluxes to parameterize OM rates which were comparable to values presented in a study in the same system (D'Andrea & Dewitt, 2009). The reviewer is of course correct that alkalinity fluxes not only depend on the mineralization rates, but also the partitioning of the pathways, and the extent of reoxidation reactions. Because these are part of the model, we feel that alkalinity fluxes can be used to tune the organic matter mineralization rate driving early diagenesis. We also added the range of OM mineralization from D'Andrea & Dewitt (2009) and clarified the sentence so that the other studies we compare our values to (Wang & Van Capellen, 1996; Krumins et al., 2013) are all from deeper environments.

L 235: "This [dissolution rate] is in line with previous reactive transport models focused on mineral dissolution." I find it strange that you're justifying your choice of dissolution rate equations by

comparing to other RTM models (which surely cite other papers for their rate equations), instead of studies focused on CaCO₃ dissolution. Furthermore, these references are all quite old, and progress has been made on constraining CaCO₃ dissolution rates in the meantime.

We appreciate the concern and to address that, we reworded 'previous RTM models' to highlight that we are actually focusing on the data synthesis carried out by those studies.

The different model runs are not clearly explained or outlined anywhere. Perhaps there should be a table of the initial parameters, as well as subsequent tests. Examples:

L 202: I had no idea what the parameters used in the spin-up simulations were, and they're only mentioned as an "(e.g., ...)". They should be explicitly listed in a table somewhere.

Reaction parameters used in spin-up were presented in methods section. We also present baseline scenario parameters in Table 5.

L 217: surficial mixing was "varied" from 4 cm to 10 cm. Is this only two depths/tests? Or was a range of values tested?

We only considered 2 depths and we justify our selection of these values based on literature.

The different CaCO₃ addition scenarios (8%, 16%) are not clearly discussed in the text. E.g., if 8% CaCO₃ addition is the "baseline", it should be identified as such earlier (L 200). Which scenario is represented in the Results, Discussion, and Figs?

We appreciate the suggestion and added a table addressing the above points (see Table 5).

Presentation of both the experimental observations and model results is confusing. E.g., Section 3.1 presents measured data, but immediately follows the lengthy model methods description. You need to more clearly specify "experiment" and "model" results.

We made changes to the overall flow of the paper which we think might help with this issue.

Mixing discussion points about calcifying organisms into both the Methods and Results section is distracting. Example: L 288.

Removed sentence to make it clear.

Minor comments:

Throughout: abbreviations are not used consistently (e.g., "rate of OM mineralization" could be "R_C," or included as a reminder, e.g., "rate of OM mineralization (R_C)" (L 210)).

Not all variables are defined.

L 149 (Equation 4): What is s?

It is defined as the stoichiometric coefficient for each species

Subsequently R_C and R_C0 are used without definition.

Defined in Table 3 caption.

Table 3: What is RC? Is it supposed to be R_C ?; What is R_M ?

R_C and R_C^0 were defined in Table 3.

Table 4: kfm and kdm are not defined

Dissolution rates were presented in section 3.1. Both dissolution and formation rate constants are added to Table 4.

L 108: the 'volumetric dissolution rate' is confusing following directly after the Equation 1. It should be a new paragraph.

Done

L 110: The jump from equation 2 to equation 3 is not obvious and needs to be explained better.

We revised this part for clarification.

L 127: What do you mean by "validation samples"? How were these used, and what were they compared to?

We used the TCO₂/PCO₂ samples to ensure our seawater treatments were correct and to validate all the alkalinity titrations. The bottle samples were simply another layer of data checking. We removed 'validation samples' for clarification.

L 180: "other acids/bases" needs to be explained

We removed this equation since the information we want to present already exist in Table 3.

L 184: RC0 is not yet defined.

Defined in previous sentence.

L 201: "respectively" does not make sense here; not needed

Removed.

L 267: aerobic respiration consumes alkalinity, so saying it produces "significantly less TA" is confusing.

Removed.

L 359: "reached similar values" is unclear. Similar to what?

Clarified as: '...under all scenarios, mineral saturation states reached similar values...'

L 372: Specify that A is Omega_calcite. Also, caption should not say "2 years after" since data are for three timepoints

Removed '2 years'. We kept Omega as is since it represents saturation state for the mineral type added.

L 415: "Loosing"

Changed to 'washing away'

L 428: Reword "... in the bay most."

Removed 'in the bay'.

L 430: "Increase of CO₂ uptake" is not accurate. The sediment is still a net source of CO₂; "decrease in CO₂ flux" would be closer to accurate

Changed as suggested.