We thank David Burdige for his time and feedback. Below we reply to comments that asked for information or clarification, and all other suggestions and corrections will be integrated in the revised text as recommended. For clarity, David Burdige's comments are in black, and our replies are in red.

In this manuscript Sulpis et al. describe a diagenetic model for marine sediments targeted for the study of deep-sea sediments (RADI). Many aspects of this model look like a number of other models that have been previously published, although there are two aspects of this work that stand out. The first is that the model incorporates a more complex (and presumably realistic) representation of carbonate dissolution kinetics, based on recent studies from the USC and CalTech groups. This is an important addition for a number of reasons and warrants eventual publication of this work.

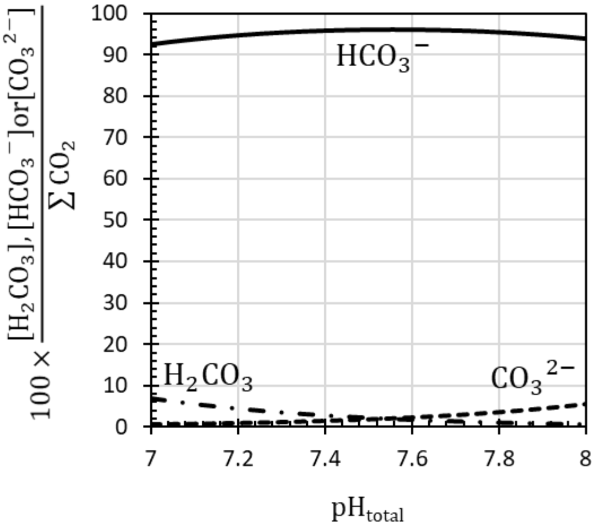
The second is that the model is explicitly discussed in the context of its ability to look at time-dependent problems. Strictly speaking, this is not exactly new since other models out there (e.g., CANDI) can, in principle, also be used to examine time-dependent problems. However, these models generally are not used in this fashion and the work shown here presents some interesting observations based on time-dependent simulations using RADI.

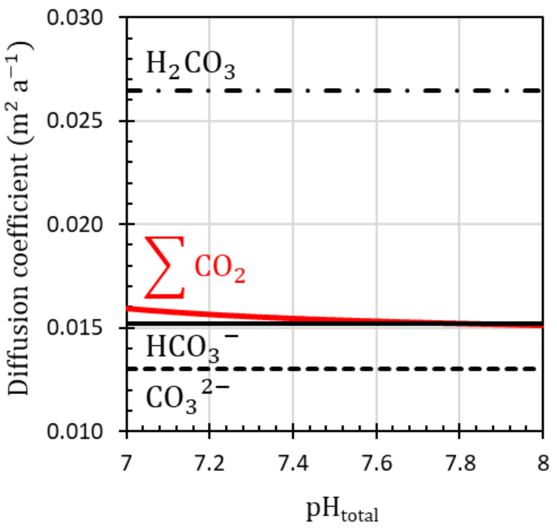
A concern I have, though, about the model is that they use total alkalinity and total DIC as solute variables, rather than calculating them from individual chemical components (I know this is touted as an advantage of this model, but I'm not as convinced that it really is). Given that a major thrust of this work is examining carbonate dissolution in deep-sea sediments this seems like a possible problem. Rather than calculating [H+] and [CO32-] from Alk and DIC profiles (see line 297) wouldn't it make more sense to model H+ and carbonate (or bicarbonate) concentrations directly in the model and then calculate alkalinity and DIC depth profiles at the end of each time step. Such a model would be just as easy to use as RADI is in terms of comparing model results with field observations and would likely be more accurate. This would probably also require the addition of an equation for borate in the model, but that would be an easy addition (see, for example, the approaches described in Hoffmann et al. [Biogeosci. 5, 227-251, 2008] and Faber et al. [Biogeosci. 9, 4087-4097, 2012]).

Transport-reaction modelling of the carbonate system is challenging, and trade-offs must be made (e.g., Boudreau, 1997; Hoffmann et al., 2008 Biogeosciences). Modelling the carbonate system in the water column normally involves transport of total alkalinity and total DIC because these model variables are conservative (Humphreys et al., 2018 Marine Chemistry), and both are transported with the water (i.e. differences in molecular diffusion among the species involved do not matter in advection dominated systems). In non-permeable sediments, molecular diffusion dominates transport and species diffuse according to their own gradient (e.g. the gradient of carbon dioxide may differ from that of the carbonate ion). Moreover, species may have different diffusion coefficients. As a consequence, a more accurate way to represent the carbonate system in non-permeable sediments is to have transport-reaction equations for all the species involved (protons, bicarbonate, carbonate, carbon dioxide) as suggested by David Burdige. The most accurate way would be to include also changes in complex formation and electroneutrality constraints (Boudreau et al., 2004 EPSL).

However, this gain in model accuracy comes at the expense of model complexity and computational demand, while the uncertainty due to lumping carbonic acid, bicarbonate and carbonate transport is usually less than other uncertainties related to thermodynamic constants needed in the calculation and tortuosity corrections for diffusion coefficients. Most of the uncertainty surrounding $CaCO_3$ saturation state estimates stems from the large uncertainty within the $CaCO_3$ equilibrium constants rather than that associated with carbonate ion (Orr et al., 2018 Marine Chemistry; Sulpis et al., 2020 Ocean Science); this uncertainty is independent of the modelling approach used.

HCO_3^- is the dominant dissolved inorganic carbon species at pH values typical of porewaters, see figure below on the left. In the figure below, on the right, we show what the diffusion of DIC would be if it was computed as a weighted arithmetic average of the diffusion coefficients of each of the DIC components. At pH ~7, the 'true' DIC diffusion coefficient (the weighted arithmetic average) is about 4% higher than the diffusion coefficient of HCO_3^- alone. That gap becomes negligible at higher pH. Thus, using the HCO_3^- diffusion coefficient as a surrogate for that of TAlk and DIC, as it has been done by other, similar models, such as that of Kanzaki et al. (2021, Geoscientific Model Development), should be acceptable as long as the pH is not too low. We will include this figure and discussion in the supplementary information.





Borate is already included in the model for solving the CO_2 system. We have not made that clear in the current version of the manuscript, but will include the following in the next version, line 298.

> "At each model time step, the total hydrogen ion concentration $[H^+]$ is computed from TAlk and $\sum CO_2$ using a single Newton-Raphson iteration from the previous time step (Humphreys et al., 2021, Geosci Model Dev Discuss):
>
> $$[H^+]_t = [H^+]_{t-1} - \frac{[TAlk]([H^+]_{t-1}, [\sum CO_2]) - [TAlk]}{d[TAlk]([H^+]_{t-1}, [\sum CO_2]) \big/ d[H^+]_{t-1}}$$
>
> where $[H^+]_t$ is the new $[H^+]$ value and $[H^+]_{t-1}$ is the $[H^+]$ from the previous time step. TAlk($[H^+]_{t-1}$, $\sum CO_2$) is the total alkalinity computed from user-specified total dissolved silicate, $[\sum PO_4]$ and total borate calculated from salinity (Uppstrom 1974), plus equilibrium constants for silicic acid (Sillen et al. 1964, Special publication of the Royal Society of Chemistry) and phosphoric acid (Yao and Millero 1995, Aquatic Geochemistry). Its derivative is computed following the approach of CO2SYS, see Humphreys et al. (2021, Geoscientific Model Development Discussions). The carbonate ion concentration is then computed as:
>
> $$[CO_3^{2-}] = \frac{[\sum CO_2] \times K_1^* \times K_2^*}{K_1^* \times K_2^* + K_1^* \times [H^+]_t + [H^+]_t^2}$$

> where K_1^* and K_2^* are the first and second dissociation constants for carbonic acid, respectively, taken from Lueker et al. (2000, Marine Chemistry)."

Maybe I'm missing something, but since one of the major efforts here is to more realistically quantify carbonate dissolution in early diagenetic models the approach taken in RADI to "directly" model Alkalinity and DIC as solute variables seems like it adds unnecessary uncertainty. It also requires that they use the bicarbonate diffusion coefficient for DIC and alkalinity (line 395), which adds further uncertainty in the calculation of carbonate ion concentration gradients and fluxes near the sediment surface, which is where most calcium carbonate dissolves in the deep sea.

See previous reply.

I also have a number of other questions and smaller concerns about this work. Note that in the rest of this review, the numbers in parentheses refer to line numbers.

(130-1) – Just so I'm clear, the "diagenetic equations" in RADI are still differential equations (also see the next comment).

That is correct, the reviewer #1 made a similar comment. We have clarified the text, and added partial differential equations ruling the model, see reply to comment #1 of reviewer #1.

(132) – How exactly does RADI compute "the concentrations of a set of solids and solutes at each time step"? This should be briefly discussed here and perhaps presented in a bit more detail in the supporting information section. Also, in addition to describing these equations part-by-part in the text it might be nice to present some sort of summary of the complete equations in the supporting information section. Perhaps only modeling "geeks" like me would want to see this, but I think it would be good for this to be available, should any reader be so interested in seeing this information.

We have clarified and complemented this section and included the model governing equation, in response to the first comment of reviewer #1. Eq. (3) is used to compute the new concentrations at each time step, and each of the R, A, D & I terms in Eq. (3) are defined later in the Model description section. In addition, we will include a summary in the supplement that will include the complete, detailed version of Eq. (3).

(181) – Why and how is Clay being modeled here? This is never really discussed (unless I missed it).

Clay is simply modelled as a non-reactive solid. We use it to assess when the simulation has reached a steady state, and because the clay accumulation flux to the sediment-water interface participates to the calculation of the solid burial velocity. We will precise this at line 181. In future versions, we plan to incorporate adsorption/desorption reactions on clay surfaces, as mentioned in section 5.

(228) - What exactly is meant by "the reactivities decline with depth"? I'm assuming the k's in eqn. (4) are constants for a given site (since based on eqns. (7a) and (7b) they only depend on the carbon rain rate to the sediment), so the overall rate of organic matter degradation at any given site should decrease with depth solely because of changes with depth in the quantity of organic matter and the relative proportions of fast and slow decay materials that are present. Am I missing something here?

This is a mistake, reactivities are actually constant with depth, as computed per equations (7a,7b). We will delete this part of the sentence.

(250) – Is there a subscript "z" missing for the k on this line?

Here and elsewhere, because the organic matter reactivities do not decrease with depth, there should not be any subscript ‘z’. We will delete this.

(268) – “This scheme …” - I would think that the way alkalinity and DIC are modeled in RADI will also make it difficult to apply this model to coastal and anoxic sediments.

We agree that below at lower pH, using the HCO_3^- diffusion coefficient for DIC and TAlk may not be adequate. We will precise that and refer to the new supplementary figure showed above in response to comment #2.

(299) – How are the concentrations of fluoride, borate and silicate obtained?

As mentioned in the reply to comment #1, we have added further information to *$CaCO_3$ dissolution and precipitation* section 2.2.3. Borate concentration was computed as a function of salinity (Uppstrom, 1974, DSR) for borate. Fluorite is not included in the current version of RADI. The silicate concentration was fixed to a typical deep-sea value of 120 µmol kg^{-1}.

(307) – It’s not clear to me how the reaction order (η) implicitly accounts for each carbonate mineral’s specific surface area. The discussion later on only talks about how the reaction order varies with Ω.

The sentence was unclear, in fact, only the dissolution rate constant accounts for the mineral surface area. The reaction order is specific to each mineral and only depends on Ω. We will rephrase to clarify.

In the caption to Fig. 2 it states that calcite and aragonite dissolution rates are based on eqns. (8) and (9) but it isn't until you read a little further that you learn that η is actually a complex function of Ω (starting on line 334). It might be good to at least mention this in the figure caption.

We will clarify this in the figure caption.

Fig. 4 has two different types of symbols in the O2 profiles. I think I figured out the differences from reading the text (lines 547-548), but this should be clarified in the figure legend and/or caption.

The squares refer to $[O_2]$ from microelectrodes and the circles refer to $[O_2]$ from porewater extracted from the retrieved box core. We will precise that in the caption.

(583) – “in the laboratory” but on-board ship? Please clarify.

Yes, that is indeed from the ship laboratory. We will clarify.

(704) - Will tides in the deep sea (water depth 4370 at station #W-2) really generate this large a change in DBL thickness (i.e., from 0.5 to 3.5 mm)?

There was a mistake in the text, in the simulation, the DBL actually varied between 0.5 and 1.5 mm-thick, as shown in Fig. 8. We will correct this in the revised manuscript. There is unfortunately no data to assess the validity of this deep-sea tidal DBL-range. Assuming that the DBL thickness depends on the current speed only, and that the seafloor is perfectly flat, i.e., no turbulence generated by sediment roughness, without tidal current, a DBL value of 1.5 mm-thick could be realistic in abyssal plains (Sulpis et al., 2018, PNAS). Since it is thought that tidal currents account for most of the overall current speed in the deep-sea, that the DBL thins to 0.5 mm every 6 hours when the tidal current is the strongest could be realistic.

(715) – Tides affect both the concentration gradient at the sediment water interface as well as the thickness of the DBL, so the combined effects should then impact the benthic flux. Do these two factors reinforce one another, cancel each other out, or do something in-between? Some of these issues are alluded to indirectly in the next section (4.3), but I wonder if this is worth looking at and/or considering here more explicitly.

This is correct. Regarding the diffusive fluxes across the sediment-water interface, interface concentration changes and DBL thickness change have generally opposite effects. Interfacial concentrations respond quickly to DBL changes, but that the gradient within the DBL also changes will attenuate the initial response. This is what is seen in section 4.3., and we will include a few pH depth profiles (see reply to next comment) to illustrate this effect. We will not discuss that in detail here because that will be the object of a manuscript currently in preparation, in which we will investigate the competing effects of DBL changes and organic matter degradation on $CaCO_3$ dissolution near the sediment-water interface.

(760-1) – "… the quick adjustment of porewater concentrations to the new diffusive boundary layer …" – Might it be worth showing these profiles (perhaps in the supporting information section)?

We will include these pH profiles in the revised supplement.

(781) – I think that trying to model carbon isotopes from POC degradation will be challenging if you use a reactive continuum approach, even if this approach is more appropriate for many studies. In part, that is why we use a similar "multi-G" approach to the one used here in our work modeling POC, DIC and DOC degradation in sediments (both total C, 13C and 14C)

We will delete the statement about switching to a continuum approach.

(787) – As noted above, I wonder if applications of the RADI model to coastal sediments will be difficult given the way alkalinity and DIC are being modelled here.

We will add a note precising that if pH is too low, assuming that both DIC and TAlk can diffuse at the same rate than a HCO_3^- will lead to inaccurate results.

We accept all the other suggestions and corrections and will include them in the revised manuscript.

Best regards,

Olivier Sulpis, Matthew P. Humphreys, Monica M. Wilhelmus, Dustin Carroll, William M. Berelson, Dimitris Menemenlis, Jack J. Middelburg, Jess F. Adkins

References

Boudreau, B.P.: Diagenetic Models and Their Implementation. Springer-Verlag, Berlin, 414 pp. 1997

Boudreau, B.P., Meysman, F.J.R., Middelburg, J.J. Multicomponent ionic diffusion in porewaters: Coulombic effects revisited. Earth and Planetary Science Letters, 222, 653-666, 2004

Hofmann, A.F., Meysman, F.J.R., Soetaert, K., Middelburg, J.J. A step-by-step procedure for pH model construction in aquatic systems. Biogeosciences 5, 227-251, 2008

Humphreys, M.P., Daniels, C.J., Wolf-Gladrow, D.A., Tyrrell, T., Achterberg, E.P. On the influence of marine biogeochemical processes over CO_2 exchange between the atmosphere and ocean. Marine Chemistry, 199, 1-11, 2018

Humphreys, M.P., Lewis, E.R., Sharo, J.D., Pierrot, D. PyCO2SYS v1.7: marine carbonate system calculations in Python. Geoscientific Model Development Discussions. 2021

Lueker, T. J., Dickson, A. G., and Keeling, C. D.: Ocean pCO_2 calculated from dissolved inorganic carbon, alkalinity, and equations for K1 and K2: validation based on laboratory measurements of CO_2 in gas and seawater at equilibrium, Mar. Chem., 70, 105–119, 2000

Kanzaki, Y., Hülse, D., Turner, S.K., Ridgwell, A. A model for marine sedimentary carbonate diagenesis and paleoclimate proxy signal tracking: IMP v1.0. Geoscientific Model Development, 14, 5999-6023, 2021

Orr, J. C., Epitalon, J.-M., Dickson, A. G., and Gattuso, J.-P.: Routine uncertainty propagation for the marine carbon dioxide system, Mar. Chem., 207, 84–107, 2018

Sillén, L.G., Martell, A.E., Bjerrum, J., Schwarzenbach, G.K. Stability Constants of metal-ion complexes. The Chemical Society (London), Special Publ. 17:751, 1964

Sulpis, O., Boudreau, B.P., Mucci, A., Jenkins, C.J., Trossman, D.S., Arbic, B.K. and Key, R.M.: Current $CaCO_3$ dissolution at the seafloor caused by anthropogenic CO_2. Proceedings of the National Academy of Sciences, 115, 11700-11705, 2018

Sulpis, O., Lauvset, S.K., Hagens, M. Current estimates of K_1* and K_2* appear inconsistent with measured CO_2 system parameters in cold oceanic regions. Ocean Science 16(4), 847-862, 2020

Uppström, L. R.: The boron/chlorinity ratio of deep-sea water from the Pacific Ocean, Deep-Sea Research and Oceanographic Abstracts, 21, 161-162, 1974

Yao, W. and Millero, F. J.: The chemistry of the anoxic waters in the Framvaren Fjord, Norway, Aquat. Geochem., 1, 53–88, 1995