Geoscientific Model Development Discussions

Geosci. Model Dev. Discuss., referee comment RC2
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Comment on gmd-2020-447

Anonymous Referee #2

Referee comment on "SolveSAPHE-r2 (v2.0.1): revisiting and extending the Solver Suite for Alkalinity-PH Equations for usage with CO2, HCO3- or CO32- input data" by Guy Munhoven, Geosci. Model Dev. Discuss., https://doi.org/10.5194/gmd-2020-447-RC2, 2021

General comments

Guy Munhoven has written a very interesting manuscript which is a follow-up on his 2013 paper describing SolveSAPHE. In this manuscript, he extended his previous work on solving the Alk_T - C_T pair by providing solutions for the three different inorganic carbon species in combination with Alk_T. Strongly supported by mathematics, he shows that while the combinations of Alk_T with CO_2 and HCO_3^- only have one physically meaningful solution, this does not hold for the Alk_T – CO_3^{2-} pair. He then continues to define the different cases that can take place (i.e. no, one or two physically meaningful solutions, of which the latter case is mostly relevant for oceanographic applications) and comes up with clever algorithms to take this behaviour into account. These algorithms were implemented in FORTRAN 90 and thoroughly tested with a high amount of case studies.

Understandably, the manuscript is not written for the broader scientific community working on the carbonate system because of its technical focus, and overall it is well written. However, I do think that some efforts can be made in making the paper more appealing to a wider audience. For example, more context can be given as to why it is important to include solutions for the CO_2 - Alk_T, HCO_3^- - Alk_T and especially CO_3^{2-} - Alk_T pairs. While pCO_2 has already been a commonly measured parameter for decades, CO_3^{2-} can currently be regarded as the fifth parameter that can be measured to describe the carbonate system. Recent adoption of direct CO_3^{2-} measurements by experimentalists (e.g. Easley et al., 2013; doi:10.1021/es303631g or Patsavas et al., 2015; doi:10.1016/j.marchem.2014.10.015) actually provide scientific ground for this manuscript and this is even strengthened given that CO_3^{2-} was found to be best paired with A_T (or C_T; Sharp and Byrne, 2018; doi:10.1016/j.marchem.2018.12.001).

Another comment I have along the same line is that I felt that a discussion was lacking on which pH value to take in the case that there are two solutions for the CO_3^{2-} - Alk_T pair. Later I noticed that Reviewer 1 has this exact comment and worked this out very nicely in their comment. I would therefore suggest Guy Munhoven to take this point into account and perhaps even create a figure similar to that by Reviewer 1 in the manuscript. Such a figure would also aid the less technical reader (as well as the reader who has difficulties in interpreting Deffeyes diagrams) in understanding the importance of this work. However, I also agree with Reviewer 1 that a justification of this choice is probably beyond the scope

of this manuscript.

Finally, it might be interesting to include some other case studies. Specifically, I was thinking about pore waters where the concentrations of various acid-base systems may be higher, especially the relative contributions of non-carbonate bases to Alk_T.

Overall, after taking into account the minor comments in this review, I recommend publication of this manuscript. I look forward to these solvers being implemented in some of the more routinely used carbonate chemistry solvers, such that the broader scientific community can benefit from this work.

Minor and technical comments

- L.10-11: "longer"/ "more time"--> than what exactly?
- L.12-13: "It outperforms the Newton-Raphson based one by a factor of four"--> In terms of what, calculation time?
- L.15: "For Alk_T & CO_3^{2-} data pairs" would read better here
- L.27-29: Depending on the purpose, some modellers will use pH in combination with C_T; I suggest to write "most modellers" instead.
- L.38-39: Not sure what is meant with "this best had to be one pair of input data only".
- L.40-44: I would suggest to finish the introduction and start a new manuscript section after presenting the aim.
- L.50: "whose"
- L.176: "in Fig. 2"
- L.187: better write "I" instead of "we" (single author)
- L.193: $[H^+]$ >> (something appears to be missing here)
- L.270-271: I suggest to provide one sentence here to explain the difference between both solvers, for example by moving the current L.324-326 which explains that one is the Newton-Raphson solver, while the other uses the secant scheme.
- L.275 "developments"
- L.290: CO_3^{2-} instead of CO_3^{-2}.
- L.322: "in Fig. 4"
- L.324: "in Fig. 5"