Dear Sandra,

please find below my point to point listing of the changes made to the manuscript in response to the referees’ comments and suggestions. For the sake of brevity, I do not repeat here the justifications that were given in the Author’s Comments in reply to the Referees Comments. A latexdiff version of the manuscript highlighting the insertions and deletions in the text has also been uploaded alongside the revised manuscript.

I hope the manuscript is now acceptable for publication.

Best regards,

Guy

Revisions in response to comments by Anonymous Referee #1

General Comments

Anonymous Referee #1, hereafter AR#1, essentially has only one major comment, or more precisely question:

When calculating pH from alkalinity and carbonate ion concentration in typical seawater […] one obtains two solutions and the question is 'Which one to take?’ In order to shed some light on this problem I have calculated the concentrations of all carbonate system parameters for a fixed alkalinity (Alk_T = 2300 µmol kg\(^{-1}\)) as a function of pH (Fig. 1). For [CO_3^{2-}] = 500 µmol kg\(^{-1}\) one obtains two solutions: pH_1 = 8.70 and pH_2 = 10.75 with quite different DIC values. The higher pH value is discarded because the DIC is ‘unrealistically’ low and that pH = 8.70 would be the chosen answer. This [choice] has been taken, for example, by Zeebe & Wolf-Gladrow (2001, p. 277, ‘use the larger one’): they recommend using the real solution with the largest H\(^+\) concentration (lowest pH). Although this choice works out fine in common seawater, it has not been properly justified. And the justification is actually beyond mathematics.
Added Figure with a graph similar to the Figure provided by AR#1, but adapted to the results presented here (more complex AlkT composition, more extended pH range).

In the manuscript I wrote that the existence of two roots for the AlkT & CO$_3^-$ pair system was a little known fact. As AR#1 illustrates “little known” does not mean “unknown”… [Zeebe and Wolf-Gladrow (2001), pp. 276–277] did mention it: “Roots: two positive (use the larger one), three negative.” I have added a mentioning of this in the manuscript (line [XXX] in the latexdiff report)

Added extra discussion regarding the choice of the root

Specific/technical comments

Units of alkalinity: I suggest replacing meq (outdated) by mmol (compare, for example, Dickson et al., 2007, Chapter 5, Table 2)

OK, corrected as recommended.

L50 typo: whoe? whose

OK, corrected.

L51 ‘s is a factor to convert from that scale to the free scale: it might be useful to mention that the value of s is close to 1

The sentence at lines 51–52 has been rewritten as follows:

“s depends on temperature, pressure and salinity of the sample and its value is close to 1 (typically between 1.0 and 1.3).”

Fig. 1: axes labels (quantities & units) missing, same for color bars; remove titles (numbers); y-axes from 1 to 0 to 3 or from −1 to 3 (??); a bit more explanation/discussion might be in order.

The annotations of Fig. 1 in the manuscript were partly lost during the processing of the submitted manuscript file (where the figure was complete) to produce the preprint posted on the GMDD forum.

L174 typo: eq. (12 then → eq. (12) then

OK, corrected.

L193 [H$^+$] $\gg$: something missing here

This has been replaced by “as [H$^+$] → +∞.”

L210 $H_1 < H_{\text{min}}$ and $H_2 > H_{\text{min}}$ might be shortened to $H_1 < H_{\text{min}} < H_2$

I prefer to leave it as is—nothing changed.

L229 ‘exact knowledge determination’ ???

“determination” has been deleted so that the sentence now reads “[…] for which the exact knowledge of $H_{\tan}$ is not indispensable.”
API is a standard acronym in computer science and stands for “Application Programming Interface” – the definition has been added (line 393 in the latexdiff.

There was a spurious blank between “development” and the “s” that follows. Corrected to read “In the course of the developments related to […]”

Discarded “function”

This was about the caption of Fig. 7 (now Fig. 8), and has been corrected.

Sup. Mathematical and Technical Details

Typos:
2.3.1 $B(OH)\rightarrow B(OH)_3$
2.3.3 $H_3(PO)_4 \rightarrow H_3PO_4$
2.3.4 $H_4(SiO)_4 \rightarrow H_4SiO_4$

OK, corrected.
Revisions in response to comments by Anonymous Referee #2

General comments

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 Alk$_T$ (or C$_T$; Sharp and Byrne, 2018; doi:10.1016/j.marchem.2018.12.001).

The introduction was reorganised, partly rewritten and extended along the lines proposed by Anonymous Referee #2 (hereafter AR#2).

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.

- A two-panel figure was added (new Fig. 2 in the revised manuscript). The top panel is similar to the figure presented by AR#1, but has been completed to make it compatible with the alkalinity composition used to produce Fig. 1 (i.e., including borate alkalinity). The target $[CO_3^{2-}]$ line intersecting the CO$_3^{2-}$ distribution function is not shown in order to avoid overloading the graph. The second panel shows a selection of carbonate ion distribution functions obtained for different Alk$_T$ values.
- The graphs of the new figure are discussed in the text, and the possibilities of zero, one or two roots explored.
- Discussion about which one of the roots to chose when there are two has been added in a new section 2.4.2 (two pages).

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$_T$.

I had difficulties to secure sufficiently complete data sets for porewater chemistry to design a realistic representative test case as requested by AR#2. As the purpose was to cover samples where “[... ] the concentrations of various acid-base systems may be higher, especially the relative contributions of non-carbonate bases to Alk.” I finally resorted to using the data of [Yao and Millero(1995)] for the anoxic waters of the Framvaren Fjord, Norway, as a starting point. The water column in this fjord is anoxic below 20 m depth, and at depths greater than 100 m, it is characterised by H$_2$S concentrations between about 4.5 and 5.8 mM, as well as NH$_4^+$ concentrations between about
1.3 and 1.6 mM. Yao and Millero (1995) provide data for all the acid-systems currently considered in the Fortran 90 implementation of SOLVEr2.

For the new test case ABW5, where “ABW” stands for anoxic brackish water, I then use average concentrations between 100 and 170 m depth for all components except Alk$_T$ and C$_T$, for which roughly rounded ranges over that depth interval are adopted: $T = 7.56^\circ C$, $S = 22.82$, $D = 135 m$, $[H_2S] = 5.1 \text{ mmol kg}^{-1}$, $[PO_4^{3-}] = 0.1 \text{ mmol kg}^{-1}$, $[NH_4^+] = 1.5 \text{ mmol kg}^{-1}$, $[SiO_2] = 0.6 \text{ mmol kg}^{-1}$, Alk$_T = 17 - 20 \text{ mmol kg}^{-1}$, $C_T = 15 - 17.5 \text{ mmol kg}^{-1}$. All reported concentrations are assumed to represent total concentrations of their respective acid systems.

In order not to lengthen the manuscript unnecessarily, the results for SW1, which covers a subset of SW2) have been removed from Figs. 5 and 6 (now Figs. 6 and 7) and those for ABW5 included instead.

**Specific comments**

Throughout

“on Fig. n” changed to “in Fig. n” as suggested repeatedly.

L.10-11: “longer”/“more time” ---> > than what exactly?

There was actually an error on line 11: “while Alk$_T$ & CO$_2$ requires about four times as much time.” should actually have read “while Alk$_T$ & CO$_3^{2-}$ requires about four times as much time.”

Lines 10–11 have been rewritten to read (see lines 10–12 in the latexdiff report):

“The Alk$_T$ & CO$_2$ pair is numerically the most challenging. With the Newton-Raphson based solver, it takes about five times as long to solve as the companion Alk$_T$ & C$_T$ pair; the Alk$_T$ & CO$_3^{2-}$ pair requires on average about four times as much time as the Alk$_T$ & C$_T$ pair.”

L.12-13: “It outperforms the Newton-Raphson based one by a factor of four’ ---> > In terms of what, calculation time?

In terms of the required number of iterations. This has been reformulated more precisely as

“It outperforms the Newton-Raphson based one by up to a factor of four in terms of average numbers of iterations and execution time and yet reaches equation residuals that are up to seven orders of magnitude lower.”

L.15: “For Alk$_T$ & CO$_3^{2-}$ data pairs” would read better here

OK – changed as suggested.

L.27-29: Depending on the purpose, some modellers will use pH in combination with $C_T$; I suggest to write “most modellers” instead.

OK – changed as suggested.

L.38-39: Not sure what is meant with “this best had to be one pair of input data only”.
This means that users should only have to provide the absolutely necessary information (i.e., the pair of data), but no further auxiliary information, such as a bracketing interval or starting values for an iterative process. As in SOLVE SAPHE v1, the algorithm should be able to derive that kind of information autonomously without having to rely on user input.

Lines 36–39 (see lines 60–67 in the latexdiff report) have been rewritten:

“Here, we do not focus on these aspects, but on the design of algorithms that can solve the underlying mathematical problem with as little user input as possible. The aim is to reduce user input to the bare essentials: besides the fundamental information about temperature, salinity, pressure and the thermodynamic data, this ideally had to be any physically meaningful data pair only; the algorithm should be able to derive any other auxiliary information, such as root brackets or starting values for iterations, on its own.”

L.40-44: I would suggest to finish the introduction and start a new manuscript section after presenting the aim.

The section heading “2 Theoretical Considerations” has been moved before the earlier line 44, followed by a new subsection title “2.1 Revisiting the mathematics of the alkalinity-pH equation” The first sentence of the new subsection has been reformulated.

L.50: “whose” OK – changed as suggested.

L.187: better write “I” instead of “we” (single author)

Actually on L. 188, but changed as suggested anyway.

L.193: \([H^+] \rightarrow +\infty\).

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.

The paragraph starting at line 270 has been rewritten (see lines 389–397 in the latexdiff report):

“The SOLVE SAPHE Fortran 90 library from Munhoven (2013) – hereafter SOLVE SAPHE v. 1 – has been revised, cleaned up and upgraded to allow the processing of the additional three pairs. For the purpose of this paper, only the two main solvers have been kept: these are solve_at_general, which uses a Newton-Raphson method, and solve_at_general_sec, which uses the secant method. Both can be still be used with the same Application Programming Interface (API) as in v1. The instances in SOLVE SAPHE-r2 are nevertheless only wrappers to the newly added Newton-Raphson based solve_at_general2 and secant (or more precisely regula falsi) based solve_at_general2_sec both of which are able to process problems that have two roots. They return the number of roots of the problem, as well as their actual values, if any.”
L.275 “developments”
   OK – corrected.

L.290: $\text{CO}_3^{2-}$ instead of $\text{CO}_3^{-2}$
   OK – corrected.
Author’s own changes

Revised graphs

Jean-Pierre Gattuso has drawn my attention to issues with the rainbow colour scheme that I had adopted for most of my figures. The colour schemes of all the figures in the manuscript and in the Supplement have been changed from the rainbow scheme to a colour-blind friendlier one.

Test cases: naming scheme and inter-comparison set-up

There was an inconsistency in the naming of the test cases: SW4 actually is for brackish water and not seawater, as the “SW” in the name might suggests.

SW4 has been renamed to BW4, where “BW” stands for brackish water.

While setting up the new test case ABW5 I realised that the currently defined ones are not consistent when it comes to comparing the computational requirements of the Alk$_T$ & C$_T$, Alk$_T$ & CO$_2$, Alk$_T$ & HCO$_3^-$ and Alk$_T$ & CO$_3^{2-}$ versions against each other, for a each of SW1, SW2, SW3 and BW4. Although the [CO$_2$], [HCO$_3^-$] and [CO$_3^{2-}$] ranges for each test case had been defined on the basis of their respective distributions calculated from the Alk$_T$-C$_T$ results, they did not cover exactly the same “samples.” To make the results for the different pairs actually comparable, the test case definitions were therefore adapted for the inter-comparison of the performances of the four data pairs. Each test case is first carried out with the Alk$_T$-C$_T$ pair, for each set of temperature, salinity and pressure, and the results stored. For the other three pairs, the pH distribution obtained with the Alk$_T$-C$_T$ pair for the chosen set of temperature, salinity and pressure is first read in and the corresponding [CO$_2$], [HCO$_3^-$] or [CO$_3^{2-}$] distributions calculated on the underlying Alk$_T$-C$_T$ grid. The so-obtained arrays of species concentrations are then used to define the set of Alk$_T$-CO$_2$, Alk$_T$-HCO$_3^-$ and Alk$_T$-CO$_3^{2-}$ data pairs the benchmark calculations. This way the experiments for the four different characteristic carbonate system concentrations cover exactly the same set of samples.

The description of the test cases in Sect. 3.2.1 and the discussion in Sect. 3.2.2 have been adapted accordingly.

Figure 1

• The HCO$_3^-$ concentration in C$_T$-Alk$_T$ space was added between the pH and [CO$_2$] panels.
• The panels in the lower row of Fig. 1 have been rearranged so that they are in CO$_2$–HCO$_3^-$–CO$_3^{2-}$ order.
• Star symbols have been added to the two panels with the CO$_3^{2-}$ concentration distributions to illustrate a case with two roots (to extend the amendments suggested by the referees).
• The figure caption has been amended.

Discussion of Figure 1 in the text

Similarly to Alk$_T$ & CO$_3^{2-}$, the C$_T$ & HCO$_3^-$ pair generally has two pH roots, but the diagnosis is much more straightforward. This is now also discussed in the text and the solution recipe in Appendix A has been amended.
Figures 7 and 8 (previously Figures 6 and 7)

- Removed panel for test case SW1 (subset of SW2).
- Added panel for the new test case ABW5.
- Amended the maximum numbers of iterations to the slightly changed results as a result of the modified intercomparison setup

Figure 8 (previously Figure 7)

- Added an insert with a histogram to the figure to make better usage of the free blank space and to make the information quantitatively more expressive.
- Amended the caption to explain the insert.

Appendix A: The direct cases

The recipe for solving the C$\text{T}$ & HCO$^{-3}$ was not correct. Unlike for C$\text{T}$ & CO$_2$ and C$\text{T}$ & CO$_3^-$, the quadratic equation to solve for [$H^+$] does not always have roots, and most often have two of them. The HCO$^{-3}$ fraction in DIC does have to fulfill an additional constraint; being lower than 1 is not sufficient.

The recipe for C$\text{T}$ & HCO$^{-3}$ is now treated separately and presented and discussed in more detail.

Supplement: Additional Results

- Added Tables S2 and S3 with additional details about the test case definitions.
- Introduced ABW5 results into Tables S2 and S3 (now Tables S4 and S5).
- Added results for the new test case ABW5 where suitable: added new Figs. S5 and S12; added one panel to Figs. S10–S19 (now Figs. S13–S22).
- Added new Fig. S9 with results for the test case SW3-sc that had been missing.
- Fig. S20 (now Fig. S23): added histogram inserts to the four panels of the figure to make better usage of the free blank space and to make the information quantitatively more expressive and amended the caption to explain the insert.

Minor changes

Title

Added new code version number (v2.0.1) in the title to reflect code changes during the revision.

Throughout the manuscript and the Supplement:

- The manuscript text and the figure annotations has been revised to adhere more closely to the Copernicus house style (abbreviations such as “Fig.”, Eq.”, “Table” never being abbreviated, spelling of sulfur-related components and processes as sulf[xyz], power notation for units, etc.)

- Remaining “DIC” instances have been replaced by “C$\text{T}$”, which is the notation used everywhere else in the manuscript.
• Corrected a few English errors
• Added details of the medians and most probable numbers of iterations in section 3.2.2 (see lines 503–505 in the latexdiff report).

**Tables**

The table captions have been moved above the tables.

**Figure 4 (now Figure 5)**

The figure caption has been slightly reformulated.

**Code availability section:**

• Archived the codes on Zenodo and amended the section text accordingly, giving the references of the archives.
• Added notice that SolveSAPHE-r2 has been ported to R and made available on the Comprehensive R Archive NETwork (CRAN) under [https://cran.r-project.org/package=SolveSAPHE](https://cran.r-project.org/package=SolveSAPHE)

**References**

