SolveSAPHE-r2: revisiting and extending the Solver Suite for Alkalinity-PH Equations for usage with CO_2, HCO_3^- or CO_3^{2-} input data

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Abstract. The successful and efficient approach at the basis of SOLVESAPHE (Munhoven, 2013), which determines the carbonate system speciation by calculating pH from total alkalinity (Alk_T) and dissolved inorganic carbon (C_T), and which converges from any physically sensible pair of such data, has been adapted and further developed for work with Alk_T & CO_2, Alk_T & HCO_3^- and Alk_T & CO_3^{2-}. The mathematical properties of the three modified alkalinity-pH equations are explored. It

5 is shown that the Alk_T & CO_2 and Alk_T & HCO_3^- problems have one and only one positive root for any physically sensible pair of data (i.e, such that, resp., $[CO_2] > 0$ and $[HCO_3^-] > 0$). The space of Alk_T & CO_3^{2-} pairs is partitioned into regions where there is either no solution, one solution or where there are two. The numerical solution of the modified alkalinity-pH equations is far more demanding than that for the original Alk_T-C_T pair as they exhibit strong gradients and are not always monotonous. The two main algorithms used from SOLVESAPHE v. 1 had to be revised in depth to reliably process the three additional data

10 input pairs. 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, while Alk_T & CO_2 requires about four times as much time. All in all, it is nevertheless the secant based solver that offers the best performances. It outperforms the Newton-Raphson based one by up to a factor of four, to reach equation residuals that are up to seven orders of magnitude lower. Just like the pH solvers from routines from the v. 1 series, SOLVESAPHE v. 2 includes automatic root bracketing and efficient initialisation schemes

15 for the iterative solvers. For Alk_T & CO_3^{2-} pairs of data, it also determines the number of roots and calculates non-overlapping bracketing intervals. An open source reference implementation in Fortran 90 of the new algorithms is made publicly available for usage under the GNU Lesser General Public Licence v. 3 or later.

1 Introduction

Among all the aspects of the ongoing global environmental changes (climate change, ocean acidification, ...), the solution

20 chemistry of carbon dioxide (CO_2) is one of the best known. The related chemistry of the carbonate system in the oceans and other aqueous environments is well understood and routinely monitored and modelled. The equilibrium between the carbonate system species involves four variables: $[CO_2]$ (or equivalently the partial pressure of CO_2, pCO_2, or its fugacity, fCO_2), $[HCO_3^-]$, $[CO_3^{2-}]$ and $[H^+]$ (or equivalently pH). The speciation, i.e., the determination of the concentrations of the individual

species, therefore also requires four constraints. Two constraints are given by the equilibrium constants that characterize the
equilibria between dissolved CO_2 and HCO_3^- on one hand, and between HCO_3^- and CO_3^{2-} on the other hand, assuming
that these are known or can be calculated. Two more independent constraints are thus required to completely characterize the
system. Depending on the applications, different types of information are used: modellers will call upon the total concentration
of Dissolved Inorganic Carbon, $C_T = [CO_2] + [HCO_3^-] + [CO_3^{2-}]$ and total alkalinity, Alk_T, which are both measurable, but
most important, conservative and thus appropriate suitable for a budgeting approach; experimentalists use the pair that best
suits their analytical equipment and expertise. With these additional constraints, the concentrations of the individual species
can then be calculated. Such calculations are performed to an advanced level of detail with dedicated and highly specialised
packages. The review of Orr et al. (2015) offers a systematic analysis of subsisting uncertainties and inconsistencies between
ten such packages, focusing on the equilibrium constants adopted, pressure corrections applied, etc. Here, we do not focus
on the best set of equilibrium constants to use, nor on details related to temperature or salinity scales, or parametrisations
of the water density. Please refer to the comprehensive review of Orr et al. (2015) (and also Orr and Epitalon (2015)) and
references therein for these and related aspects. Here, we focus on the design of algorithms that can solve the underlying
mathematical problem with as little user input as possible – if possible such inputs should reduce to the bare essentials: besides
the fundamental information about temperature, salinity, pressure and the thermodynamic data, this best had to be one pair of
input data only.

In the companion paper (Munhoven, 2013), such autonomous algorithms with robust convergence properties for a wide range
of environmental conditions had been developed for usage with the Alk_T & C_T pair. For the present study, we are revisiting
that approach, extending and adapting it so that the Alk_T & CO_2, Alk_T & HCO_3^- and Alk_T & CO_3^{2-} can be processed with
the same reliability.

Cornerstone to the speciation calculation is the resolution of the following equation, that derives from the definition of Total
Alkalinity

$$R_T([H^+]) \equiv Alk_{nW}([H^+]) + \frac{K_W}{[H^+]} - \frac{[H^+]}{s} - Alk_T = 0, \tag{1}$$

i. e., eq. (21) from Munhoven (2013), where

$$Alk_{nW}([H^+]) = \sum_i Alk_{A_{[i]}}([H^+])$$

is that part of the total alkalinity not related to the water self-ionization, with i denumbering the acid systems resulting from
the dissolution of acids $A_{[i]}$ whoe dissolution products contribute to total alkalinity. $[H^+]$ is the proton concentration expressed
on one of the commonly used pH scales (total, seawater) and s is a factor to convert from that scale to the free scale. s depends
on temperature, pressure and salinity of the sample. For the purpose of this study, $Alk_{nW}([H^+])$ is partitioned into carbonate
alkalinity, $Alk_C([H^+])$, and non-carbonate alkalinity, $Alk_{nWC}([H^+])$,

$$Alk_{nW}([H^+]) = Alk_C([H^+]) + Alk_{nWC}([H^+])$$

since the relevant carbonate system parameters (the concentrations of CO_2, HCO_3^- and CO_3^{2-} and their sum, C_T) are all
directly related to Alk_C. Similarly to Alk_{nW}, Alk_{nWC} admits an infimum and a supremum which can both be derived from the

total concentrations of all the acid-base systems considered. We denote these two by $\text{Alk}_{\text{nWCinf}}$ and $\text{Alk}_{\text{nWCsup}}$, respectively. Eq. (1) is thus formally rewritten as

$$R_{\text{T}}([\text{H}^+]) \equiv \text{Alk}_{\text{C}}([\text{H}^+]) + \text{Alk}_{\text{nWC}}([\text{H}^+]) + \frac{K_{\text{W}}}{[\text{H}^+]} - \frac{[\text{H}^+]}{s} - \text{Alk}_{\text{T}} = 0, \tag{2}$$

60 The carbonate alkalinity term writes, as a function of C_{T}

$$\text{Alk}_{\text{C}}([\text{H}^+]) = \frac{K_1[\text{H}^+] + 2K_1 K_2}{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1 K_2} \, C_{\text{T}} \tag{3}$$

where K_1 and K_2 are the first and second stoichiometric dissociation constants of carbonic acid. The individual carbonate species fractions of C_{T} can be expressed as a function of $[\text{H}^+]$:

$$[\text{CO}_2] = \frac{[\text{H}^+]^2}{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1 K_2} \, C_{\text{T}} \tag{4}$$

65 $$[\text{HCO}_3^-] = \frac{K_1[\text{H}^+]}{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1 K_2} \, C_{\text{T}} \tag{5}$$

$$[\text{CO}_3^{2-}] = \frac{K_1 K_2}{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1 K_2} \, C_{\text{T}}. \tag{6}$$

Accordingly, $\text{Alk}_{\text{C}}([\text{H}^+])$ may be rewritten in one of the following forms

$$\text{Alk}_{\text{C}}([\text{H}^+]) = \frac{K_1[\text{H}^+] + 2K_1 K_2}{[\text{H}^+]^2} \, [\text{CO}_2] \tag{7}$$

$$\text{Alk}_{\text{C}}([\text{H}^+]) = \frac{K_1[\text{H}^+] + 2K_1 K_2}{K_1[\text{H}^+]} \, [\text{HCO}_3^-] \tag{8}$$

70 $$\text{Alk}_{\text{C}}([\text{H}^+]) = \frac{K_1[\text{H}^+] + 2K_1 K_2}{K_1 K_2} \, [\text{CO}_3^{2-}] \tag{9}$$

which will be used hereafter.

2 Theoretical Considerations

In the following, it is assumed that the temperature T, salinity S and applied pressure P are given and that adequate values for all the required stoichiometric equilibrium constants are available. It is furthermore assumed that the total concentrations
75 of all the other relevant acid systems (borate, hydrogen sulphate, phosphate, silicate, etc.) are known or can be derived from adequate parametric relationships.

Eleven out of the fifteen different possible pairs of independent parameters of the carbonate system do not require any complex iterative schemes, but can be directly solved or require at most the resolution of a quadratic equation. For the sake of completeness – and with minimal details only – "recipes" for solving these straightforward cases are provided in the appendix.
80 Alternative approaches can be found in the literature, such as in the *Guide to Best Practices for Ocean CO_2 Measurements* (Dickson et al., 2007). Dickson et al. (2007) also provide pathways for usage with triplets or quartets of input data. These only require the knowledge of one of the two dissociation constants or of their ratio, or none of them. That kind of approach is, however, not considered in this study.

The remaining four pairs require iterative procedures. Besides the A_T & C_T pair which was addressed in full detail by Munhoven (2013) these are (1) A_T & CO_2, (2) A_T & HCO_3^- and (3) A_T & CO_3^{2-}. As will be shown below, the SOLVESAPHE approach of Munhoven (2013), which is based upon the use of a hybrid iterative solver safeguarded by intrinsic brackets that can be calculated a priori, can be easily adapted for the A_T & CO_2 and A_T & HCO_3^- pairs. The A_T & CO_3^{2-} pair, for which there are ranges of combinations that do not allow any compatible pH value, and other ranges where there are two of them, requires additional analysis. We show below that it is nevertheless possible to diagnose these different situations and, in case there are two solutions, to derive bracketing intervals for each of the two and to isolate them efficiently. For each pair, we (1) establish the analytical properties of the modified pH-alkalinity equation; (2) derive brackets for the root(s); (3) develop a reliable and safe algorithm to solve the problem; (4) design an efficient initialisation scheme. We will now in turn analyse the mathematical properties of the alkalinity-pH equation that results from the substitution of C_T by the concentration of one of its individual species.

2.1 Alk$_T$ & CO$_2$

The Alk$_T$ & CO_2 pair can be dealt with in a similar way to the Alk$_T$ & C_T pair in the original SOLVESAPHE. The Alk$_C$([H^+]) term in eq. (2) is written as in eq. (7) and eq. (2) becomes

$$\left(\frac{K_1}{[H^+]} + \frac{2K_1K_2}{[H^+]^2} \right)[CO_2] + Alk_{nWC}([H^+]) + \frac{K_W}{[H^+]} - \frac{[H^+]}{s} - Alk_T = 0. \tag{10}$$

Just like the Alk$_C$([H^+]) expression from eq. (3) is monotonously decreasing with [H^+] for C_T fixed, that from eq. (7) is monotonously decreasing with [H^+] for [CO_2] fixed. The expression at the left-hand side of eq. (10) decreases from $+\infty$ to $-\infty$ for [CO_2] > 0 as [H^+] varies from 0^+ to $+\infty$. Eq. (10) thus always has exactly one positive solution.

2.1.1 Root bracketing

Intrinsic brackets for the solution of eq. (10) can be derived similarly to what is done in section 5.1 in Munhoven (2013). The lower bound H_{inf} can be chosen such that

$$\left(\frac{K_1}{H_{inf}} + \frac{2K_1K_2}{H_{inf}^2} \right)[CO_2] + \frac{K_W}{H_{inf}} - \frac{H_{inf}}{s} = Alk_T - Alk_{nWCinf}$$

i.e., as the positive root of the cubic equation

$$\frac{H^3}{s} + (Alk_T - Alk_{nWCinf})H^2 - (K_1[CO_2] + K_W)H - 2K_1K_2[CO_2] = 0$$

Let us denote this cubic by $P(H)$. It is important to notice that $P(0) = -2K_1K_2[CO_2] < 0$ and $P'(0) = -(K_1[CO_2] + K_W) < 0$. The equation $P(H) = 0$ has therefore one and only one positive root.

Similarly, the upper bound H_{sup} can be chosen such that

$$\left(\frac{K_1}{H_{sup}} + \frac{2K_1K_2}{H_{sup}^2} \right)[CO_2] + \frac{K_W}{H_{sup}} - \frac{H_{sup}}{s} = Alk_T - Alk_{nWCsup}$$

i.e., as the positive root of the cubic equation

$$\frac{H^3}{s} + (\text{Alk}_T - \text{Alk}_{\text{nWCsup}})H^2 - (K_1[\text{CO}_2] + K_W)H - 2K_1K_2[\text{CO}_2] = 0$$

which has also one and only one positive root, for the same reasons as above.

115   The positive roots of these cubic equations can be found by adopting a strategy similar to that used for the cubic initialisation of the iterative solution in SOLVESAPHE (Munhoven, 2013, sec. 3.2.2):

1. Locate the local minimum of the cubic, in $H_{\min} > 0$;

2. Develop the cubic as a quadratic Taylor expansion, $Q(H)$, around that minimum;

3. Solve $Q(H) = 0$ which has two roots and chose the one that is greater than $H_{\min}$.

120   In this particular case, it is, however, not necessary to solve these equations exactly as we only need approximate bounds of the root for safeguarding the iterations while solving eq. (2). For $H_{\inf}$ we may actually chose the $H_{\min}$ of the first cubic which is lower than the positive root and thus sufficient. Regarding $H_{\sup}$, it should be noticed that $P(H) = Q(H) + (H - H_{\min})^3/s$. Accordingly, $P(H) > Q(H)$ for $H > H_{\min}$ and therefore the greater root of $Q(H)$ for the second cubic is greater than the positive root of that cubic. The greater of the two roots of $Q(H)$ is therefore a sufficient upper bracket and may be used instead
125   of the exact $H_{\sup}$.

Any bracketing root-finding algorithm can then be used to solve the modified pH-alkalinity equation (10).

2.2 Alk_T & HCO_3^-

For the Alk_T & HCO_3^- pair, the $\text{Alk}_C([\text{H}^+])$ term in eq. (2) is written as in eq. (8):

$$\left(1 + \frac{2K_2}{[\text{H}^+]}\right)[\text{HCO}_3^-] + \text{Alk}_{\text{nWC}}([\text{H}^+]) + \frac{K_W}{[\text{H}^+]} - \frac{[\text{H}^+]}{s} - \text{Alk}_T = 0. \tag{11}$$

130   The $\text{Alk}_C([\text{H}^+])$ expression used in eq. (8) is again monotonously decreasing with $[\text{H}^+]$ for $[\text{HCO}_3^-]$ fixed. The expression at the left-hand side of eq. (11) decreases from $+\infty$ to $-\infty$ for $[\text{HCO}_3^-] \geq 0$ as $[\text{H}^+]$ varies from 0^+ to $+\infty$. Eq. (11) thus always has exactly one positive solution.

2.2.1   Root bracketing

The lower bound $H_{\inf}$ can be chosen such that

$$\left(1 + \frac{2K_2}{H_{\inf}}\right)[\text{HCO}_3^-] + \frac{K_W}{H_{\inf}} - \frac{H_{\inf}}{s} = \text{Alk}_T - \text{Alk}_{\text{nWCinf}}$$

i. e., as the positive root of the quadratic equation

$$\frac{H^2}{s} + (\text{Alk}_T - \text{Alk}_{\text{nWCinf}} - [\text{HCO}_3^-])H - (2K_2[\text{HCO}_3^-] + K_W) = 0.$$

Similarly, the upper bound H_{sup} can be chosen such that

$$\left(1 + \frac{2K_2}{H_{\text{sup}}}\right)[\text{HCO}_3^+] + \frac{K_W}{H_{\text{sup}}} - \frac{H_{\text{sup}}}{s} = \text{Alk}_T - \text{Alk}_{\text{nWCsup}}$$

140   i. e., as the positive root of the quadratic equation

$$\frac{H^2}{s} + (\text{Alk}_T - \text{Alk}_{\text{nWCsup}} - [\text{HCO}_3^-])H - (2K_2[\text{HCO}_3^-] + K_W) = 0.$$

Both equations always have two roots, one positive and one negative — their product is negative as indicated by the constant term. With the respective positive roots, we have again bounds for the solution of the modified pH-alkalinity equation and any bracketing root-finding algorithm can be used to solve it.

145   2.3   Alk$_T$ & CO$_3^{2-}$

Whereas any physically meaningful Alk$_T$ & [CO$_2$] or Alk$_T$ & [HCO$_3^-$] concentration pairs will always provide one and only one [H$^+$] (or equivalently pH) value as demonstrated above, this cannot be the case for Alk$_T$-[CO$_3^-$] pairs, as can be deduced from Fig. 1b and 1c. On one hand, there are two compatible C_T, and equivalently two pH values for most Alk$_T$-[CO$_3^-$] pairs. This little-known fact was already documented in the 1960s (see, e. g., Deffeyes (1965)). On the other hand, there are also
150   Alk$_T$-[CO$_3^-$] pairs that do not allow for any solution, as they lead to negative carbonate alkalinity. To our best knowledge, none of the currently used carbonate system speciation programs takes this possibility into account.

The solution of the Alk$_T$-[CO$_3^-$] problem thus requires a more in-depth preliminary mathematical analysis. To start, we write out eq. (2) with the Alk$_C$ expression for [CO$_3^-$] (eq. (9)):

$$\frac{K_1[\text{H}^+] + 2K_1K_2}{K_1K_2}[\text{CO}_3^{2-}] + \text{Alk}_{\text{nWC}}([\text{H}^+]) + \frac{K_W}{[\text{H}^+]} - \frac{[\text{H}^+]}{s} - \text{Alk}_T = 0.$$

155   Let us collect all the terms that are related to carbonate or water self-ionization alkalinity at the left-hand side, introduce the shorthand

$$\gamma = \frac{[\text{CO}_3^{2-}]}{K_2} - \frac{1}{s}.$$

and rewrite the equation as

$$\gamma[\text{H}^+] + \frac{K_W}{[\text{H}^+]} + 2[\text{CO}_3^{2-}] = \text{Alk}_T - \text{Alk}_{\text{nWC}}([\text{H}^+]). \tag{12}$$

160   The value of γ is one of the main controls on the number of roots that this equation has.

1.   If $\gamma < 0$, the equation has similar mathematical characteristics as the usual pH-alkalinity equation (eq. (1). It has exactly one root which can be calculated using similar procedures as in the original SOLVESAPHE. Please notice though that this means that $[\text{CO}_3^{2-}] < \frac{K_2}{s}$. Since K_2 is of the order of 10^{-9} mol/kg-SW and s is of the order of 1, this case is only relevant for CO$_3^{2-}$ concentrations of the order of 1 nmol/kg-SW and less.

165   2.   If $\gamma = 0$ (i. e., if $[\text{CO}_3^{2-}] = \frac{K_2}{s}$), the equation has exactly one root if $\text{Alk}_T - 2[\text{CO}_3^{2-}] - \text{Alk}_{\text{nWCinf}} > 0$, no root otherwise.
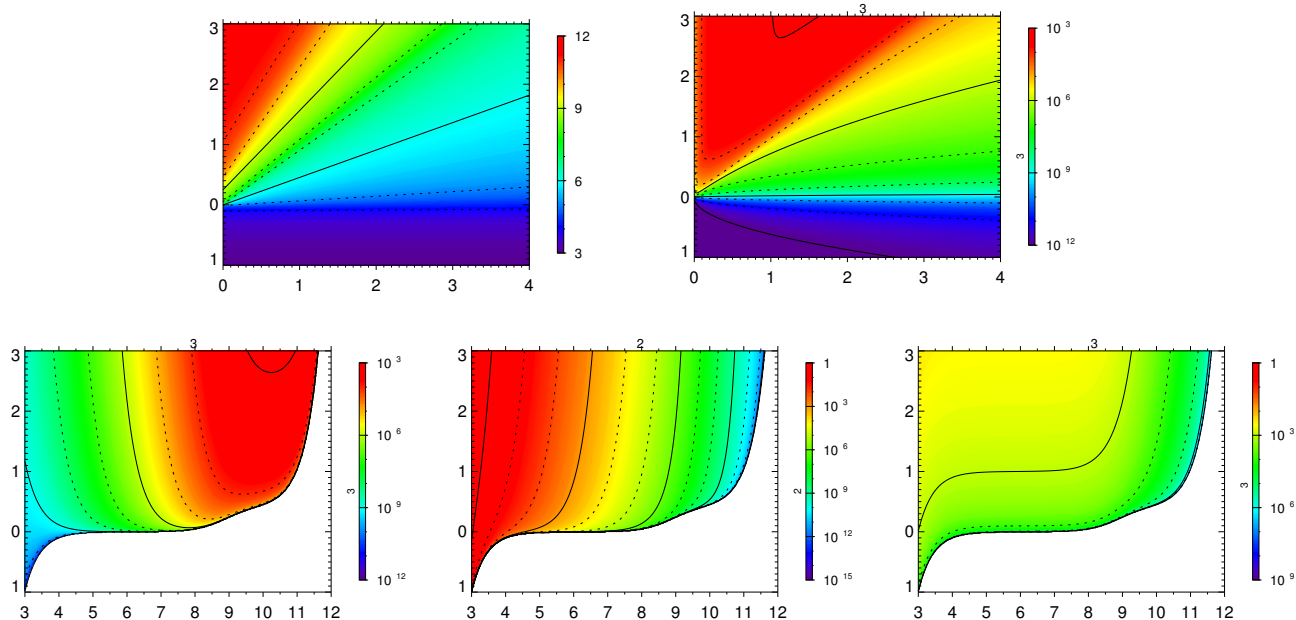
Figure 1. (a) pH isolines; (b) CO_3^{2-} concentration isolines in C_T-Alk_T space; (c) CO_3^{2-}, (d) CO_2 and (e) HCO_3^- concentration isolines in pH-Alk_T space. These distributions were calculated with SOLVESAPHE version 1.0.3. For (c), (d) and (e), carbonate alkalinity, Alk_C, was derived by using eq. (2), combined with with eqs. (9), (7) and (8) to derive $[CO_3^{-2}]$, $[CO_2]$ and $[HCO_3^-]$, resp. Blank areas represent the pH-Alk_T combinations that lead to negative Alk_C. Fig. 3 in Deffeyes (1965) is similar to (b).

3. If $\gamma > 0$, the left-hand side is not monotonous: it decreases from $+\infty$ in $[H^+] = 0^+$ to a minimum (see below) and then increases back to $+\infty$ as $[H^+] \rightarrow +\infty$. The right-hand side is bounded and strictly increasing over the same interval (Munhoven, 2013). As a result, the equation has no root if the right-hand side is too low, exactly one if the two curves become tangent and two roots if the right-hand side is great enough.

2.3.1 Mathematical analysis and root bracketing

To alleviate notation let us define the two parametric functions

$$L([H^+]; \gamma) = \gamma[H^+] + \frac{K_w}{[H^+]} + 2[CO_3^{2-}] \tag{13}$$

$$R([H^+]; A) = A - Alk_{nWC}([H^+]), \tag{14}$$

where $[H^+]$ is the independent variable and γ and A (alkalinity) are parameters. With these two function definitions, eq. (12then rewrites $L([H^+]; \gamma) = R([H^+]; Alk_T)$. Schematic representations of the three γ cases and of the L and R functions are shown on Fig. 2.
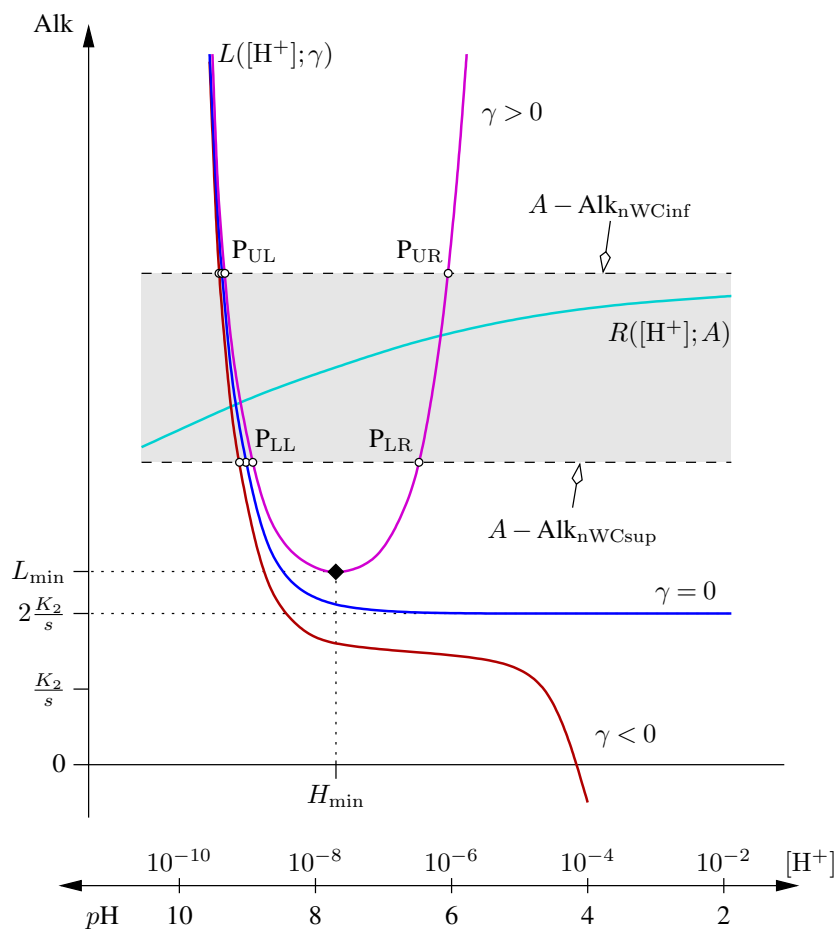
Figure 2. Schematic representation of the general characteristics of the $L([H^+]; \gamma)$ and $R([H^+]; A)$ components of the pH-alkalinity equation for the $\mathrm{Alk_T} - \mathrm{CO_3^{2-}}$ pair. The grey band delimits the (monotonous) variations of $R([H^+]; A)$, for a given alkalinity A. The band moves up and down without being distorted as A is increased, resp., decreased. For a given pair of $\mathrm{Alk_T}$ and $\mathrm{CO_3^{2-}}$ concentrations, the actual equation to solve is $L([H^+]; \gamma) = R([H^+]; \mathrm{Alk_T})$, where $\gamma = \frac{[\mathrm{CO_3^{2-}}]}{K_2} - \frac{1}{s}$. $\gamma = 0$ thus corresponds to $[\mathrm{CO_3^{2-}}] = \frac{K_2}{s}$.

Case $\gamma < 0$

The first case can be handled similarly to the $\mathrm{Alk_T}$ & CO_2 and $\mathrm{Alk_T}$ & HCO_3^- pairs. Eq. (12) always has exactly one root with $\gamma < 0$ as the equation function is monotonous and strictly decreasing with $[\mathrm{H}^+]$. Upper and lower bounds for that root can be

180   derived by solving the (quadratic) equations

$$\gamma H_{\mathrm{inf}} + \frac{K_{\mathrm{W}}}{H_{\mathrm{inf}}} + 2[CO_3^{2-}] = \mathrm{Alk_T} - \mathrm{Alk_{nWCinf}} \tag{15}$$

for H_{inf} and

$$\gamma H_{\mathrm{sup}} + \frac{K_{\mathrm{W}}}{H_{\mathrm{sup}}} + 2[CO_3^{2-}] = \mathrm{Alk_T} - \mathrm{Alk_{nWCsup}} \tag{16}$$

for H_{sup}, and retaining the respective positive roots of each.

185   **Case $\gamma = 0$**

The second case might be considered to be only mathematically of importance as it only applies for one exact (and thus improbable) CO_3^{2-} concentration value. For the sake of completeness, we nevertheless solve it.

As mentioned above, if $\gamma = 0$, eq. (12) has one solution if and only if $\mathrm{Alk_T} - \mathrm{Alk_{nWCinf}} > 2[CO_3^{2-}]$, and no solution else. The root can be easily bracketed from below. It is sufficient to chose H_{inf} such that

190    $$\frac{K_{\mathrm{W}}}{H_{\mathrm{inf}}} = \mathrm{Alk_T} - 2[CO_3^{2-}] - \mathrm{Alk_{nWCinf}}$$

leading to $L(H_{\mathrm{inf}}; \gamma) - R(H_{\mathrm{inf}}; \mathrm{Alk_T}) > 0$. The analogue equation for H_{sup}, with $\mathrm{Alk_{nWCinf}}$ replaced by $\mathrm{Alk_{nWCsup}}$ (cf. eqs. (15) and (16)) does not work if $\mathrm{Alk_T} - \mathrm{Alk_{nWCsup}} \leq 2[CO_3^{2-}]$. The newly derived asymptotic approximation for $\mathrm{Alk_{nWC}}([\mathrm{H}^+])$ for $[\mathrm{H}^+] \gg$ (see the *Mathematical and Technical Details* report in the Supplement) nevertheless provides a means to derive an upper bound. It is sufficient to chose H_{sup} such that

195    $$\frac{K_{\mathrm{W}}}{H_{\mathrm{sup}}} = \mathrm{Alk_T} - 2[CO_3^{2-}] - \mathrm{Alk_{nWCinf}} - \frac{\sum_i [\Sigma \mathrm{A}_{[i]}] K_{1,[i]}}{H_{\mathrm{sup}}}$$

where i denumbers the acid systems considered, except for the carbonate system, $[\Sigma \mathrm{A}_{[i]}]$ is the total amount of the acid i dissolved and $K_{1,[i]}$ is the first dissociation constant of the acid system i. This equation always has a solution and, taking into account that

$$\mathrm{Alk_{nWC}}([\mathrm{H}^+]) < \mathrm{Alk_{nWCinf}} + \frac{\sum_i [\Sigma \mathrm{A}_{[i]}] K_{1,[i]}}{[\mathrm{H}^+]},$$

200   which is valid for $[\mathrm{H}^+] > 0$, it is straightforward to show that $L(H_{\mathrm{sup}}; \gamma) - R(H_{\mathrm{sup}}; \mathrm{Alk_T}) < 0$ with this choice. Eq. (12), which is equivalent to $L(H; \gamma) - R(H; \mathrm{Alk_T}) = 0$ thus has one single root between H_{inf} and H_{sup}.

Case $\gamma > 0$

The third case is the most commonly encountered, and the most challenging. With $\gamma > 0$, $L([\mathrm{H}^+]; \gamma)$ has a minimum and the location of that minimum is a critical parameter in the analysis of this case. Let us denote the location of that minimum by

205 $H_{\min}$ and the value that L takes there by $L_{\min}$:

$$H_{\min} = \sqrt{\frac{K_W}{\gamma}} \quad \text{and} \quad L_{\min} = 2\sqrt{\gamma K_W} + 2[CO_3^{2-}].$$

There are two ranges of Alk_T values where firm conclusions can be drawn right away.

1. If $R(H_{\min}; Alk_T) > L_{\min}$, i. e., if $Alk_T > L_{\min} + Alk_{nWC}(H_{\min})$, eq. (12) has two distinct roots, since $R(H; Alk_T)$ is bounded. Furthermore, the roots — let us provisionally denote the lower one H_1 and the greater one H_2 — are such that

210 $H_1 < H_{\min}$ and $H_2 > H_{\min}$. $H_{\min}$ can thus be used as an upper bracket for H_1 and as a lower bracket for H_2. However, if $Alk_T - Alk_{nWCsup} > L_{\min}$, the abscissae of the intersection points P_{LL} and P_{LR} (see Fig. 2), which are solutions of

$$\gamma H + \frac{K_W}{H} = Alk_T - 2[CO_3^{2-}] - Alk_{nWCsup}$$

provide tighter brackets than $H_{\min}$.

2. If $Alk_T - Alk_{nWCinf} \leq L_{\min}$, i. e., if $Alk_T \leq L_{\min} + Alk_{nWCinf}$, eq. (12) does not have any roots.

215 For intermediate values of Alk_T, no firm quantitative statement regarding the root(s) of eq. (12) can be made a priori. As Alk_T decreases from $L_{\min} + Alk_{nWC}(H_{\min})$ to $L_{\min} + Alk_{nWCinf}$, eq. (12) will at first still have two roots, but both are greater than or equal to $H_{\min}$. At some intermediate value, $L([H^+]; \gamma)$ and $R([H^+]; Alk_T)$ become tangent. At this point, eq. (12) has one double root, which is the abscissa of that tangent point, $H_{\tan}$. $H_{\tan}$ is actually a universally valid separation limit between two roots, if there are any. For lower values of Alk_T, the problem does not have any solutions.

220 The limiting Alk_T value for which the two curves are tangent and the corresponding $H_{\tan}$ value can be calculated with a common algorithm to characterize a bracketed local minimum, such as Brent's algorithm (Brent, 1973). To start, we reconsider $L([H^+]; \gamma) - R([H^+]; A) = 0$ not as an equation in $[H^+]$ for given parameter value γ (or, equivalently, $[CO_3^{2-}]$) and A, but rather as an implicit definition for A as a function of $[H^+]$, for a given γ (here $\gamma > 0$). This implicit function definition can actually be solved explicitly here:

225 $A([H^+]) = L([H^+]; \gamma) + Alk_{ncW}([H^+]).$

Figure 3 shows how the two problems are related and which information can be derived from the analysis of $L([H^+]; \gamma)$ and $R([H^+]; A)$ to contribute to the solution of the minimization of $A([H^+])$. The determination of $H_{\tan}$ is costly, generally more costly even than the subsequent resolution of the pH equation itself. As mentioned right at the beginning of this section, there are extended ranges of Alk_T values for which the exact knowledge determination of $H_{\tan}$ is not indispensable. In these

230 situations $H_{\min}$ may be a sub-optimal but nevertheless sufficient separation limit for the roots (or equal to the double root itself), and cheap to calculate. If available, $H_{\tan}$ can be used as an upper bound for the lower and as a lower bound for the greater of the two roots. To start the minimization algorithm to derive $H_{\tan}$, we can use the three characteristic $[H^+]$ values from Fig. 3 as initial conditions. These are $H_{\min}$ together with the abscissae H_L and H_R of the intersection points between $L([H^+]; \gamma)$ and the horizontal line at $Alk_{\min} - Alk_{nWCinf}$, which are the roots of

235 $\gamma H^2 - (Alk_{\min} - 2[CO_3^{2-}] - Alk_{nWCinf})H + K_W = 0.$
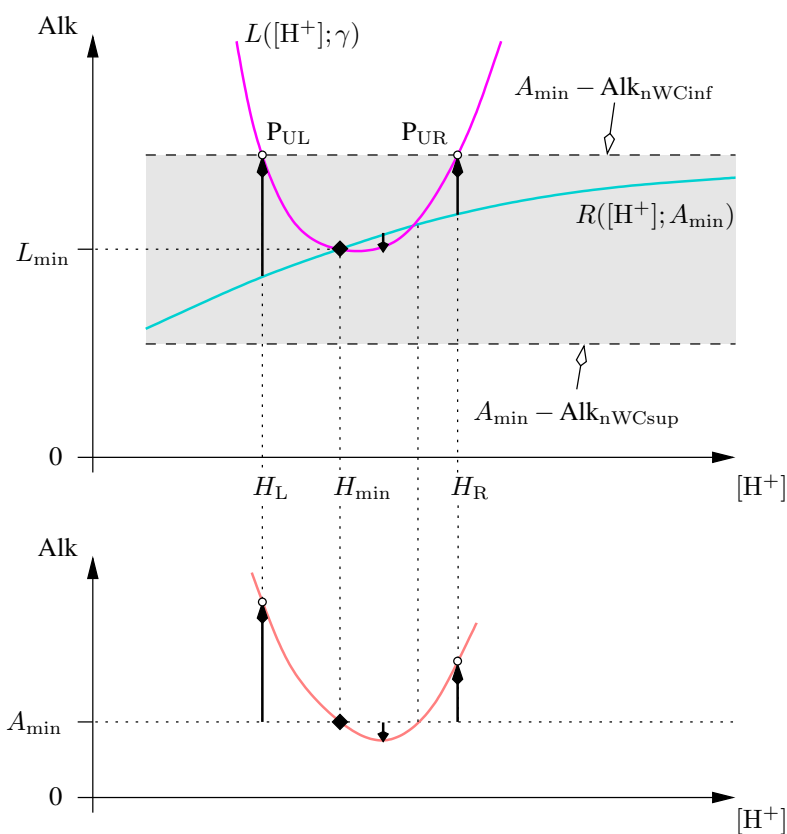
Figure 3. Determination of the A value for which the $L([H^+]; \gamma)$ and $R([H^+]; A)$ curves become tangent, or, equivalently, the lowest Alk_T value for which the equation $L([H^+]; \gamma) - R([H^+]; Alk_T) = 0$ has a solution. The top panel shows how relevant characteristic points can be derived by considering the particular $R([H^+]; A)$ curve that intersects $L([H^+]; \gamma)$ at its minimum. The bottom panel shows the locus of the solutions of $L([H^+]; \gamma) - R([H^+]; Alk_T) = 0$ in an $[H^+] - Alk_T$ graph, i.e., the curve $Alk_T = L([H^+]; \gamma) + Alk_{ncW}([H^+])$. Please notice that $A_{min} = L_{min} + Alk_{ncW}(H_{min})$ denotes the alkalinity value obtained for $[H^+] = H_{min}$, and not the minimum value of the curve shown on the bottom panel. See text for details.

By construction, $\text{Alk}_{\min} - \text{Alk}_{\text{nWCinf}} > L_{\min} = 2\sqrt{\gamma K_{\text{W}}} + 2[\text{CO}_3^{2-}]$. The discriminant of this quadratic equation is therefore strictly positive and the equation has two positive roots (their sum and their product are positive) as required. It is possible to show that the second derivative of $R([\text{H}^+]; A)$ with respect to $[\text{H}^+]$ is positive provided that the successive dissociation constants $K_{j,[i]}$ of the different acid systems (denumbered by i) resulting from the dissociation of an acid $\text{H}_{n_{[i]}}\text{A}_{[i]}$ are such that $K_{j,[i]} < \frac{1}{2}K_{j-1,[i]}, j = 2, \ldots, n_{[i]}$ — a very weak constraint as these constants generally generally differ by a few orders of magnitude. This has been verified to be the case for acid systems with $n_{[i]} = 1, \ldots, 12$ The underlying technical developments can be found in the *Mathematical and Technical Details* report in the Supplement. $R([\text{H}^+]; A)$ is thus concave, while $L([\text{H}^+]; \gamma)$ is convex for $\gamma > 0$. $A([\text{H}^+])$ thus has only one single local minimum comprised between H_{L} and H_{R}.

Once H_{tan} is known, the root brackets can be completed by the intersection points between $L([\text{H}^+]; \gamma)$ and the horizontal line at $\text{Alk}_{\text{T}} - \text{Alk}_{\text{nWCinf}}$ – corresponding to the P_{UL} and P_{UR} points on Fig. 2 with the grey band shifted down to include the minimum – i. e., by solving the same quadratic equation than for H_{L} and H_{R}, with $\text{Alk}_{\min}$ replaced by Alk_{T}. We have again $\text{Alk}_{\text{T}} - \text{Alk}_{\text{nWCinf}} > L_{\min}$ and the equation has two positive roots. With these brackets on the two roots, any safeguarded iterative procedure, such as those implemented in SOLVESAPHE can be used to find the two roots in a controlled way.

2.4 Initialisation: rationale

Since we have bracketing intervals for each of the root(s), we may always use the fall-back initial value $H_0 = \sqrt{H_{\text{inf}}H_{\text{sup}}}$. This value is, however, often far from optimal. The efficient initialisation strategy of Munhoven (2013) can be generalized and adapted to each of the three pairs. For each case, we chose the most complex Alk_{T} approximation that leads to a cubic equation. If the cubic polynomial behind that equation does not have a local minimum and a local maximum, we use the fall-back value. If such a local minimum and maximum exist, we use the quadratic Taylor expansion around the relevant extremum — this will normally be the maximum if the coefficient of the cubic term is negative, and the minimum if that coefficient is positive. If that quadratic does not have any positive roots, the fall-back initial value is used. The roots for that quadratic are then determined. For problems that have only one positive $[\text{H}^+]$ solution (Alk_{T} & CO_2, Alk_{T} & HCO_3^- and the Alk_{T} & CO_3^{2-} with $\gamma < 0$), we consider that root of the quadratic expansion that is greater than the greatest location of the two extrema: if that root is lower than H_{inf}, we use $H_0 = H_{\text{inf}}$; if it is greater than H_{sup}, we set $H_0 = H_{\text{inf}}$. For problems that have two positive $[\text{H}^+]$ solutions (Alk_{T} & CO_3^{2-} with $\gamma > 0$ and sufficiently great Alk_{T}), the initial value for determining the greater of the two $[\text{H}^+]$ solutions can be chosen exactly the same way; the initial value required to calculate the lower of the two $[\text{H}^+]$ solutions may be more tricky. If the location of the right-hand side extremum is too close to 0, the estimated root of the cubic may be negative. In this case, the quadratic fitted to left-hand extremum should be considered as well and the greater of its roots tested. Because of the symmetries of a cubic, that root can be calculated with a few extra additions only.

The developments for each of the three input pairs are presented in full detail in the *Mathematical and Technical Details* report in the Supplement.

3 Numerical Experiments

3.1 Reference Fortran 90 implementation

The SOLVESAPHE Fortran 90 library from Munhoven (2013) – hereafter SOLVESAPHE 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. `solve_at_general` and `solve_at_general_sec` are still available with the same API as in v. 1.
The instances in the new v. 2 are nevertheless only wrappers to `solve_at_general2` and `solve_at_general2_sec`
which are able to process problems that have two roots. They return the number of roots of the problem, as well as the actual
roots.

In the course of the development s related to the Alk_T & CO_2 pair the Newton-Raphson based algorithm showed a few
weaknesses. With the Alk_T & C_T pair that SOLVESAPHE v. 1 had been designed for, each non-water alkalinity term was
bounded, just like its derivative. Once CO_2 takes the role of C_T these favourable properties are lost: with $[CO_2]$ fixed, the
carbonate alkalinity term and its derivative with respect to $[H^+]$ become unbounded. Newton iterates can then change by large
amounts and floating point over- and underflow errors on the exponential correction became common. The rate of change
for Newton-Raphson iterates during each step was therefore limited to a factor of 100. With high CO_2 concentration values
prescribed, there was another loss of control on the iteration sequence that had not been encountered before. At some iterations,
most often at the first one, it happened that one of the two root brackets, say the upper one, was reduced to the iteration value.
In the next iteration, that same bound was exceeded by the trial Newton-Raphson iterate, which was then rejected and replaced
by a bisection iterate on the interval delimited by the previous iterate and the upper bracket. Since both were identical, the
bisection actually produced no variation and falsely led to convergence diagnosis. This has been fixed by changing the interval
whereon the bisection step is performed to that delimited by the lower and the upper brackets of the root, which are always
different.[1] The unbounded variations of the carbonate alkalinity term when one of the individual species was used instead of C_T
furthermore required to modify the stopping criterion for the iterations: in SOLVESAPHE v. 1 iterations are stopped as soon
as the relative difference between successive iterates falls below a set tolerance ϵ ($\epsilon = 10^{-8}$ by default). However, iterations for
Alk_T & CO_2 and for the greater root of Alk_T & CO_3^{-2} were prone to early termination with that stopping criterion, as iterates
only slowly changed due to the extreme gradients in the Alk_C term of the equation function. The stopping criterion is therefore
now based upon the width of the bracketing interval and iterations are stopped as soon as $(H_{max} - H_{min}) < \epsilon \frac{1}{2}(H_{max} + H_{min})$,
where H_{max} and H_{min} are resp. the upper and lower brackets of the root, which are continuously updated as iterations progress.
As a consequence of this change, the number of bisection steps considerably increased. In order to speed up convergence, most
bisection steps were replaced by regula falsi steps on $[H_{min}, H_{max}]$. Bisection steps are only used occasionally when either the
minimum or maximum root bracket gets updated too often in a row (three times by default) which indicates that the equation
values at H_{max} and H_{min} have strongly different magnitudes. Unfortunately, the number of iterations required for the original
SOLVESAPHE pair Alk_T & C_T increase with this stopping criterion, without any appreciable gain in precision (compare,

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[1]Both corrections have been backported to the v. 1 branch of SOLVESAPHE and are included in v. 1.1 in the SOLVESAPHE archive on Zenodo
(DOI:10.5281/zenodo.3752250).

		SW1		SW2		SW3		SW4	
	scale	min	max	min	max	min	max	min	max
Alk_T/[meq/kg]	linear	2.20	2.50	2.20	3.50	-1	5	0	1.5
C_T/[mmol/kg]	linear	1.85	2.45	1.85	3.35	0	6	0	1.2
$[CO_2]$/[mol/kg]	log.	10^{-6}	10^{-3}	10^{-7}	10^{-3}	10^{-14}	10^{-2}	10^{-12}	10^{-3}
$[HCO_3^-]$/[mmol/kg]	linear	1.20	2.40	0.60	3.20	0	5	0	1
$[CO_3^{2-}]$/[mol/kg]	log.	10^{-5}	10^{-3}	10^{-6}	10^{-3}	10^{-14}	10^{-2}	10^{-9}	10^{-3}

Table 1. Ranges of variation for the input variables for the SW1, SW2 and SW3 test cases. Experiments always considered Alk_T and either one of C_T, $[CO_2]$, $[HCO_3^-]$ or $[CO_3^{2-}]$.

e. g., the number of iterations from Fig. 3b and the residuals from Fig. 1d in Munhoven (2013), with the number of iterations
300 required here as reported on Fig. 5 for SW3 and the synthetic overview of the equation residuals reported in Tables S2 and
S3 in the *Additional Results* in the Supplement). For modelling purposes, where Alk_T & C_T is generally the relevant pair
of data, SOLVESAPHE v. 1 remains the most efficient choice. Tests have shown that the two safe-guarded algorithms from
SOLVESAPHE v. 1 typically require 40–45% less computing time than their new v. 2 counterparts.

Finally, as explained above, some Alk_T & CO_3^{2-} combinations require the solution of an auxiliary minimisation problem.
305 For this purpose, Brent's algorithm was implemented into SOLVESAPHE (translated to Fortran 90 from the Algol 60 version in
Brent (1973, sect. 5.8), taking into account the author's errata reported on https://maths-people.anu.edu.au/~brent/pub/pub011.
html and his modifications to the original algorithm as implemented in https://www.netlib.org/go/fmin.f).

3.2 Results and discussion

3.2.1 Test cases

310 Results from the three test cases SW1, SW2 and SW3 from Munhoven (2013) were used to define ranges of CO_2, HCO_3^- and
CO_3^{2-} concentrations to drive the test case experiments (see Figs. S1–S4 in the *Additional Results* in the Supplement). For
the sake of simplicity, we keep the corresponding denominations here. A supplementary 'SW4' was added for brackish water
(with $S = 3.5$). For CO_2 and CO_3^{2-}, which are most conveniently handled on a logarithmic scale, the representative ranges
were adapted so that the range endpoints are integer powers of ten. The adopted ranges and scales are reported in Tab. 1. Each
315 of the tests cases is complemented with temperature, salinity and pressure conditions for four typical environments (surface
cold, surface warm and deep cold seawater, as well as surface brackish water.
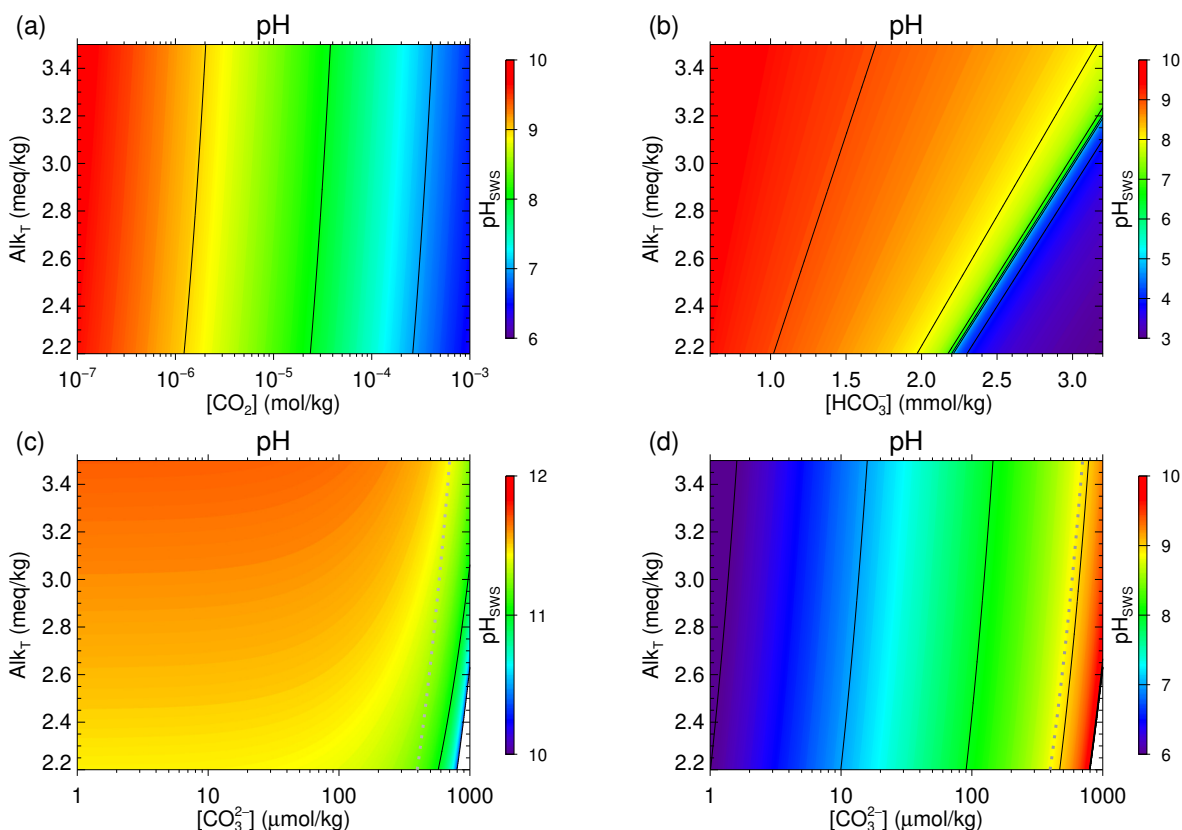
Figure 4. pH distributions for the SW2 test case under cold surface conditions ($T = 273.15\,\mathrm{K}$, $S = 35$ and $P = 0\,\mathrm{bar}$), obtained with `solve_at_general2_sec`: (a) Alk_T & CO_2; (b) Alk_T & HCO_3^-; (c) the lower $[H^+]$ root (higher pH root) of Alk_T & CO_3^{2-}; (d) the greater $[H^+]$ root (lower pH root) of Alk_T & CO_3^{2-}. The thick grey dashed line in (c) and (d) shows the critical limit above which the Alk_T & CO_3^{2-} always has two roots. Below this limit further calculations are required to determine the number of solutions. More details are given in the text and in the Supplement. Please notice the different scales on the horizontal axes and for the pH colour coding in the four panels.

3.2.2 Results

While all the test cases have their specific relevance, we are going to focus on SW2 for most of our discussion here. SW2 covers currently observed sea-water samples, thus encompassing SW1, and conditions expected to occur over the next 50,000
320 years as derived from simulation experiments carried out with MBM-MEDUSA (Munhoven, 2009). A wider selection of results also for the other cases presented in the *Additional Results* in the Supplement. pH distributions for the SW2 test case are shown on Fig. 4.

The difficulties posed by Alk_T & CO_2 that were at the origin of most of the amendments to the solver algorithms show up in the histograms for the number of iterations required to reach convergence shown on Fig. 5 for `solve_at_general` which
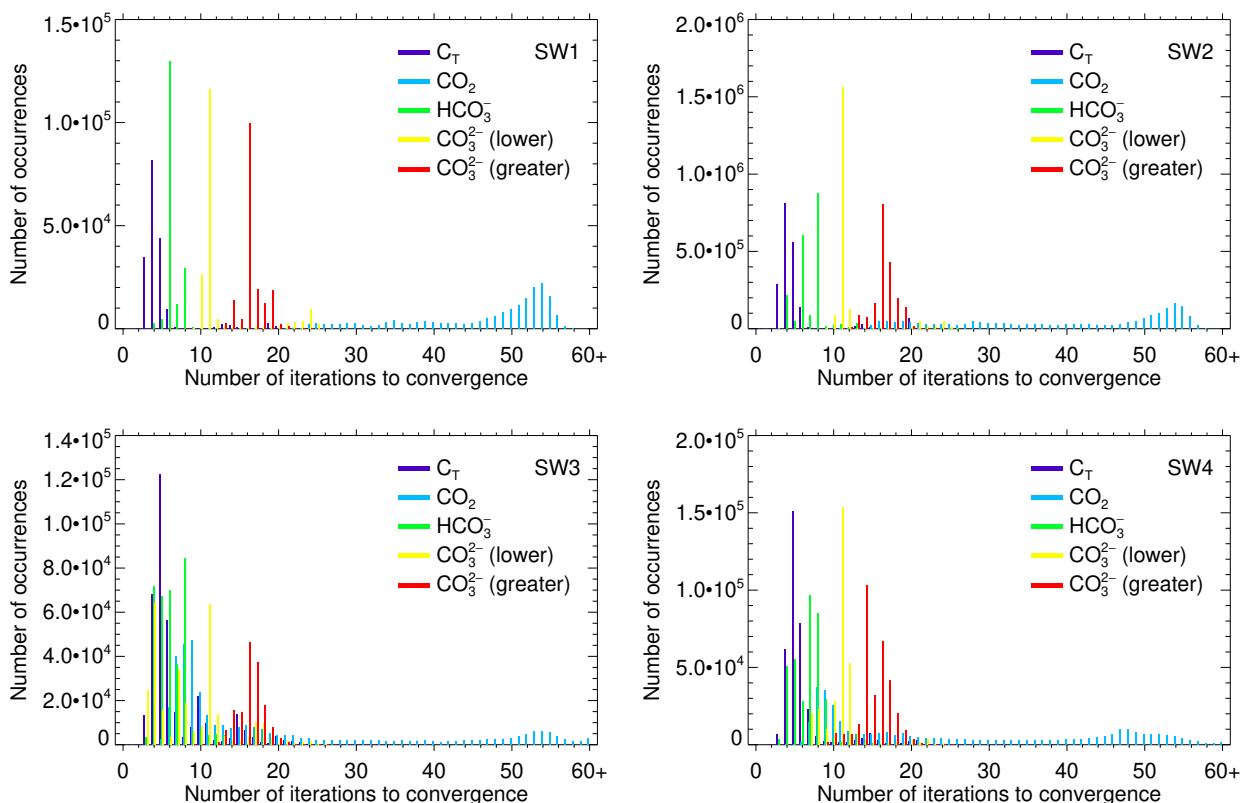
Figure 5. Number of iterations to convergence required by the various data pairs (separately for the lower and the greater $[H^+]$ roots of the Alk_T & CO_3^{2-}), for each of the four test cases, carried out with `solve_at_general` (using a hybrid Newton-Raphson–regula falsi–bisection method). The absolute maximum numbers of iterations were 58, 58, 68 and 66, for SW1 to SW4, resp.

325 uses the hybrid Newton-Raphson–regula falsi–bisection scheme and on Fig. 6 for `solve_at_general_sec` which uses the hybrid secant–regula falsi–bisection scheme. With both solvers, Alk_T & CO_2 problems require in general more iterations to conclude than the other three pairs. This is especially pronounced with `solve_at_general` (Fig. 5), where a considerable fraction of the Alk_T & CO_2 samples require 45 to 55 and more iterations. In comparison, Alk_T & C_T samples typically require about four to eight iterations for naturally occurring compositions, and only in some rare instances more than twenty for the

330 extreme SW3. The other pairs range between these two, Alk_T & HCO_3^- coming closest to Alk_T & C_T.

Finally, Figs. 5 and 6 demonstrate the superiority of `solve_at_general_sec` over `solve_at_general`. All in all, the former requires only one fourth to one half of the number of iterations than the latter, and it produces root approximations characterised by equation residuals that are up to seven orders of magnitude lower than those obtained with the former (see Tabs. S2 and S3 in the *Additional Results*).
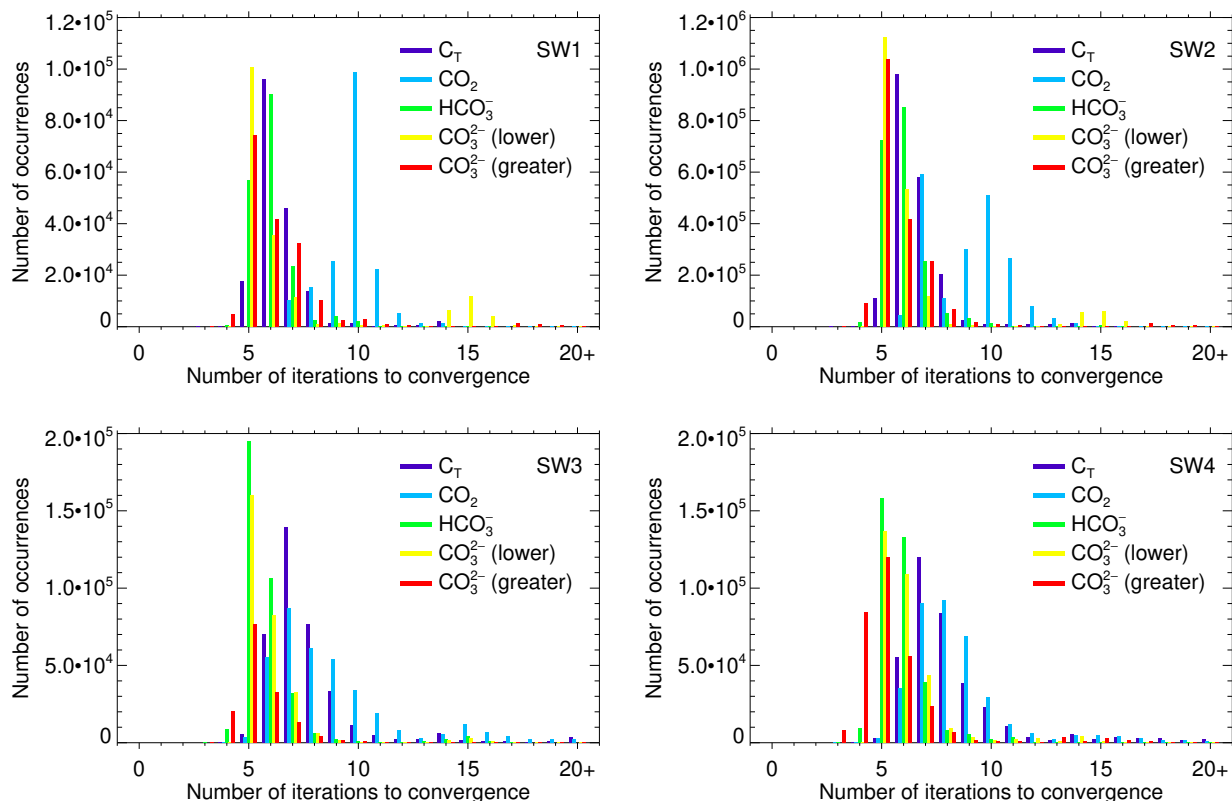
Figure 6. Number of iterations to convergence required by the various data pairs (separately for the lower and the greater $[\mathrm{H}^+]$ roots of the Alk_T & CO_3^{2-}), for each of the four test cases, carried out with `solve_at_general_sec` (using a hybrid secant–regula falsi–bisection method). The absolute maximum numbers of iterations were respectively 22, 23, 29 and 27, for SW1 to SW4, resp.

335   All these observations are also reflected in the execution times of the two solvers. The Newton-Raphson based solver takes more than five times as much time for the SW2 test case with Alk_T & CO_2 than with Alk_T & C_T; for Alk_T & CO_3^{2-} it takes four times as much (for both roots though). For Alk_T & HCO_3^-, the difference is only 20%. With the secant based method, the picture is completely different: Alk_T & CO_2 takes only about 30% more time than Alk_T & C_T, Alk_T & CO_3^{2-} twice as much, whereas Alk_T & HCO_3^- executes even about 5% faster. For the Alk_T & CO_2 pair of input data the difference between the two

340 solvers is greatest: the secant based one takes less than one fourth of the time taken by the Newton-Raphson based one.

     Another key factor that influences the execution times is the initialisation scheme, although the comparisons are not as clear-cut as in Munhoven (2013). Safe initialisation with the geometric mean of the root brackets (the fall-back initialisation value mentioned in Sect. 2.4) results in 40–60% increases of the execution times for the Alk_T & C_T and the Alk_T & HCO_3^- input pairs, compared to the standard cubic polynomial one. Similar increases are obtained with a constant uniform $p\mathrm{H} = 8$
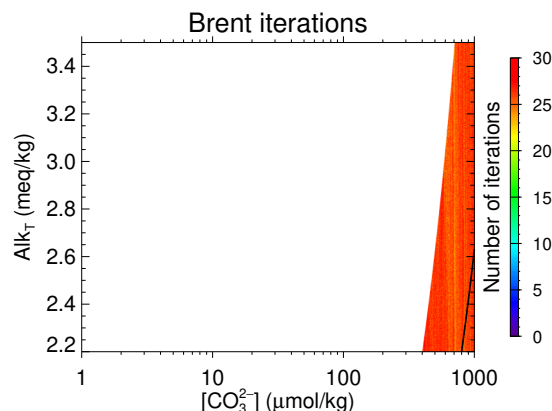
Figure 7. Number of iterations required by Brent's algorithm in the SW2 test case to solve the auxiliary minimisation problem whose solution determines the number of roots of the Alk_T & CO_3^{2-} pair and also provides the separation between the two roots The white areas covers the region where the solution of the minimisation problems is not required as Alk_T is sufficiently high so that there were two roots). The black line in the lower right corner traces the limit between regions with two roots and without roots – cf. Fig. 4c.

345   initialisation. For Alk_T & CO_2 and Alk_T & CO_3^{2-}, the differences are much smaller and range between a decrease or an increase of up to 5%. With these two, the quality of the root brackets seems to be more critical than the initial value.

In the analysis in section 2.3.1, two characteristic thresholds for Alk_T have been made out for $\gamma > 0$: an upper one at $L_{min} + Alk_{nWC}(H_{min})$, above which the problem always has two $[H^+]$ solutions, and a lower one at $L_{min} + Alk_{nWCinf}$, below which the problem does not have any solution at all. For intermediate values of Alk_T it is necessary to determine H_{tan} and

350   Alk_{tan} to find out how many roots the problem has, and, in case there are two, where the separation between them lies. The minimisation procedure required to determine H_{tan} is computationally expensive as can be seen on Fig. 7. The most probable number of iterations is in all cases 25, the median number is 27–28, due to the skew-symmetric nature of the distribution of the number of iterates (not shown). The subsequent computation of the roots is much cheaper: for the lower root, the secant based algorithm most probably takes five iterations, and only occasionally 15–16, and for the greater root, most probably four

355   and only rarely more than nine. The total number of samples in the SW2 test case is 1.95 million. 10,500 (0.54%) of these do not have any root for the Alk_T & CO_3^{2-} pair and the solution of the minimisation problem is required for 173,445 samples (8.89%), because H_{tan} is required to separate the two roots. The lower threshold essentially turns out as useless: it ranges at about $-28\,meq/kg$. This is is due to the hydrogen sulphate acid system which strongly dominates the Alk_{nW} minimum in seawater, because of the high total sulphate concentration in sea-water ($S_T \simeq 28\,mmol/kg$). For carbonate ion concentrations

360   below $400\,\mu mol/kg$, i.e., for most of the naturally occurring waters, the Alk_T & CO_3^{2-} problem will always have two roots and the solution of the auxiliary minimisation problem is not required to characterise them.

4 Conclusions

The approach adopted in SOLVESAPHE (Munhoven, 2013) to safely determine carbonate speciation in particular, and speciation calculations of mixtures of acids in aqueous solution in general, knowing only the total concentrations of the different acid systems and the total alkalinity of the system was adapted and extended here to use $[CO_2]$, $[HCO_3^-]$ and $[CO_3^{2-}]$ instead of the total inorganic carbon concentration, C_T. The rationale can be entirely transposed to these three pairs: (1) the amended alkalinity-pH equations for Alk_T & CO_2 and for Alk_T & HCO_3^- still have one and only one positive solution while Alk_T & CO_3^{2-} may have no solution, or one or two; (2) intrinsic brackets that only depend on a priori available information can be derived for the root of the Alk_T & CO_2 and Alk_T & HCO_3^- problems, as well as for the two roots of Alk_T & CO_3^{2-} problems that may have to be solved for naturally occurring sample compositions. More uncommon but physically realistic Alk_T & CO_3^{2-} problems may additionally require the solution of an auxiliary minimisation problem to determine the threshold Alk_T value below which the problem does not have any roots and above which it has two of them. The solution of this problem also provides a separation value of the two roots. To our best knowledge, SOLVESAPHE is the first package to offer a complete solution of the Alk_T & CO_3^{2-} problem, autonomous above all.

The two safeguarded numerical solvers from SOLVESAPHE v. 1 have been adapted to allow for the solution of problems that may have up to two roots. The Newton-Raphson–bisection based solver required extensive modifications for the reliable solution of the numerically far more challenging Alk_T & CO_2, Alk_T & HCO_3^- and Alk_T & CO_3^{2-} problems. Most bisection steps have been replaced by regula falsi steps for increased convergence speed. The secant–bisection solver only required minimal adaptations. A Fortran 90 reference implementation, SOLVESAPHE v. 2, was prepared and used to evaluate the performances of the different methods for solving four benchmark problems. While the secant–bisection method was already slightly superior to the Newton-Raphson–bisection method in SOLVESAPHE v. 1, that advantage has now become overwhelming: in SOLVESAPHE v. 2, it typically requires two to four times less iterations, and for the newly handled pairs, the equation residuals are orders of magnitude lower than the Newton-Raphson–regula falsi–bisection based solver (typically of the order of $10^{-19} - 10^{-18}$ compared to $10^{-13} - 10^{-12}$).

For carbonate speciation problems posed by Alk_T and either one of $[CO_2]$, $[HCO_3^-]$ or $[CO_3^{2-}]$ the secant based routine from SOLVESAPHE v. 2, `solve_at_general2_sec`, is thus clearly the method of choice; for calculations on the basis of Alk_T & C_T, both `solve_at_general` and `solve_at_general_sec` from SOLVESAPHE v. 1 will perform better, although the secant based solver is marginally faster, once again.

Code availability. All the Fortran 90 codes of SOLVESAPHE v. 1 series are available from Zenodo under DOI:10.5281/zenodo.3752250 for use under the GNU Lesser General Public Licence Version 3 (LGPLv3) or later. The codes for v. 2 that are decribed in this manuscript are included in the Supplement and made available for use under the same licence.

Author contributions. GM did the mathematical analyses presented here, developed all the codes, carried out the numerical experiments, processed the results, produced the graphs and wrote the paper.

Competing interests. The author declares that there is no conflict of interest.

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Appendix A: The direct cases

For the sake of completeness, we provide here succinct "recipes" to calculate all the different carbonate system related variables, knowing two of them. Many of these were already known in the 1960s (see, e.g., Park (1969)). The *Guide to Best*
400 *Practices for Ocean CO_2 Measurements* (Dickson et al., 2007) lists the most commonly used pairs and furthermore includes procedures for selected triplets and quartets, for which not all of the equilibrium constants are required. In the following, we assume that there are direct and invertible relationships between $[CO_2]$ and the fugacity ($f CO_2$) or the partial pressure ($p CO_2$) of CO_2 and between pH and $[H^+]$ on any chosen pH scale. We therefore restrict ourselves to $[CO_2]$ and $[H^+]$.

In the following, the conditions for the existence of a solution are generally that the species concentrations, the H^+ and
405 DIC are strictly positive. In some instances, the input data must fulfil additional constraints that are, however, not always straightforward to quantitatively state a priori.

DIC & CO_2, DIC & HCO_3^-, DIC & CO_3^{2-} — (1) The species fraction for the given species concentration leads to a quadratic equation in $[H^+]$ that always allows for exactly one positive solution; (2) calculate the remaining two species concentrations from their respective species fraction; (3) Alk_T from eq. (1). In addition to the positivity of the species concentra-
410 tions, the following constraints must be met: $[CO_2] <$ DIC, $[HCO_3^-] <$ DIC and $[CO_3^{2-}] <$ DIC.

CO_2 & HCO_3^- — (1) $[H^+]$ from K_1; (2) $[CO_3^{2-}]$ from K_2; (3) C_T can be calculated from the three carbonate species concentrations; (4) Alk_T from eq. (1).

CO_2 & CO_3^{2-} — (1) $[HCO_3^-]$ from $[HCO_3^-]^2 = K_1/K_2[[CO_2][CO_3^{2-}]$; (2) C_T from the three carbonate species concentrations; (3) $[H^+]$ from K_1 or K_2; (4) Alk_T from eq. (1).

415 **HCO_3^- & CO_3^{2-}** — (1) $[H^+]$ from K_2; (2) $[CO_2]$ from K_1; (3) C_T from the three carbonate species concentrations; (4) Alk_T from eq. (1).

CO_2 & H^+ — (1) calculate $[HCO_3^-]$ from K_1; (2) calculate $[CO_3^{2-}]$ from K_2; (3) C_T from the three carbonate species concentrations; (4) Alk_T from eq. (1).

HCO$_3^-$ & H$^+$ — (1) calculate [CO$_2$] from K_1; (2) calculate [CO$_3^{2-}$] from K_2; (3) C_T from the three carbonate species concentrations; (4) Alk$_T$ from eq. (1).

CO$_3^{2-}$ & H$^+$ — (1) calculate [HCO$_3^-$] from K_2; (2) calculate [[CO$_2$] from K_1; (3) C_T from the three carbonate species concentrations; (4) Alk$_T$ from eq. (1).

Alk$_T$ & H$^+$ — (1) C_T from eq. (2); (2) individual species concentrations from the species fractions.

As illustrated on Fig. 1c–e in section 2.3, there are Alk$_T$ & H$^+$ combinations that lead to physically unrealistic negative Alk$_C$. The shape of the blank area depends on the non-carbonate contributors to the total alkalinity. In practice, such incompatible combinations are unlikely to arise from measurements, except if the adopted set of A$_T$ contributors is inappropriate.

C$_T$ & H$^+$ — Individual species concentrations from the species fractions; Alk$_T$ from eq. (1).

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