Supplementary Material to

"The Mathematics of the Total Alkalinity–*p*H Equation: Pathway to Robust and Universal Solution Algorithms"

Additional Results

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Abstract

We provide here additional graphs and results to complete the test cases presented in the main paper. Results essentially cover additional temperature and pressure conditions. In addition, we provide two more test cases: the Random Time Step (RTS) series and the Random Total Concentration (RTC) series. The first series provides a statistical analysis of the idea of Follows et al. (2006), who suggest that one single fixed-point iteration with the method that we call the Iterative Carbonate Alkalinity Correction (ICAC) in the main paper at any given time step in a biogeochemical model simulation experiment already provides a sufficiently accurate proton concentration to calculate acceptable pCO_2 values. The second test series is meant to test the robustness of the different methods when used with data that differ considerably from the typical present-day situation.

In addition, we establish the recursion formulae for the coefficients of the polynomials in $[H^+]$ at the numerator of the derivative of the alkalinity component of any given acid system with respect to $[H^+]$. These formulae are useful to directly calculate the polynomials that make up the rational functions in the total alkalinity-*p*H aquation.

1 Additional Tests

1.1 Simulation of Random Time Steps (RTS)

This test case is is an add-on to the test cases SW1, SW2 and SW3 from the main paper.

It is common practice in simulation experiments to start iterative pH calculation schemes with the pH value at the previous time step. Here we analyse the efficiency of that approach. We simulate this time-stepping framework by initialising the calculation scheme for each C_T-Alk_T pair on the grids with pH values randomly distributed around the actual root previously calculated. We adopt a normal distribution, with a standard deviation of 0.1. One hundred instances are considered for each pair. We focus on three aspects for our analysis:

1. the total computation time;
2. the average error (in absolute value) of the first iterate;
3. the average error (in absolute value) of the third iterate.

Computation time is used here as an index to compare the for computational cost of the different methods used. The second of these analyses focuses on the idea of Follows et al. (2006) who suggest that one iteration of the fixed-point ICAC is enough to derive sufficiently accurate pCO_2 estimates, if the iteration at one time-step is initialised with the result from the preceding one (where it is expected that pH values vary by less than 0.1 from step to step). With Bacastow's method the first secant iteration, which is the third iteration in the scheme, is expected to provide a significant improvement over the first two ones (reasons for this will become clear below). `driver_at_logging.f90` was also used for this analysis.

1.2 Random Total Concentrations (RTC)

The aim of this series is to test the robustness of the different algorithms. It represents a highly demanding stresstest for the solvers. We chose randomly generated values of total alkalinity, total carbonate, total borate, total phosphate, total silicate, total ammonium, and total sulphide around chosen central values. All random values are generated by adopting $A_T = A_{T,0} \times 10^{rn_o}$, where $A_{T,0}$ stands for the central value of any of the acid concentrations considered in Alk_T or for Alk_T itself, r is a normally distributed random variate, with zero mean and unit variance, and n_o is the number of order of magnitudes by how much the concentrations may vary. Values of 0.01, 0.05, 0.1, 0.5, 1, 2, and 3 were taken for n_o.

Two variants are considered for the central values:

RTC1 – $Alk_T = 2.4\,\mathrm{mmol/kg}$, $C_T = 2.2\,\mathrm{mmol/kg}$, $P_T = 0.5\,\mathrm{mmol/kg}$, $Si_T = 5.0\,\mu\mathrm{mol/kg}$, $[NH_4]_T = 0.0\,\mu\mathrm{mol/kg}$ and $[H_2S]_T = 0.0\,\mu\mathrm{mol/kg}$; S_T, F_T and B_T are calculated from salinity;

RTC2 – all central values are set to 1 mmol/kg. As we are only interested in testing for robustness in this test, we accept the inconsistency that arises from using different sulphate and fluoride concentrations in the thermodynamic constants (which are still directly derived from salinity) and in the samples themselves.

As previously, we adopt a temperature of 275.15 K, a salinity of 35 and apply a pressure of 0 bar. As initial values we furthermore either use the cubic equation based initialisation or randomly generated initial values for $[H^+]$, from uniformly distributed *p*H values between 0 and 14. One million instances are simulated each time for statistical analysis. These tests were done with `driver_at_random.f90` provided in the companion Fortan 90 codes.

2 Results

2.1 Random Total Concentrations (RTC)

Both `general` and `general_sec` passed the two Random Total Concentrations (RTC) tests without a single failure; failure fractions for the `icacfp` and `bacastow` are reported in Table S1.

2.2 Random Time Step Simulation (RTS)

2.2.1 Execution times

The Random Time Step (RTS) timings show a similar exectution time picture than the SW1 SW2 and SW3 results (see Table S2, and compare with Table 1 from the main paper). Bacastow's method is once again the fastest, but the advance on `general_sec` is much smaller than before. `icacfp` remains the slowest; `ocmip` here completes the three test series, but still remains about 70% slower than `bacastow`, and about 60–65% slower than `general_sec`.

2.2.2 First and Third Iterates: Comparative Errors

Figure S1 shows the average relative error of the first iterate obtained with `general` and by `icacfp`, for test case SW2. Close inspection shows that, for typical present-day seawater samples,which would range in the lower left corner of the domain, the error of the cubic initialisation is smaller than that of `icacfp` by a factor of three to ten. Follows et al. (2006) advocated that the first iterate in a time-dependent simulation experiment, obtained by the fixed-point ICAC method that is at one time step started with the value at the previous time-step, is sufficient to yield acceptable pCO_2 values. Obviously, the initial value designed for the cubic polynomial equation provides, on average, a better estimate of $[H^+]$ than this first iterate.

With Bacastow's method, the two first iterates are the same as with the plain fixed-point ICAC; the third iterate is the first original one provided by that method. We therefore also analyse the quality of the third iterate for the

Table S1: Fraction of divergent iterations (in %) in the RTC1 and RTC2 test series for the fixed-point ICAC and Bacastow's methods, for cubic (cub) and random (rand) initialisation. The `general` and `general_sec` routines did not present a single failure to converge. n_o is the order of magnitude of the interval of changes for the total concentrations (see text).

	`icacfp`				`bacastow`			
	RTC1		RTC2		RTC1		RTC2	
n_o	cub	rand	cub	rand	cub	rand	cub	rand
0.01	0	37	100	100	0	37	100	94
0.05	<0.1	37	100	100	<0.1	37	99	94
0.1	2	40	99	100	1	39	88	93
0.5	39	64	77	94	30	62	68	91
1	49	71	80	93	39	69	71	91
2	69	81	88	95	55	75	82	92
3	80	87	92	96	68	80	87	93

Table S2: Execution times for the Random Time Step (RTS) simulations, normalized for each one of SW1, SW2, SW3 to the respective execution times of `general_sec`. Crosses ($\times$) indicate test series that were affected by divergences and could not be considered for time measurements. Figures were rounded to the nearest multiple of 0.01 (i.e., the order of the the largest standard deviation).

Routine	SW1	SW2	SW3
`general`	1.14	1.13	1.12
`general_sec`	**1.00**	**1.00**	**1.00**
`fast`	1.13	1.12	$\times$
`icacfp`	2.58	1.87	$\times$
`bacastow`	0.97	0.90	$\times$
`ocmip`	1.65	1.62	1.64

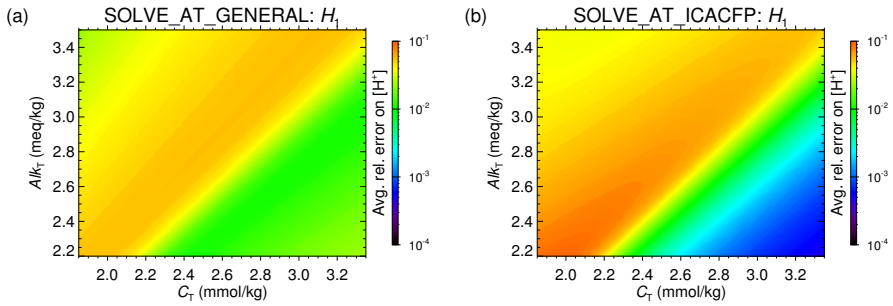

Figure S1: Average relative error (absolute values) of the first iterate (H_1) compared to the actual roots, derived from the 100 random time step simulations (RTS for SW2), for (a) `general` and (b) `icacfp`.

most important methods. Figure S2 shows the average relative error of that third iterate produced by `general`, `icacfp`, `bacastow` and `general_sec`. Again, `icacfp` has the largest errors over the range of present-day seawater compositions. `general_at_sec` globally presents the largest error. This is rather surprising, given the overall execution times of that method to final convergence. However, it should be noticed that the method uses a heuristic procedure for the second iterate (0.25 pH units away from the initial value, in the direction of the root), which in situations where the initial value is already close to the root significantly overshoot, requiring large corrections and thus possibly leading to large errors for the third iterate. The errors of the third `bacastow` iterate are only slightly greater than those of the third `general` iterate. Clearly, the errors on the third iterates are orders of magnitude smaller than those of the first iterate.

3 Additional Results for SWx Tests

3.1 Warm Surface Waters

Figures S3 to S8 show the same results as Figures 1 to 6 in the main paper, for warm surface waters ($S = 35$, $T = 298.15\,\mathrm{K}$ (25 °C) and $P = 0\,\mathrm{bar}$). Please refer to the main text for details about the various test cases mentioned. Notice also that in some instances, colour scales had to be modified in order to accommodate different ranges of variation.

3.2 Cold Deep Waters

Figures S9 to S14 show the same results as Figures 1 to 6 in the main paper, for deep cold waters ($S = 35$, $T = 275.15\,\mathrm{K}$ (2 °C) and $P = 300\,\mathrm{bar}$). Colour scales are the same as in the figures of the previous section, which may differ from those in the main paper.

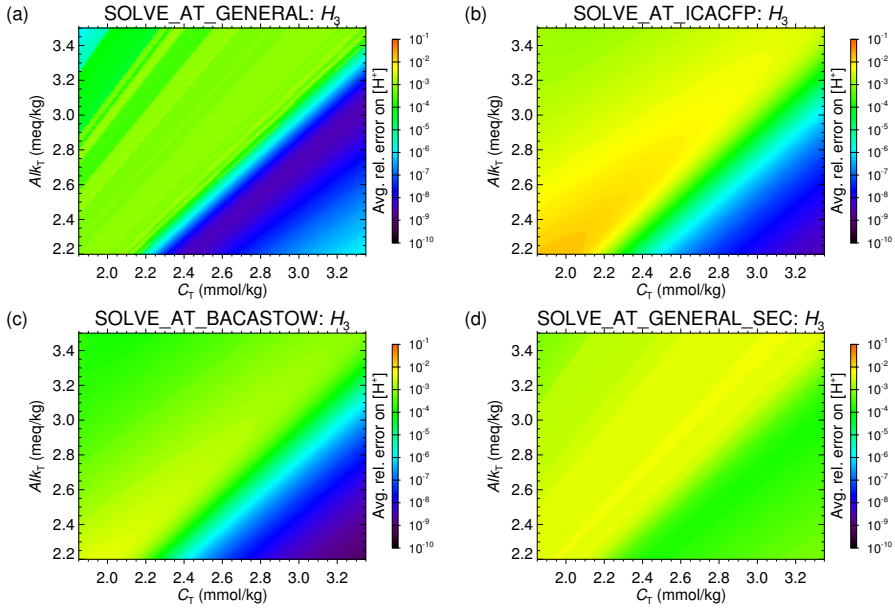

Figure S2: Average of the absolute values the relative error of the third iterate (H_3) compared to the actual roots, derived from the 100 random time step simulations (RTS for SW2), for (a) `general`, (b) `icacfp`, (c) `bacastow` with secant iterations on $[H^+]$ and (d) `general_sec`.

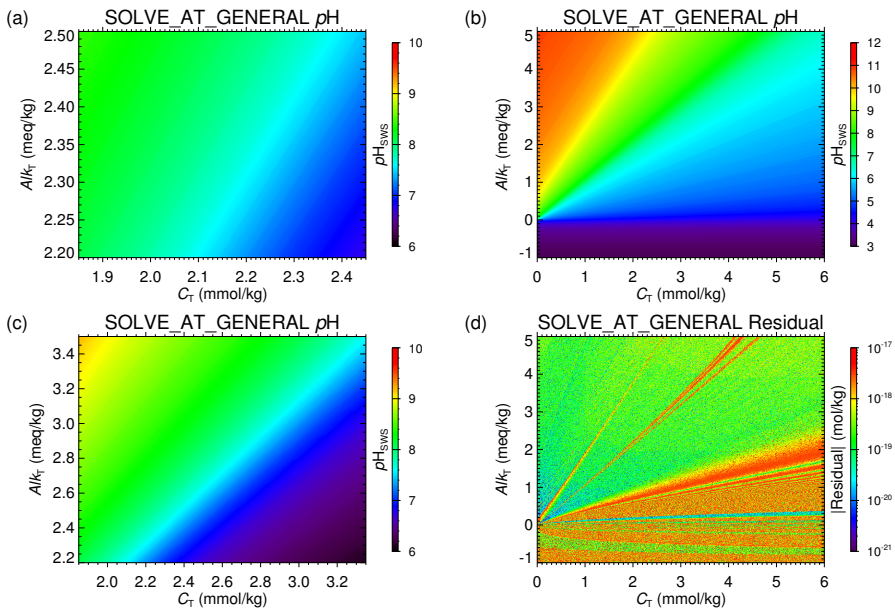

Figure S3: $p\mathrm{H}_{\mathrm{SWS}}$ values obtained for warm surface ocean water with the new universal algorithm (`general`) for test cases (a) SW1, (c) SW2 and (b) SW3 – please notice the extended colour scale. (d) Absolute value of the equation residual at the adopted root value, derived with that same algorithm started with the cubic-based initialisation to solve test case SW3. Applied convergence criterion: $|H_{n+1} - H_n|/H_n < 10^{-8}$.

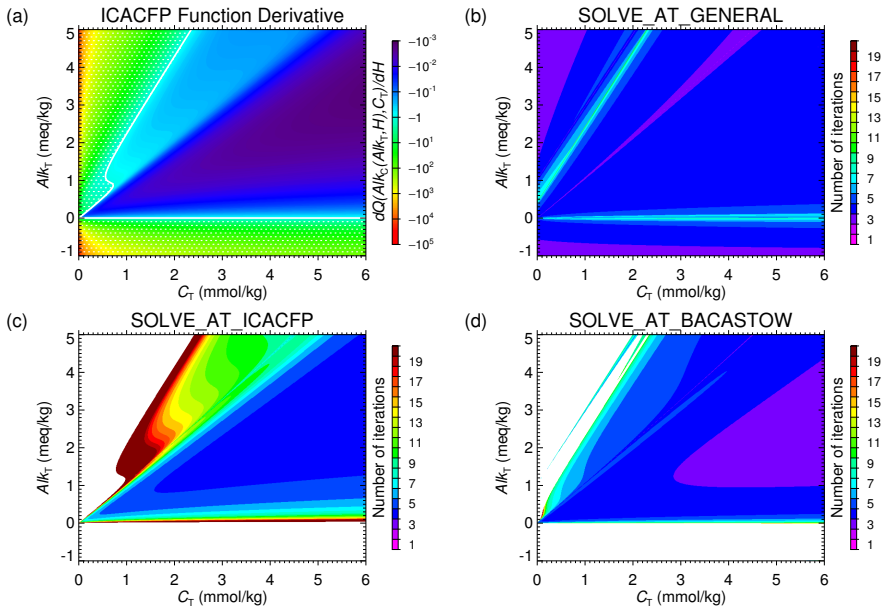

Figure S4: (a) Derivative with respect to H of the function underlying the ICAC methods, i.e., of the function Q given by equations (8) and (9) in the main paper that defines the recurrence $H_{n+1} = Q(Alk_{\mathrm{C}}(Alk_{\mathrm{T}}, H_n), C_{\mathrm{T}})$. The white line indicates where the derivative is equal to -1; in the stippled area, the derivative is strictly lower than -1. Also shown are the numbers of iterations required to meet the convergence criterion for (b) `general`, (c) `icacfp` and (d) `bacastow` with secant iterations on $[\mathrm{H}^+]$. White areas indicate no convergence or an excessive number of iterations ($n > 50$).

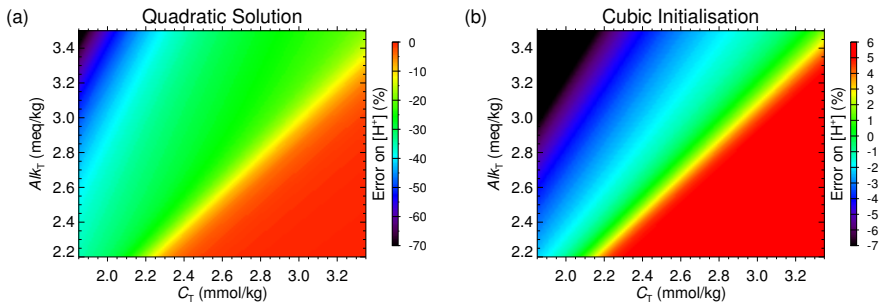

Figure S5: (a) Relative deviation (in %) of the solution of the quadratic (7) in the main paper, calculated by setting $Alk_{\mathrm{C}} = Alk_{\mathrm{T}}$, from the actual root of the complete system; (b) idem for the cubic polynomial based initial $[\mathrm{H}^+]$, calculated by setting $Alk_{\mathrm{CB}} = Alk_{\mathrm{T}}$. Please notice the strongly different colour scales. (Underlying data come from test case SW2).

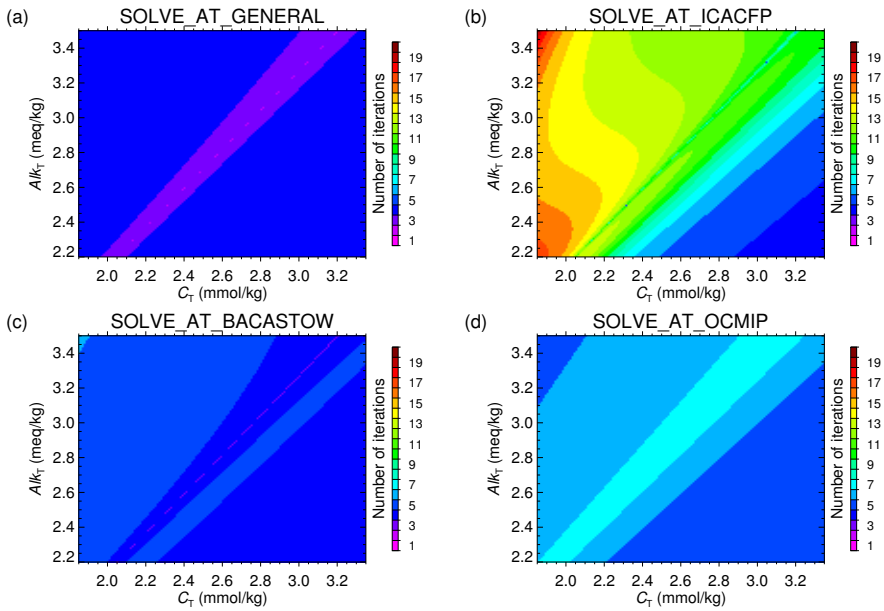

Figure S6: Number of iterations required by (a) `general`, (b) `icacfp`, (c) `bacastow` with secant iterations on $[H^+]$ and (d) `ocmip`, each one using the cubic-based initialisation procedure to solve test case SW2. Applied convergence criterion: $|H_{n+1} - H_n|/H_n < 10^{-8}$.

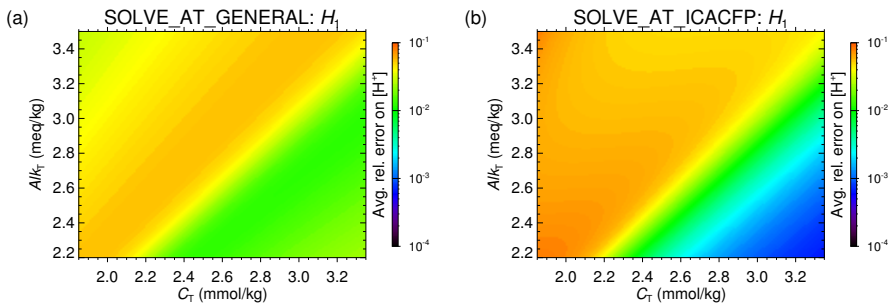

Figure S7: Average relative error (absolute values) of the first iterate (H_1) compared to the actual roots, derived from the 100 random time step simulations (RTS for SW2), for (a) `general` and (b) `icacfp`.

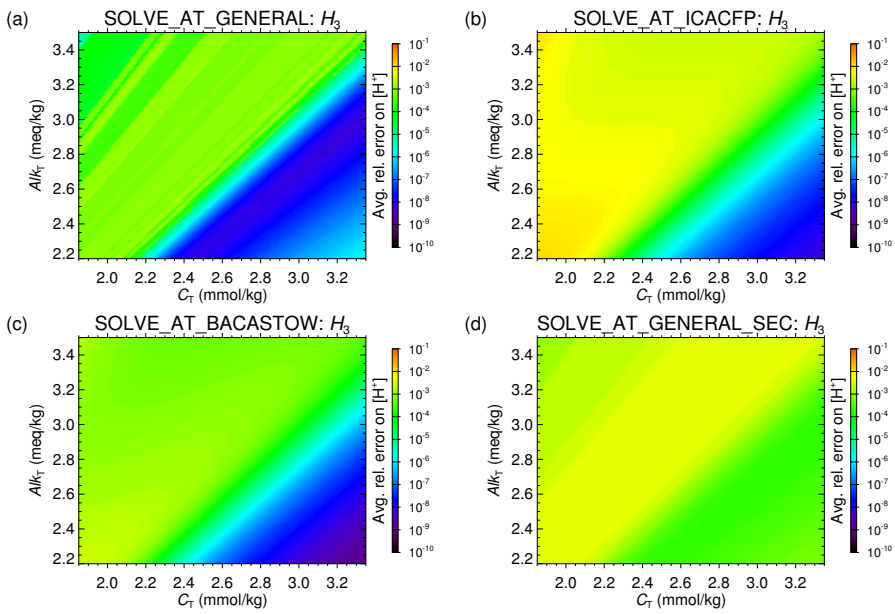

Figure S8: Average of the absolute values the relative error of the third iterate (H_3) compared to the actual roots, derived from the 100 random time step simulations (RTS for SW2), for (a) `general`, (b) `icacfp`, (c) `bacastow` with secant iterations on $[H^+]$ and (d) `general_sec`.

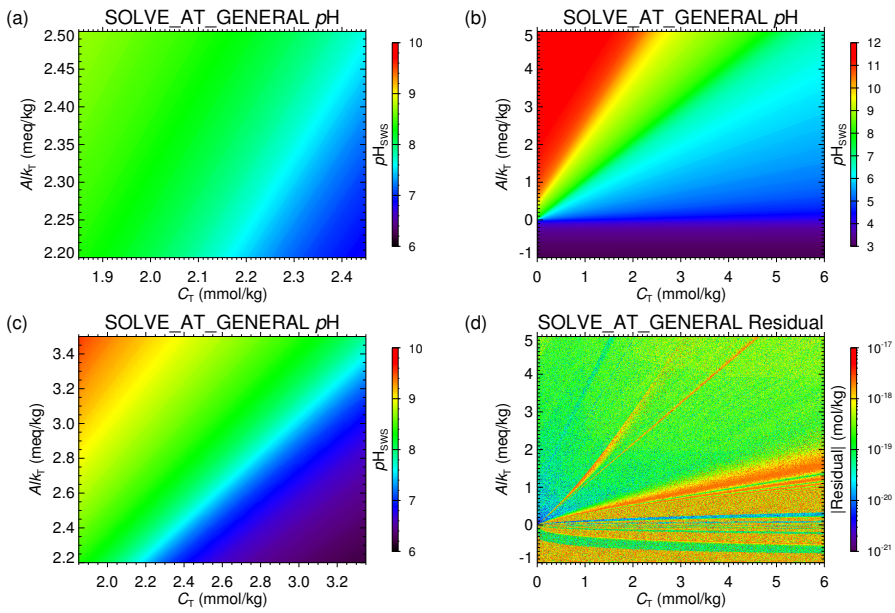

Figure S9: $p\mathrm{H}_{\mathrm{SWS}}$ values obtained for warm surface ocean water with the new universal algorithm (`general`) for test cases (a) SW1, (c) SW2 and (b) SW3 – please notice the extended colour scale. (d) Absolute value of the equation residual at the adopted root value, derived with that same algorithm started with the cubic-based initialisation to solve test case SW3. Applied convergence criterion: $|H_{n+1} - H_n|/H_n < 10^{-8}$.

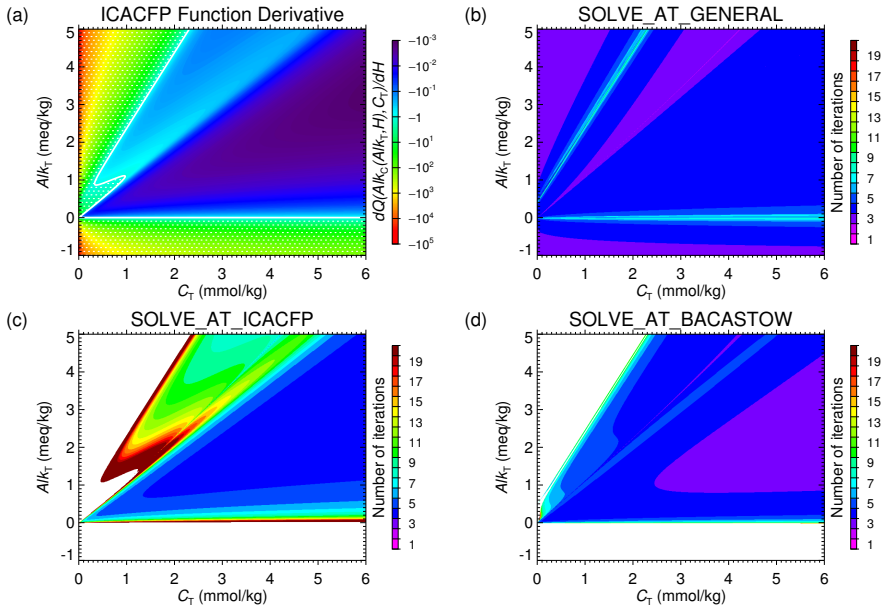

Figure S10: (a) Derivative with respect to H of the function underlying the ICAC methods, i.e., of the function Q given by equations (8) and (9) in the main paper that defines the recurrence $H_{n+1} = Q(Alk_{\mathrm{C}}(Alk_{\mathrm{T}}, H_n), C_{\mathrm{T}})$. The white line indicates where the derivative is equal to -1; in the stippled area, the derivative is strictly lower than -1. Also shown are the numbers of iterations required to meet the convergence criterion for (b) `general`, (c) `icacfp` and (d) `bacastow` with secant iterations on $[\mathrm{H}^+]$. White areas indicate no convergence or an excessive number of iterations ($n > 50$).

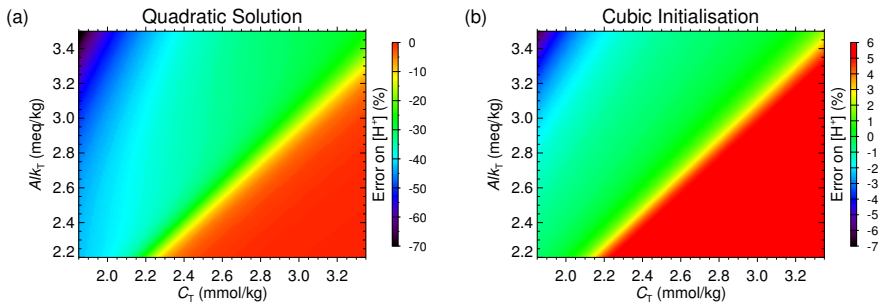

Figure S11: (a) Relative deviation (in %) of the solution of the quadratic (7) in the main paper, calculated by setting $Alk_{\mathrm{C}} := Alk_{\mathrm{T}}$, from the actual root of the complete system; (b) idem for the cubic polynomial based initial $[\mathrm{H}^+]$, calculated by setting $Alk_{\mathrm{CB}} := Alk_{\mathrm{T}}$. Please notice the strongly different colour scales. (Underlying data come from test case SW2).

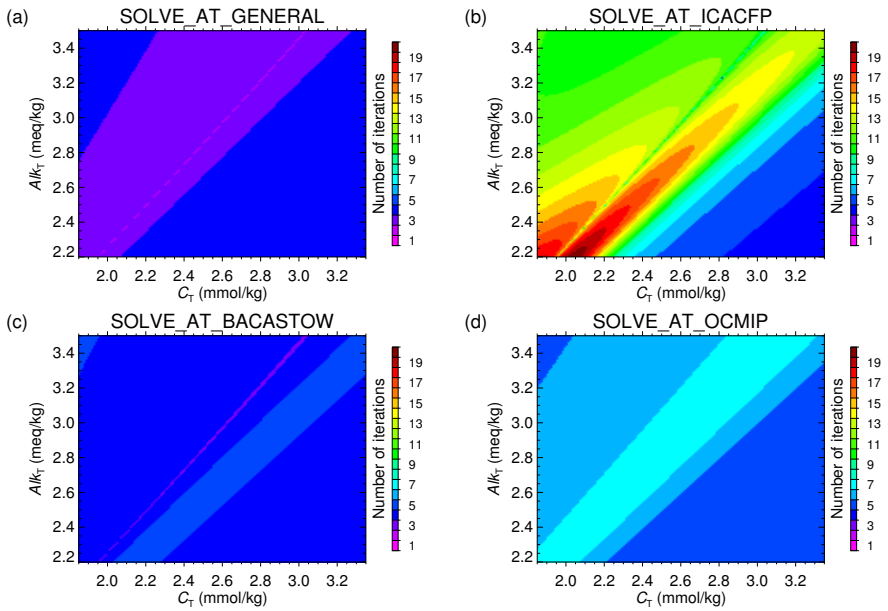

Figure S12: Number of iterations required by (a) `general`, (b) `icacfp`, (c) `bacastow` with secant iterations on $[H^+]$ and (d) `ocmip`, each one using the cubic-based initialisation procedure to solve test case SW2. Applied convergence criterion: $|H_{n+1} - H_n|/H_n < 10^{-8}$.

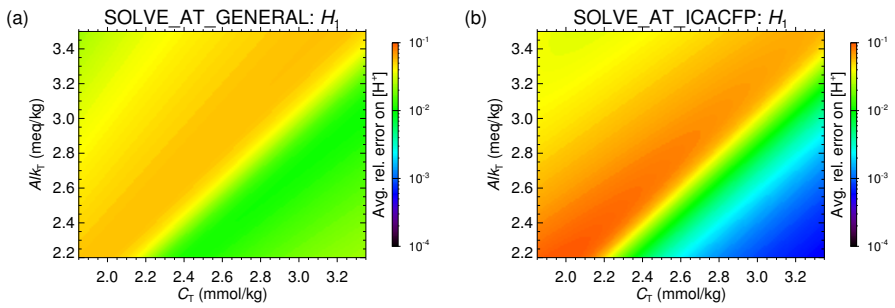

Figure S13: Average relative error (absolute values) of the first iterate (H_1) compared to the actual roots, derived from the 100 random time step simulations (RTS for SW2), for (a) `general` and (b) `icacfp`.

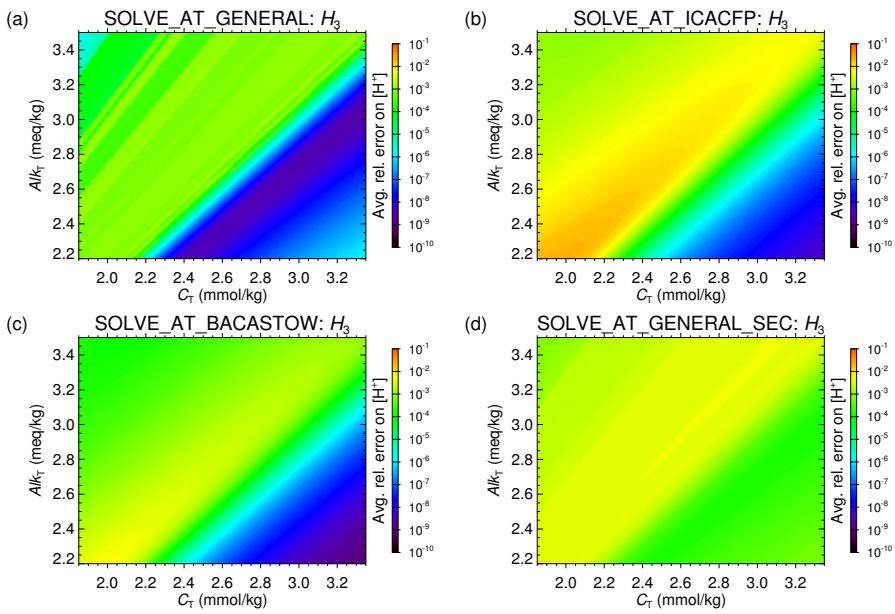

Figure S14: Average of the absolute values the relative error of the third iterate (H_3) compared to the actual roots, derived from the 100 random time step simulations (RTS for SW2), for (a) `general`, (b) `icacfp`, (c) `bacastow` with secant iterations on $[H^+]$ and (d) `general_sec`.

4 Derivative of alkalinity component expressions with respect to $[\mathrm{H}^+]$

In Appendix A in the main paper, we have established that

$$\frac{dAlk_\mathrm{A}}{d[\mathrm{H}^+]} = -A_\mathrm{T}\frac{DD_2 - D_1^2}{[\mathrm{H}^+]D^2}.$$

where

$$D = \sum_{j=0}^{n} \Pi_j [\mathrm{H}^+]^{n-j}, \quad D_1 = \sum_{j=0}^{n} j\Pi_j [\mathrm{H}^+]^{n-j}. \quad \text{and} \quad D_2 = \sum_{j=0}^{n} j^2\Pi_j [\mathrm{H}^+]^{n-j}.$$

It should be noticed that the numerator of the rational function that multiplies Alk_A is actually $(DD_2 - D_1^2)/[\mathrm{H}^+]$ and that the denominator is D^2. That was indeed the expression obtained for the numerator. It was obtained as the sum of two products between a polynomial and the derivative of a polynomial, which results in a polynomial.

We have furthermore shown by Lagrange's identity that

$$DD_2 - D_1^2 = \frac{1}{2}\sum_{j=0}^{n}\sum_{i=0}^{n} \Pi_i\Pi_j (i-j)^2 [\mathrm{H}^+]^{2n-i-j}.$$

This expression is first transformed to make the order of $[\mathrm{H}^+]$ clearly appear, by applying the index change $s = i + j$. This leads to

$$DD_2 - D_1^2 = \frac{1}{2}\sum_{j=0}^{n}\sum_{s=j}^{n+j} \Pi_j\Pi_{s-j} (s-2j)^2 [\mathrm{H}^+]^{2n-s}.$$

The actual expressions for the coefficients of the powers of $[\mathrm{H}^+]$ can be made apparent by swapping the order of summation. The required boundary information can be easily derived from the geometry of the area covered by the i and s indices. We obtain

$$\begin{aligned} DD_2 - D_1^2 \quad = \quad & \frac{1}{2}\sum_{s=0}^{n-1}\sum_{j=0}^{s} \Pi_j\Pi_{s-j} (s-2j)^2 [\mathrm{H}^+]^{2n-s} \\ & + \frac{1}{2}\sum_{j=0}^{n} \Pi_j\Pi_{n-j} (n-2j)^2 [\mathrm{H}^+]^{n} \\ & + \frac{1}{2}\sum_{s=n+1}^{2n}\sum_{j=s-n}^{n} \Pi_j\Pi_{s-j} (s-2j)^2 [\mathrm{H}^+]^{2n-s}. \end{aligned} \tag{1}$$

Additional symmetries could be made apparent, but this expression is sufficient to characterize $\frac{dAlk_\mathrm{A}}{d[\mathrm{H}^+]}$. Two simplifications are noteworthy:

1. the coefficient of the term in $[\mathrm{H}^+]^{2n}$ is zero (obtained for $s = 0$ in the first sum)

2. the constant term in the sum is zero as well (obtained for $s = 2n$).

As a consequence, the $[H^+]$ in the denominator of the derivative of Alk_A cancels out, reducing each power of $[H^+]$ in the expression for $DD_2 - D_1^2$ above by one unit, as expected by the above remark regarding the numerator of the rational function that multiplies Alk_A.

Table S3 provides the general recursion formulae for calculating the coefficients a_i of the polynomial $(DD_2 - D_1^2)/[H^+] = \sum_{i=0}^{2n-2} a_i [H^+]^i$, which represents the numerator of the rational function in $[H^+]$ that appears in the expression of the derivative of the alkalinity contribution of a generic acid H_nA (where n denotes the maximum number of protons that this acid may release into solution). The actual coefficients for the most common naturally encountered acids (i.e., $n = 1, 2, 3, 4$) are given in Table S4.

5 Conclusions

We have also produced a quantitative assessment of the idea of Follows et al. (2006), who advocate that in time-series simulations, a single iteration with the fixed-point ICAC method is sufficient at any time-step, if started from the previous timestep's pH. Our assessment is based upon the statistical analysis of 100 iteration series at each pair of C_T-Alk_T values of the test-case grids, initialised with random starting values normally distributed around the actual pH values for the pairs. We find that for common present-day conditions the average of the relative errors (in absolute value) for the first iterate of our random time series, is greater than the average of the cubic polynomial based starting procedure. One of the motivations of Follows et al. (2006) was, that adopting a single iteration only would ease the construction of the model adjoint. Since a fixed number of iterations would essentially preserve this advantage, we further analysed the quality of the third iterate, which is the first secant iterate with Bacastow's method. For the third iterate, the average of the relative errors (in absolute value) is about 1 to two orders of magnitude smaller than for the first one. However, the fixed point ICAC method `icacfp` is still performing worse than `bacastow` and `at_general`. Noting furthermore that `bacastow` offers, in the most common settings only five iterations at most to convergence, `at_general` even only four – the latter even offering with convergence guarantee – we find that fixed-point ICAC is not the most recommendable method. Bacastow's method is strongly preferable for conditions close to present-day; for strongly different conditions, the two new methods actually represent the only safe alternatives.

Acknowledgements

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Table S3: General recursive relationships defining the coefficients a_i of the polynomial $(DD_2 - D_1^2)/[\mathrm{H}^+] = \sum_{i=0}^{2n-2} a_i [\mathrm{H}^+]^i$, i.e, the numerator of $-\frac{dAlk_{\mathrm{A}}}{d[\mathrm{H}^+]}/[\Sigma A]$.

i	a_i
$2n-2$	$1^2\Pi_1\Pi_0$
$2n-3$	$2^2\Pi_2\Pi_0$
$2n-4$	$3^2\Pi_3\Pi_0 + 1^2\Pi_2\Pi_1$
$2n-5$	$4^2\Pi_4\Pi_0 + 2^2\Pi_3\Pi_1$
$2n-6$	$5^2\Pi_5\Pi_0 + 3^2\Pi_4\Pi_1 + 1^2\Pi_3\Pi_2$
$\vdots$	
$n-1$	$\frac{1}{2}\sum_{j=0}^{n} \Pi_j\Pi_{n-j}(n-2j)^2$
$\vdots$	
4	$5^2\Pi_{n-5}\Pi_n + 3^2\Pi_{n-4}\Pi_{n-1} + 1^2\Pi_{n-3}\Pi_{n-2}$
3	$4^2\Pi_{n-4}\Pi_n + 2^2\Pi_{n-3}\Pi_{n-1}$
2	$3^2\Pi_{n-3}\Pi_n + 1^2\Pi_{n-2}\Pi_{n-1}$
1	$2^2\Pi_{n-2}\Pi_n$
0	$1^2\Pi_{n-1}\Pi_n$

Table S4: Coefficients a_i of the polynomial $\sum_{i=0}^{2n-2} a_i [\mathrm{H}^+]^i = (DD_2 - D_1^2)/[\mathrm{H}^+]$ at the numerator of $\frac{dAlk_{\mathrm{A}}}{d[\mathrm{H}^+]}//[\Sigma A]$ for the most commonly encountered cases $n = 1, 2, 3, 4$.

n	a_0	a_1	a_2	a_3	a_4	a_5	a_6
1	Π_1						
2	$\Pi_1\Pi_2$	$4\Pi_2$	Π_1				
3	$\Pi_2\Pi_3$	$4\Pi_1\Pi_3$	$9\Pi_3 + \Pi_1\Pi_2$	$4\Pi_2$	Π_1		
4	$\Pi_3\Pi_4$	$4\Pi_2\Pi_4$	$9\Pi_1\Pi_4 + \Pi_2\Pi_3$	$16\Pi_4 + 4\Pi_1\Pi_3$	$9\Pi_3 + \Pi_1\Pi_2$	$4\Pi_2$	Π_1

References

Follows, M. J., Ito, T., and Dutkiewicz, S.: On the solution of the carbonate chemistry system in ocean biogeochemistry models, Ocean Modelling, 12, 290–301, doi:10.1016/j.ocemod.2005.05.004, 2006.