Supplementary Material to

"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"

Additional Results

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Abstract

We provide additional results to supplement the results and discussion in the main paper

Contents

1 Temperature, Salinity and Applied Pressure

	T	S	P
`sc`	273.15 K	35	0 bar
`sw`	298.15 K	35	0 bar
`dc`	273.15 K	35	300 bar
`sb`	273.15 K	3.5	0 bar

Table S1: Temperature, salinity and applied pressure for the four typical environmental conditions: `sc` – surface cold; `sw` – surface warm; `dc` – deep cold; `sb` – surface brackish

2 Speciation calculations with SOLVESAPHE v. 1

In this section, we present pH and carbonate system speciation calculations obtained with SOLVESAPHE v. 1. All results were obtained with `solve_at_general` (Newton-Raphson–bisection method).

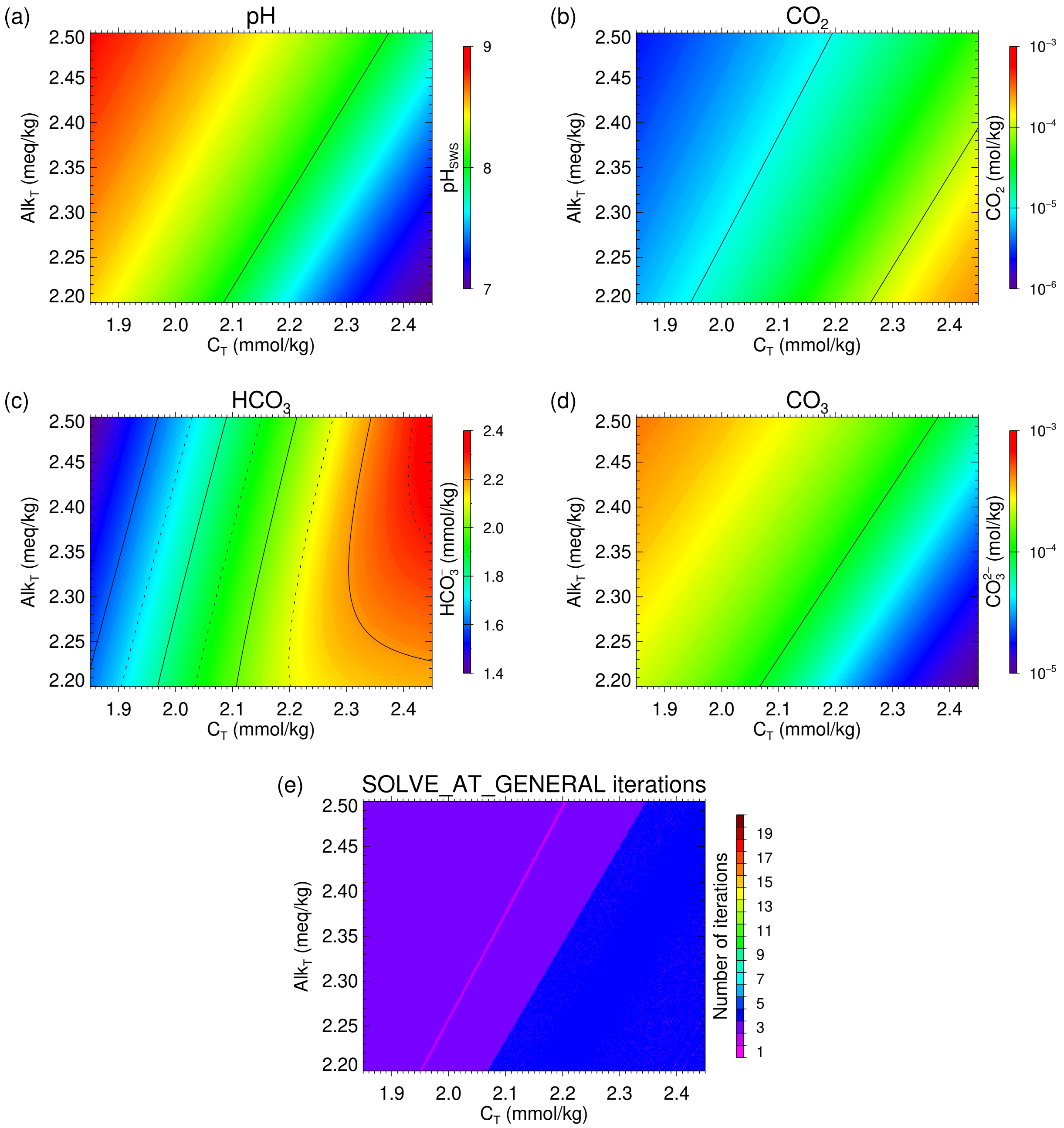

Figure S1: Test case SW1, with $T = 273.15\,\mathrm{K}$, $S = 35$, $P = 0\,\mathrm{bar}$: (top left) pH; (top right) CO_2; (bottom left) HCO_3^-; (bottom right) CO_3^{-2}

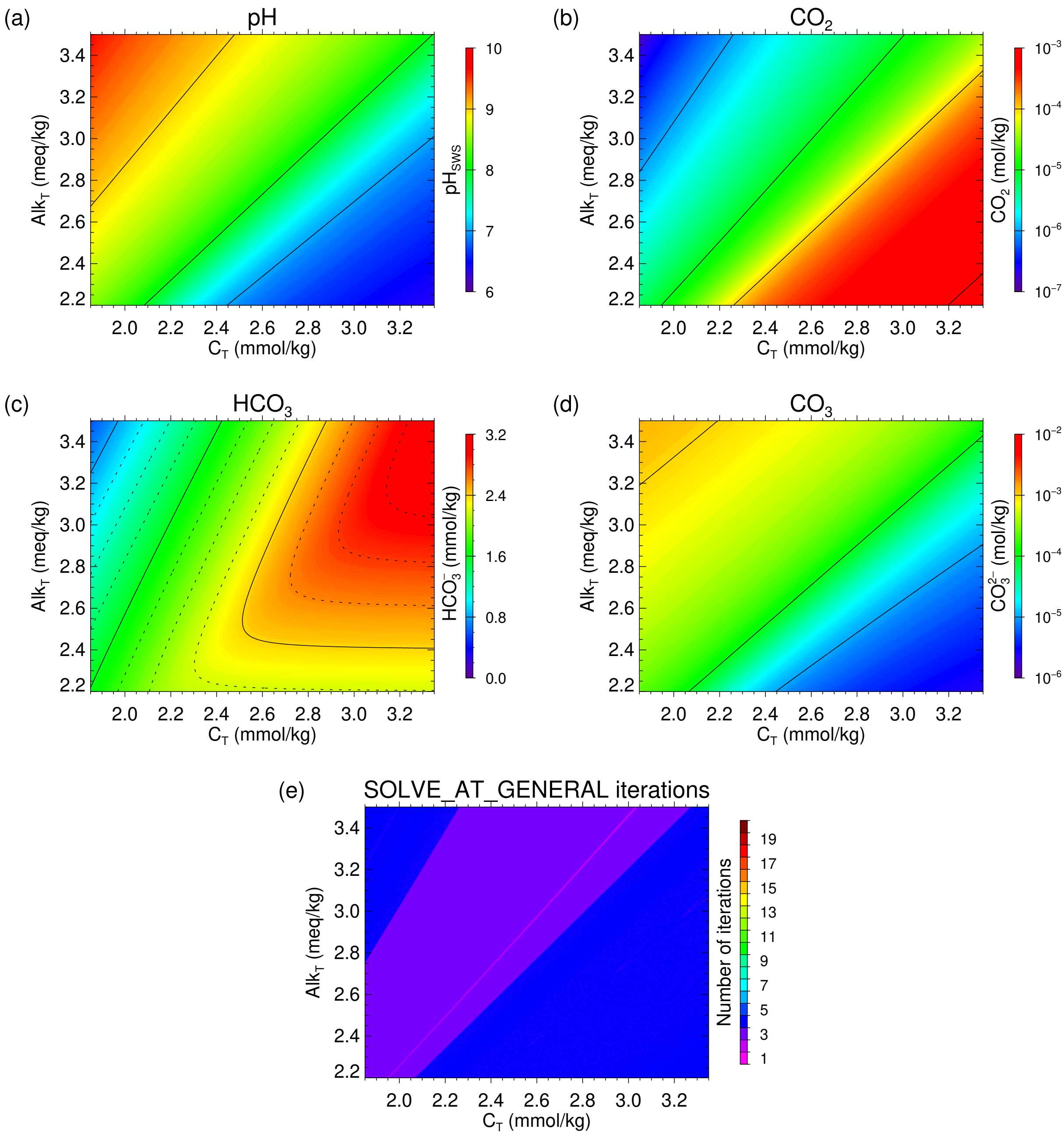

Figure S2: Test case SW2, with $T = 273.15\,\mathrm{K}$, $S = 35$, $P = 0\,\mathrm{bar}$: (top left) $p\mathrm{H}$; (top right) CO_2; (bottom left) HCO_3^-; (bottom right) CO_3^{-2}

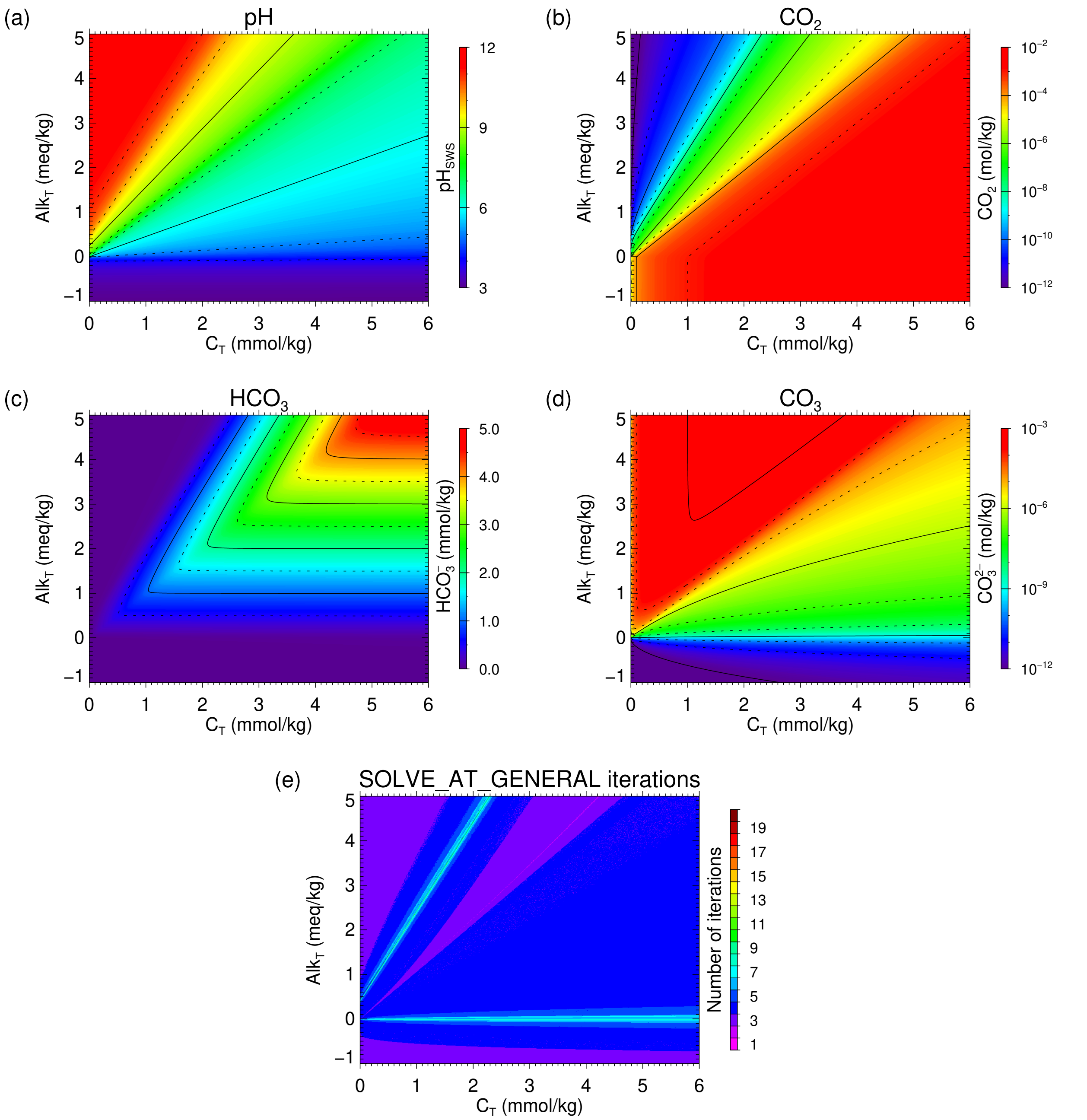

Figure S3: Test case SW3, with $T = 273.15\,\mathrm{K}$, $S = 35$, $P = 0\,\mathrm{bar}$: (top left) pH; (top right) CO_2; (bottom left) HCO_3^-; (bottom right) CO_3^{-2}

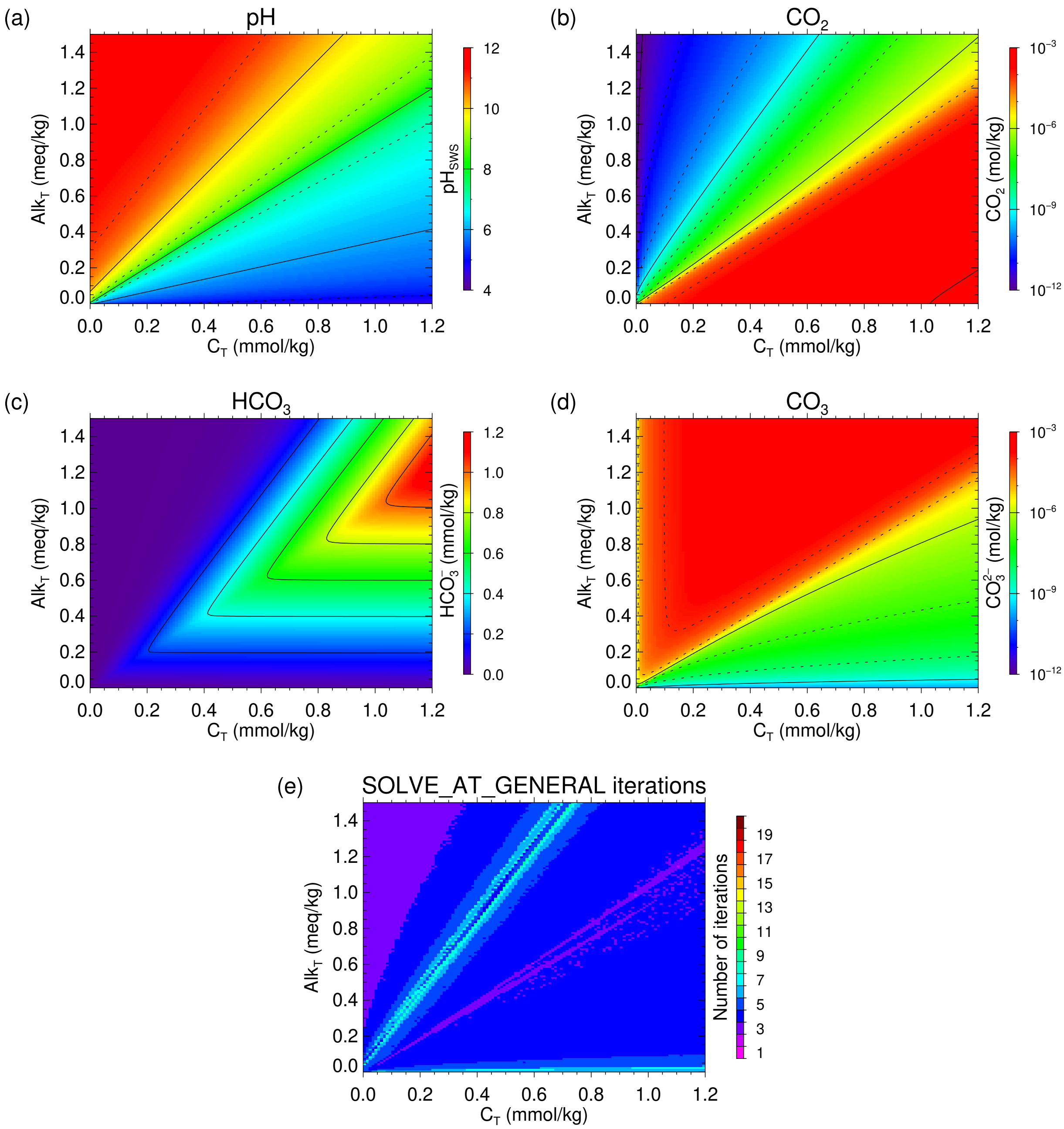

Figure S4: Test case SW4, with $T = 273.15\,\mathrm{K}$, $S = 3.5$, $P = 0\,\mathrm{bar}$: (top left) $p\mathrm{H}$; (top right) CO_2; (bottom left) HCO_3^-; (bottom right) CO_3^{-2}

3 SolveSAPHE v. 2: Additional Results and Information

Here we present additional results from all the test cases SolveSAPHE v. 2.

To illustrate the quality of the final results, the spans of equation residuals are reported in Tables S2 and S3: Table S2 shows the actual minima and maxima; Table S3 show the minima and maxima of the actual equation residuals relative to the water self-ionization alkalinity term $K_W/[H^+] - [H^+]/s$, which is common to all equations (for each input data pair, the equation residual at convergence was divided by $K_W/[H^+] - [H^+]/s$, and the minimum and maximum over the complete test taken).

	SW1		SW2		SW3		SW4	
	min	max	min	max	min	max	min	max
				`solve_at_general`				
Alk_T & C_T	−5.7E−18	1.3E−18	−3.5E−18	6.9E−18	−6.1E−18	6.3E−18	−6.5E−19	8.7E−19
Alk_T & $[CO_2]$	−2.6E−17	2.1E−17	−3.6E−17	2.7E−17	−7.8E−12	6.9E−12	−9.5E−13	1.1E−12
Alk_T & $[HCO_3^-]$	−5.9E−13	2.2E−13	−6.1E−13	1.1E−12	−1.7E−12	1.1E−12	−9.2E−13	6.6E−13
Alk_T & $[CO_3^{2-}]$	−2.7E−12	2.7E−12	−2.7E−12	2.7E−12	−6.3E−12	6.1E−12	−2.1E−12	1.8E−12
	−4.9E−12	6.9E−12	−1.0E−11	9.9E−12	−2.1E−11	2.5E−11	−2.7E−12	3.8E−12
				`solve_at_general_sec`				
Alk_T & C_T	−6.1E−18	3.0E−18	−6.5E−18	6.5E−18	−6.5E−18	6.2E−18	−8.7E−19	6.5E−19
Alk_T & $[CO_2]$	−1.3E−18	1.7E−18	−6.9E−18	6.1E−18	−6.5E−18	6.2E−18	−8.7E−19	8.7E−19
Alk_T & $[HCO_3^-]$	−6.5E−18	5.6E−18	−6.5E−18	6.5E−18	−7.2E−18	6.7E−18	−7.6E−19	8.7E−19
Alk_T & $[CO_3^{2-}]$	−8.7E−19	8.7E−19	−1.3E−18	1.3E−18	−5.9E−18	5.7E−18	−4.3E−19	4.3E−19
	−1.3E−18	1.3E−18	−1.7E−18	1.7E−18	−8.0E−15	5.3E−15	−6.5E−19	1.1E−18

Table S2: Minimum and maximum equation residuals obtained with `solve_at_general` and `solve_at_general_sec` at convergence, for the four test cases and the different input data pairs (separately for the two roots of Alk_T & CO_3^{2-} — the results for the lower root are given on the first of the two lines).

	SW1		SW2		SW3		SW4	
	min	max	min	max	min	max	min	max
				`solve_at_general`				
Alk_T & C_T	−1.0E−8	9.9E−9	−5.3E−7	4.2E−6	−4.0E−8	1.3E−7	−1.1E−8	2.0E−9
Alk_T & $[CO_2]$	−3.1E−6	5.4E−7	−5.0E−5	1.0E−5	−4.5E−5	8.0E−6	−1.6E−6	1.4E−6
Alk_T & $[HCO_3^-]$	−1.0E−6	4.1E−8	−2.1E−7	3.0E−7	−8.1E−7	2.6E−6	−1.1E−6	2.6E−6
Alk_T & $[CO_3^{2-}]$	−1.9E−9	1.9E−9	−2.0E−9	1.9E−9	−1.6E−7	1.6E−7	−1.2E−8	2.1E−8
	−2.2E−4	3.2E−4	−2.8E−3	1.0E−3	−1.4E−4	3.9E−4	−3.1E−4	5.6E−5
				`solve_at_general_sec`				
Alk_T & C_T	−1.4E−7	1.7E−8	−4.2E−6	5.3E−7	−1.4E−8	1.3E−7	−1.1E−8	2.7E−9
Alk_T & $[CO_2]$	−2.2E−8	2.7E−7	−9.7E−8	2.5E−7	−2.8E−8	3.4E−8	−1.4E−8	1.3E−8
Alk_T & $[HCO_3^-]$	−8.6E−10	1.0E−6	−1.1E−8	7.6E−8	−8.1E−9	3.4E−9	−1.3E−10	4.4E−10
Alk_T & $[CO_3^{2-}]$	−4.8E−15	8.1E−15	−7.2E−15	8.1E−15	−5.8E−11	8.8E−11	−2.5E−12	8.0E−13
	−3.5E−8	9.6E−8	−3.8E−7	3.8E−7	−1.7E−8	4.7E−9	−8.3E−8	3.4E−8

Table S3: Minimum and maximum values of the equation residuals divided by its water self-ionization alkalinity term ($K_W/[H^+] - [H^+]/s$). Derived from results obtained with `solve_at_general` and `solve_at_general_sec` at convergence, for the four test cases (all for sc conditions, except for SW4, which was used with sb conditions) and the different input data pairs (separately for the two roots of Alk_T & CO_3^{2-} — the results for the lower root are given on the first of the two lines).

3.1 Test case SW2: results for sw and dc conditions

In this section, we complete the *p*H distribution results obtained for test case SW2 with the environmental condition sets sw and dc. Results for SW2 with sc have been presented and discussed in the main text.

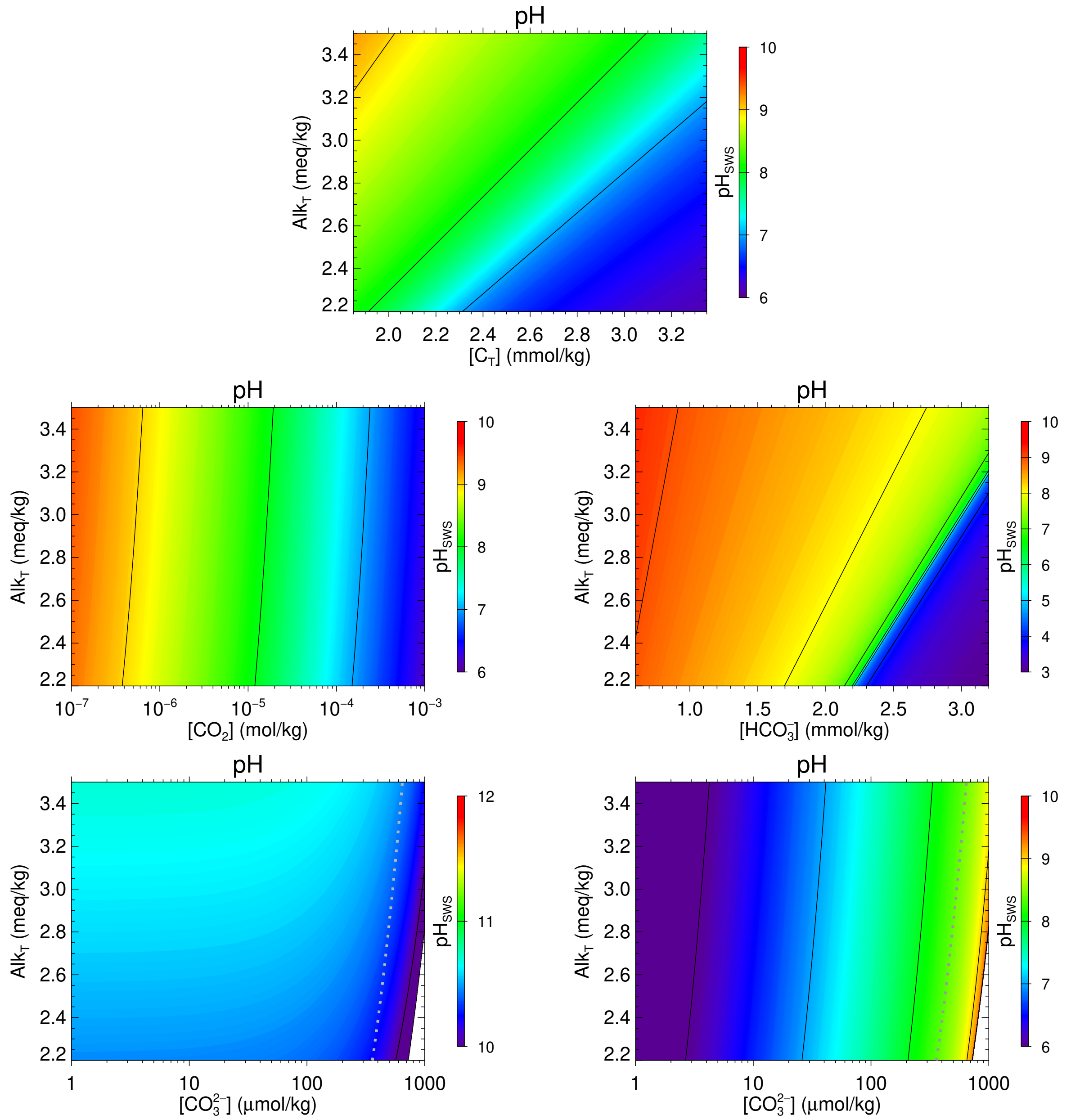

Figure S5: *p*H distributions for the SW2 test case under `sw` conditions ($T = 298.15\,\mathrm{K}$, $S = 35$ and $P = 0\,\mathrm{bar}$), obtained with `solve_at_general2_sec`: (a) $\mathrm{Alk_T}$ & C_T; (b) $\mathrm{Alk_T}$ & CO_2; (c) $\mathrm{Alk_T}$ & HCO_3^-; (d) the lower $[H^+]$ root (higher *p*H root) of $\mathrm{Alk_T}$ & CO_3^{2-}; (e) the greater $[H^+]$ root (lower *p*H root) of $\mathrm{Alk_T}$ & CO_3^{2-}. The thick grey dashed line in (d) and (e) shows the critical limit above which the $\mathrm{Alk_T}$ & CO_3^{2-} always has two roots. Below this limit further calculations are required to determine the number of solutions (please refer to the main paper and Supplement for details). Please notice the different scales on the horizontal axes and for the *p*H colour coding in the four panels.

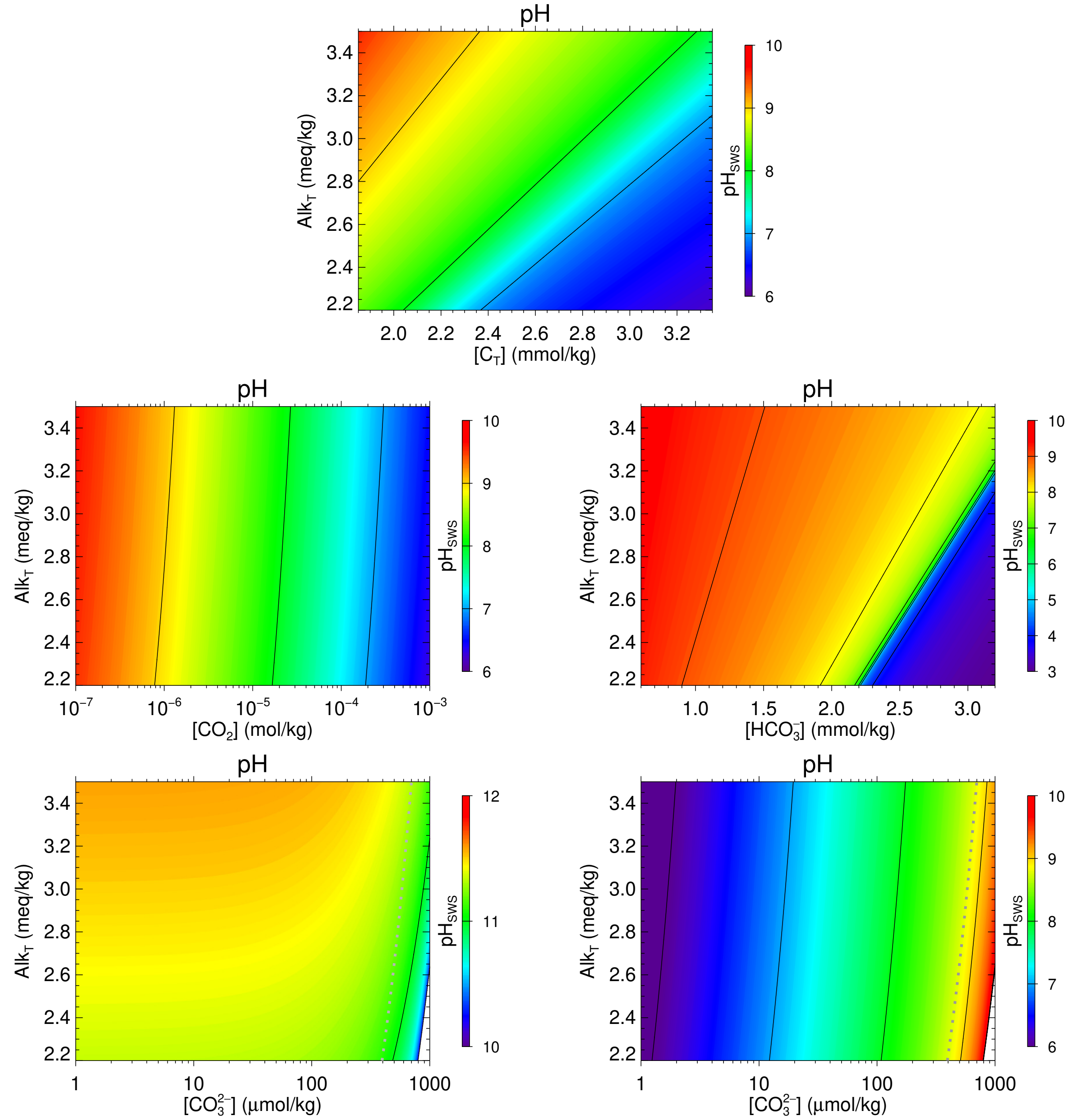

Figure S6: pH distributions for the SW2 test case under `dc` conditions ($T = 273.15$ K, $S = 35$ and $P = 300$ bar), obtained with `solve_at_general2_sec`: (a) Alk_T & C_T; (b) Alk_T & CO_2; (c) Alk_T & HCO_3^-; (d) the lower $[H^+]$ root (higher pH root) of Alk_T & CO_3^{2-}; (e) the greater $[H^+]$ root (lower pH root) of Alk_T & CO_3^{2-}. The thick grey dashed line in (d) and (e) 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 main 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 Test case SW3: results for sc, sw and dc conditions

In this section, we present the pH distributions obtained for the test case SW3 with the environmental condition sets sc, sw and dc.

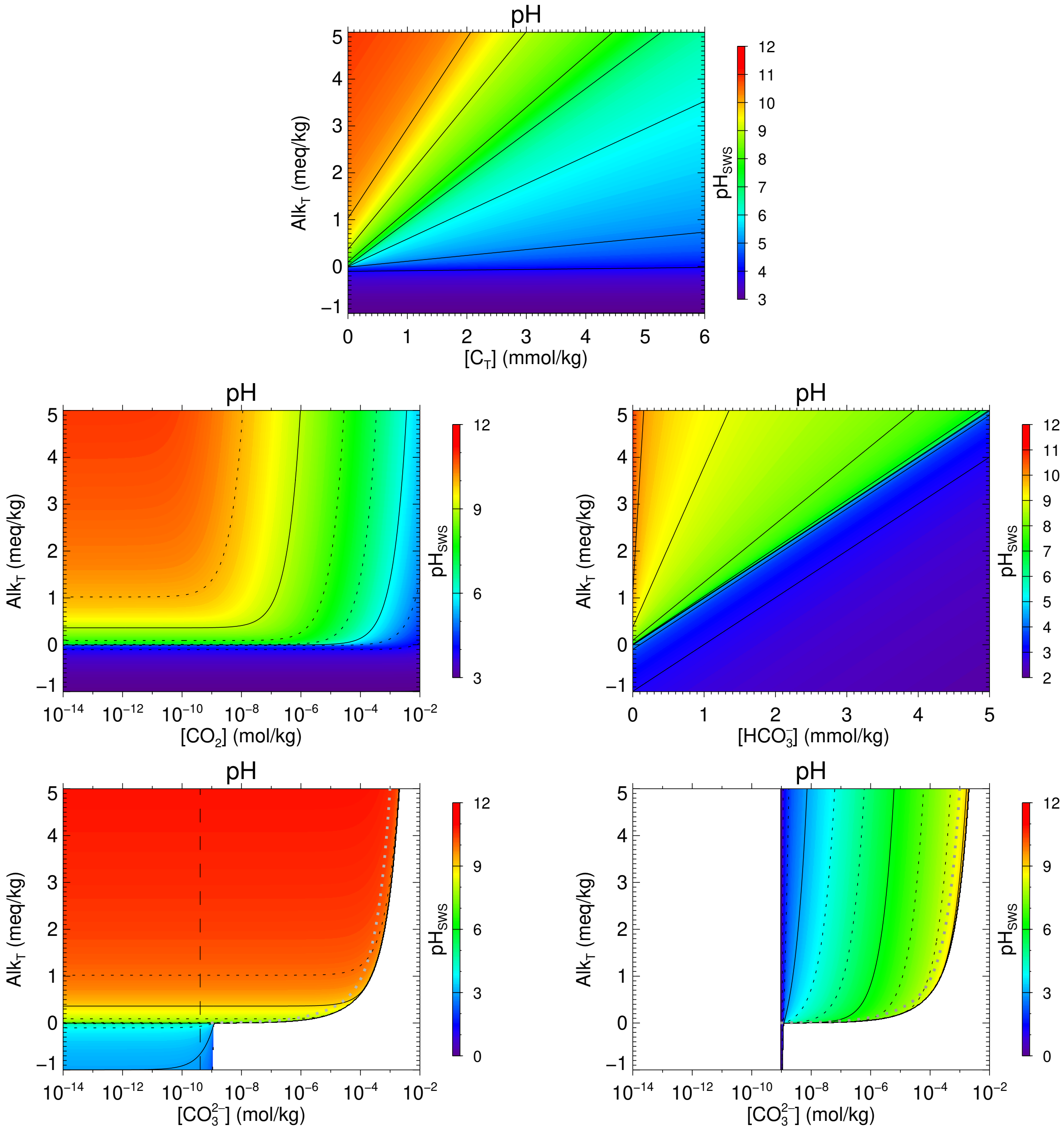

Figure S7: pH distributions for the SW3 test case under `sw` conditions ($T = 298.15\,K$, $S = 35$ and $P = 0\,bar$), obtained with `solve_at_general2_sec`: (a) Alk_T & C_T; (b) Alk_T & CO_2; (c) Alk_T & HCO_3^-; (d) the lower $[H^+]$ root (higher pH root) of Alk_T & CO_3^{2-}; (e) the greater $[H^+]$ root (lower pH root) of Alk_T & CO_3^{2-}. The thick grey dashed line in (d) and (e) 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 main text and in the Supplement. Please notice the different scales on the horizontal axes and for the pH colour coding in the four panels.

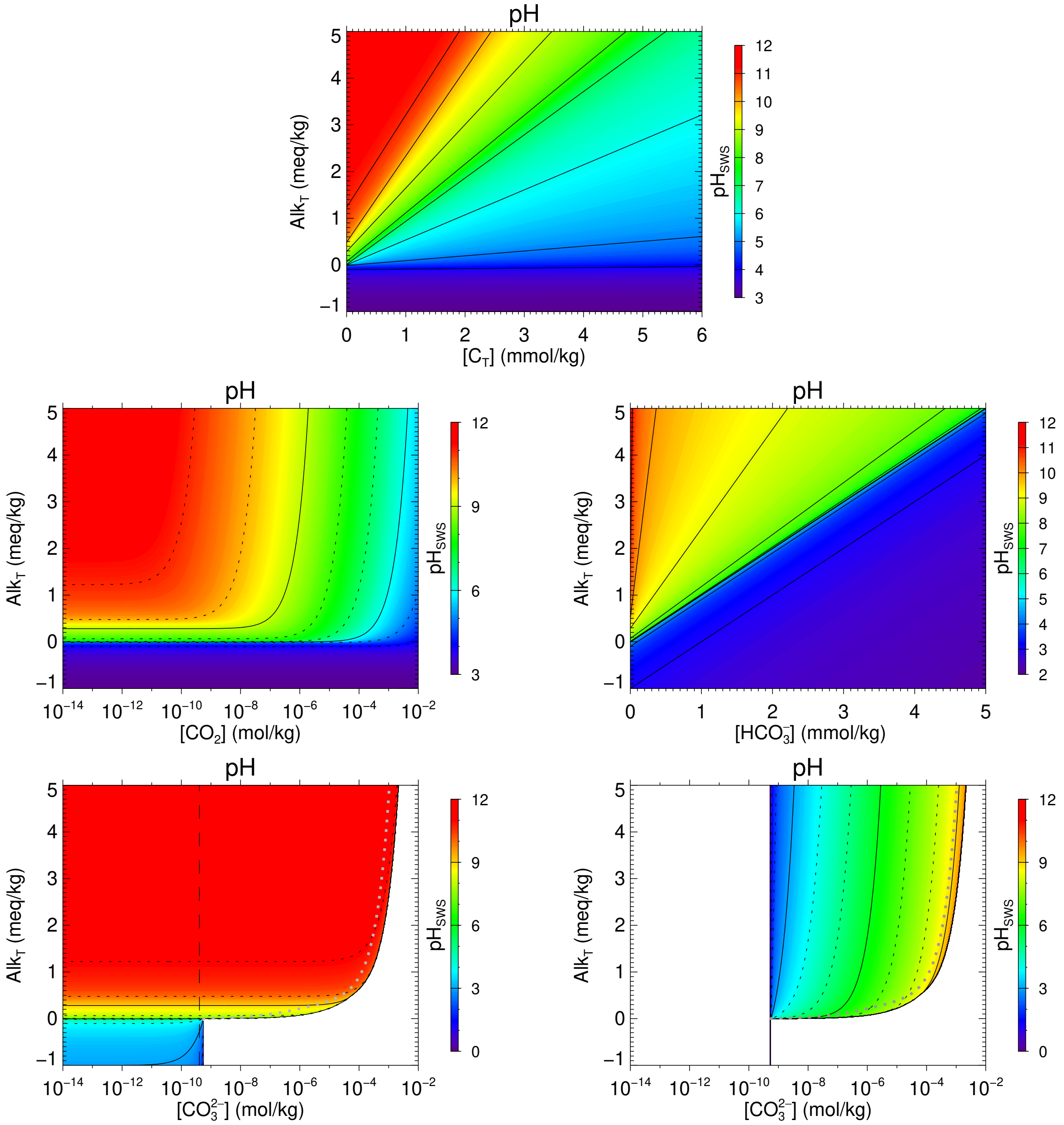

Figure S8: pH distributions for the SW3 test case under dc conditions ($T = 273.15\,\mathrm{K}$, $S = 35$ and $P = 300\,\mathrm{bar}$), obtained with `solve_at_general2_sec`: (a) $\mathrm{Alk_T}$ & C_T; (b) $\mathrm{Alk_T}$ & $\mathrm{CO_2}$; (c) $\mathrm{Alk_T}$ & $\mathrm{HCO_3^-}$; (d) the lower $[\mathrm{H^+}]$ root (higher pH root) of $\mathrm{Alk_T}$ & $\mathrm{CO_3^{2-}}$; (e) the greater $[\mathrm{H^+}]$ root (lower pH root) of $\mathrm{Alk_T}$ & $\mathrm{CO_3^{2-}}$. The thick grey dashed line in (d) and (e) shows the critical limit above which the $\mathrm{Alk_T}$ & $\mathrm{CO_3^{2-}}$ always has two roots. Below this limit further calculations are required to determine the number of solutions. More details are given in the main text and in the Supplement. Please notice the different scales on the horizontal axes and for the pH colour coding in the four panels.

3.3 Test case SW4: results for sb conditions

In this section, we present the *p*H distributions obtained for the test case SW4, with environmental conditions sb.

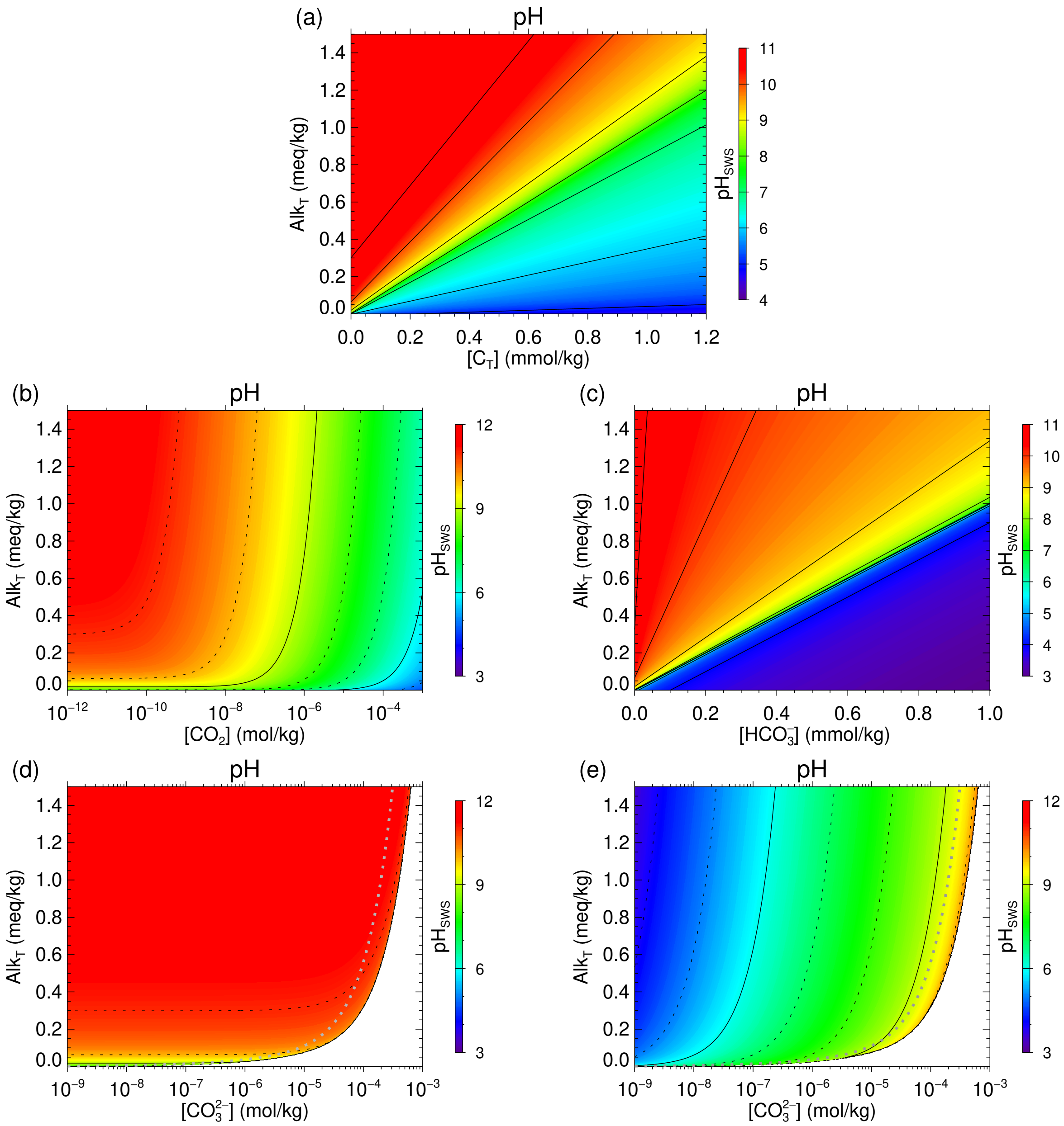

Figure S9: *p*H distributions for the SW4 test case under cold brackish surface conditions ($T = 273.15\,\mathrm{K}$, $S = 3.5$ and $P = 0\,\mathrm{bar}$), obtained with `solve_at_general2_sec`: (a) $\mathrm{Alk_T}$ & C_T; (b) $\mathrm{Alk_T}$ & CO_2; (c) $\mathrm{Alk_T}$ & HCO_3^-; (d) the lower $[H^+]$ root (higher *p*H root) of $\mathrm{Alk_T}$ & CO_3^{2-}; (e) the greater $[H^+]$ root (lower *p*H root) of $\mathrm{Alk_T}$ & CO_3^{2-}. The thick grey dashed line in (d) and (e) shows the critical limit above which the $\mathrm{Alk_T}$ & 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 main text and in the Supplement. Please notice the different scales on the horizontal axes and for the *p*H colour coding in the four panels.

3.4 Numbers of iterations

This section presents maps of the distributions of the numbers of iterations required for the four data input pairs, each time first the maps for the Newton-Raphson based method (all tests cases), followed by the maps for the secant based method. For $\mathrm{Alk_T}$ & $\mathrm{CO_3^{2-}}$, separate maps are shown for the two roots. In addition maps with the numbers of iterations required to solve the auxiliary minimisation problem are presented for this case.

3.4.1 $\mathrm{Alk_T}$ & C_T

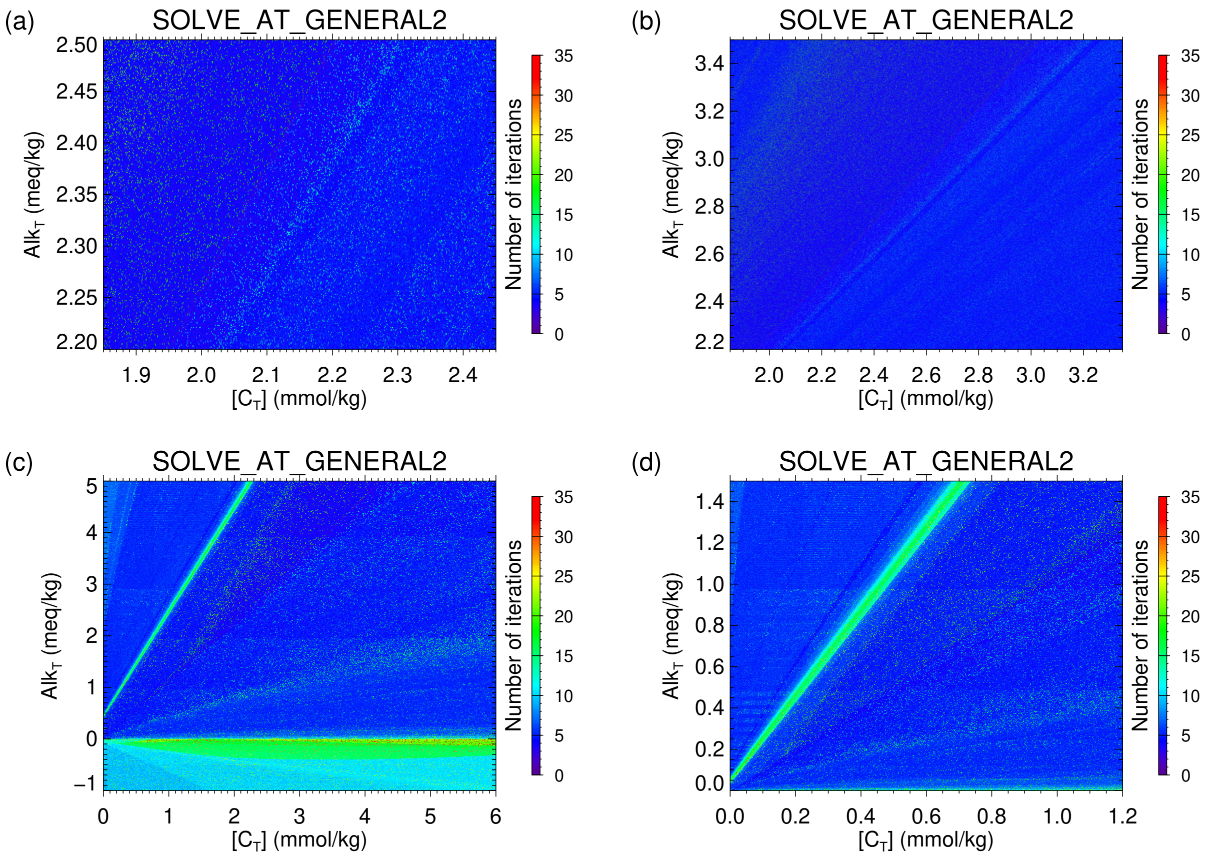

Figure S10: Number of iterations to convergence required by `solve_at_general2` for the $\mathrm{Alk_T}$ & C_T pair: (a) SW1; (b) SW2; (c) SW3 – all with sc conditions; (d) SW4, with sb conditions.

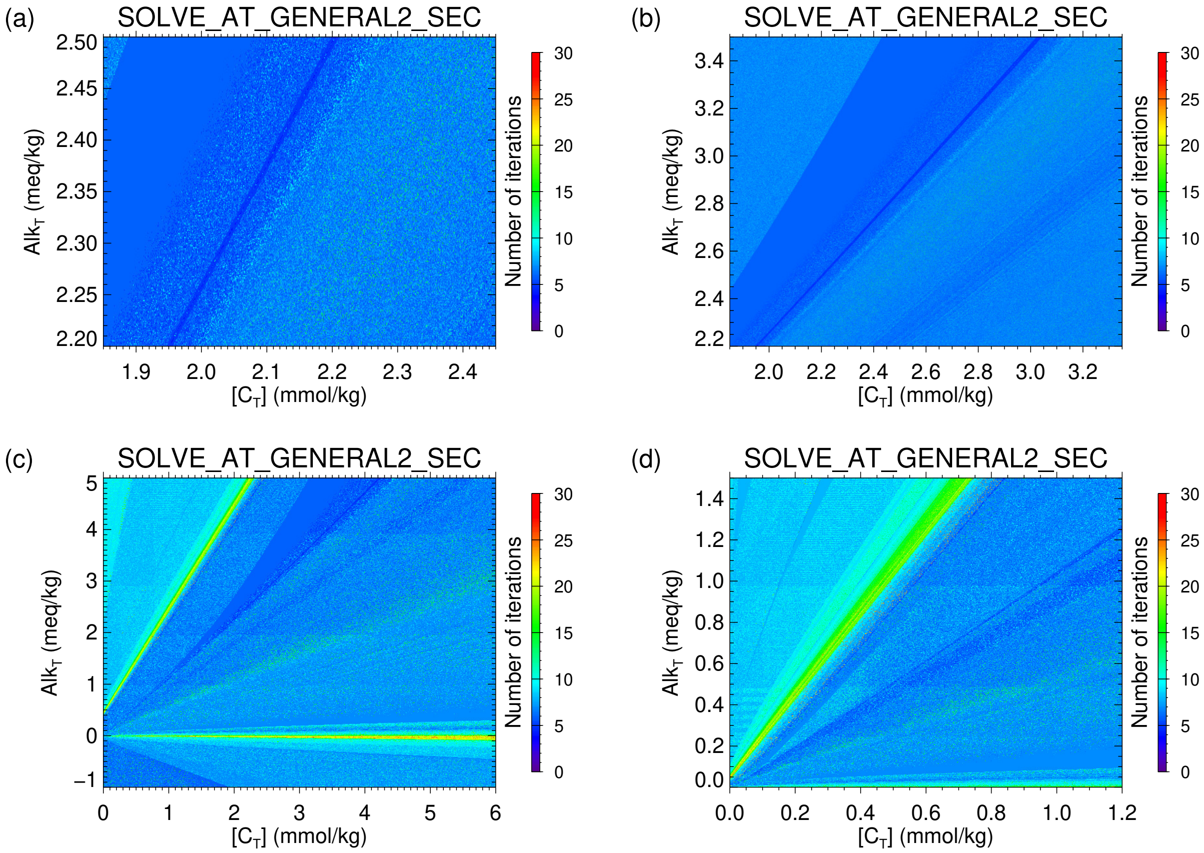

Figure S11: Number of iterations to convergence required by `solve_at_general2_sec` for the $\mathrm{Alk_T}$ & C_T pair: (a) SW1; (b) SW2; (c) SW3 – all with sc conditions; (d) SW4, with sb conditions.

3.4.2 Alk_T & CO_2

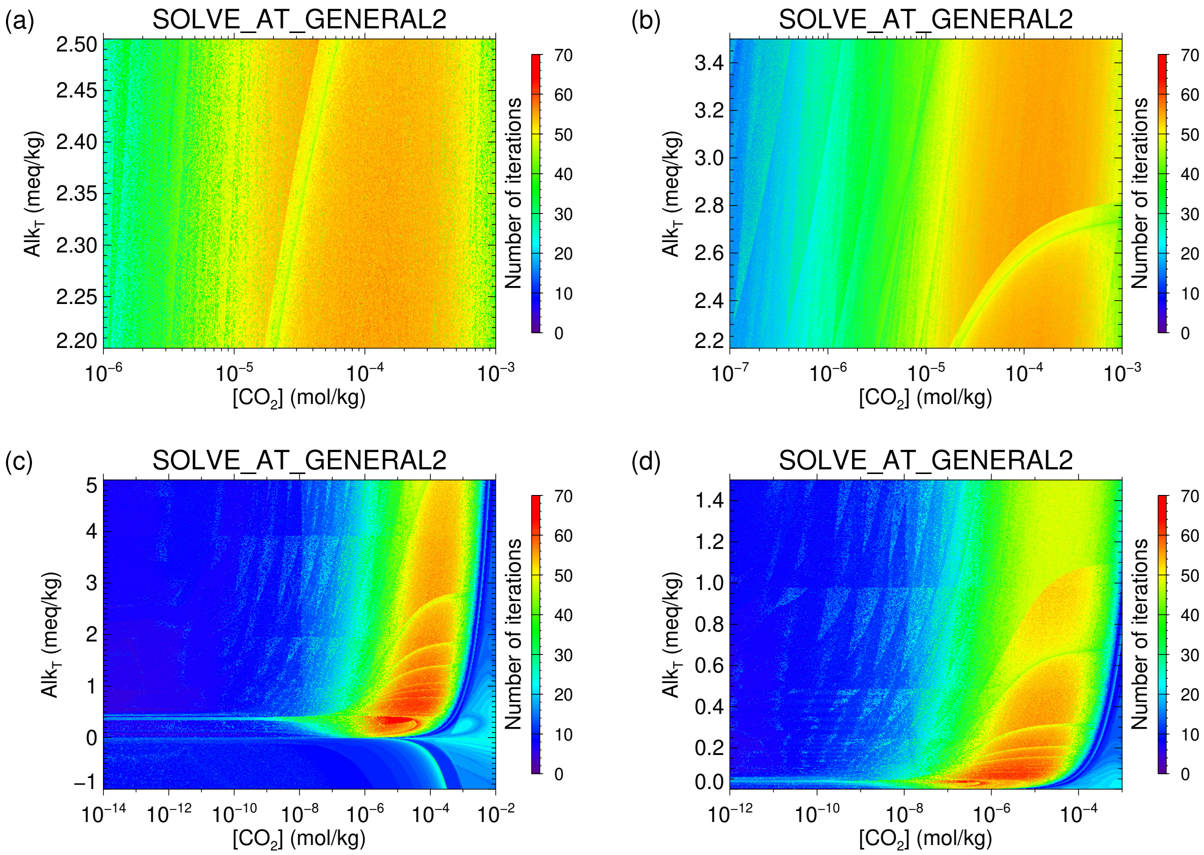

Figure S12: Number of iterations to convergence required by `solve_at_general2` for the Alk_T & CO_2 pair: (a) SW1; (b) SW2; (c) SW3 – all with sc conditions; (d) SW4, with sb conditions.

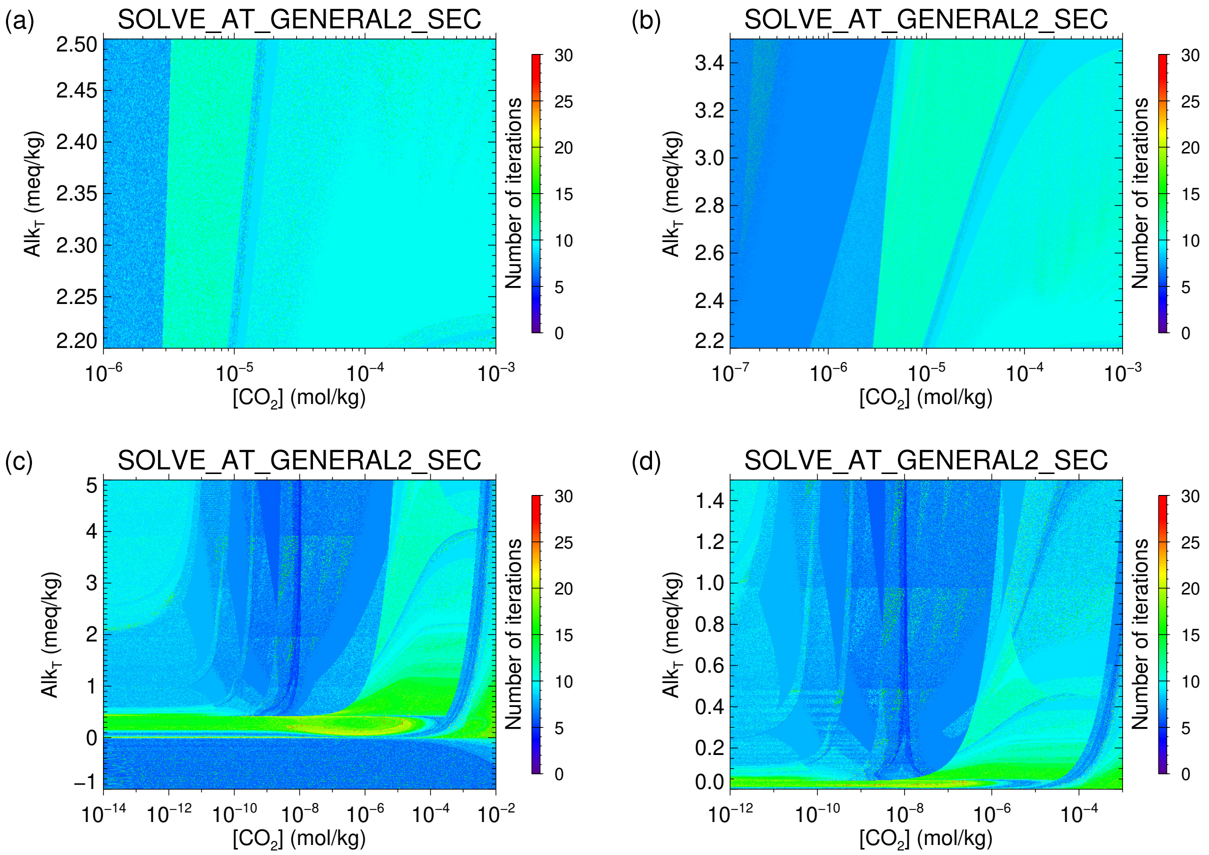

Figure S13: Number of iterations to convergence required by `solve_at_general2_sec` for the Alk_T & CO_2 pair: (a) SW1; (b) SW2; (c) SW3 – all with sc conditions; (d) SW4, with sb conditions.

3.4.3 $\mathrm{Alk_T}$ & $\mathrm{HCO_3^-}$

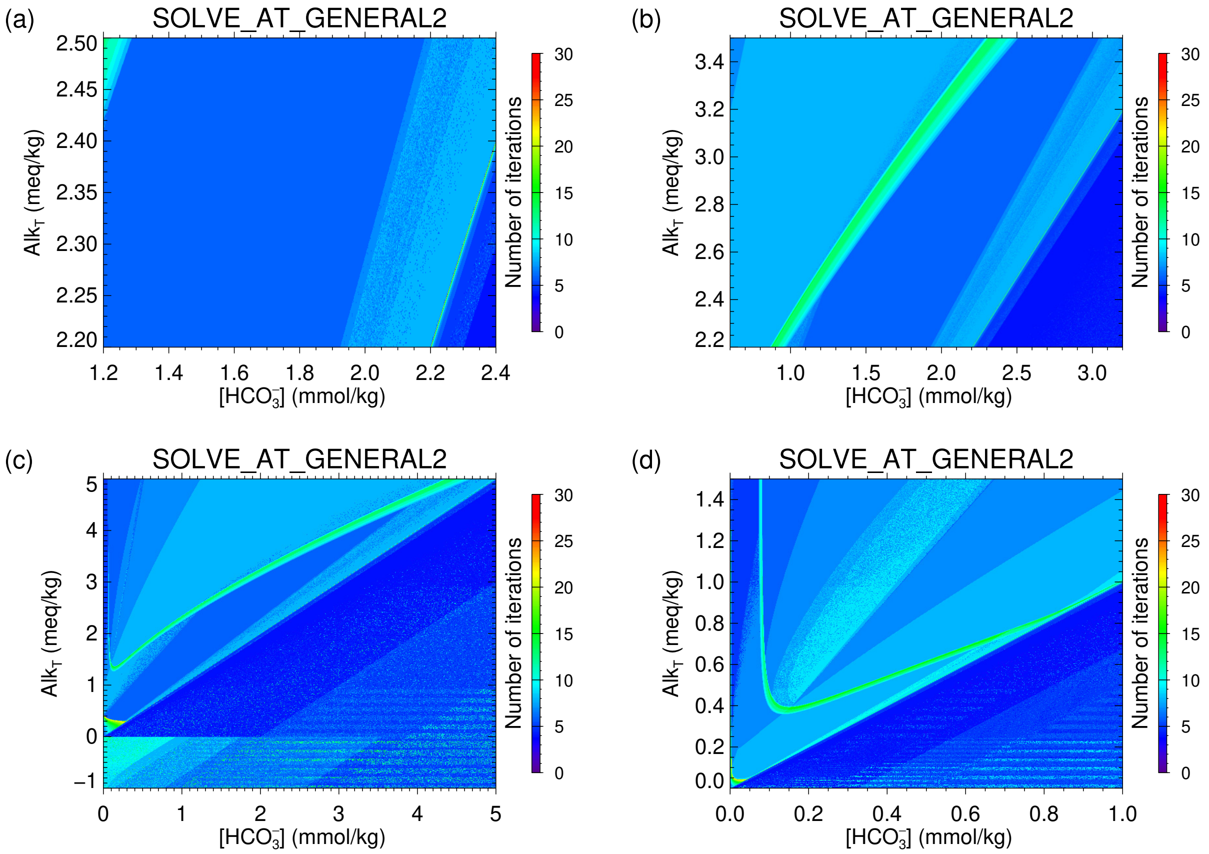

Figure S14: Number of iterations to convergence required by `solve_at_general2` for the $\mathrm{Alk_T}$ & $\mathrm{HCO_3^-}$ pair: (a) SW1; (b) SW2; (c) SW3 – all with sc conditions; (d) SW4, with sb conditions.

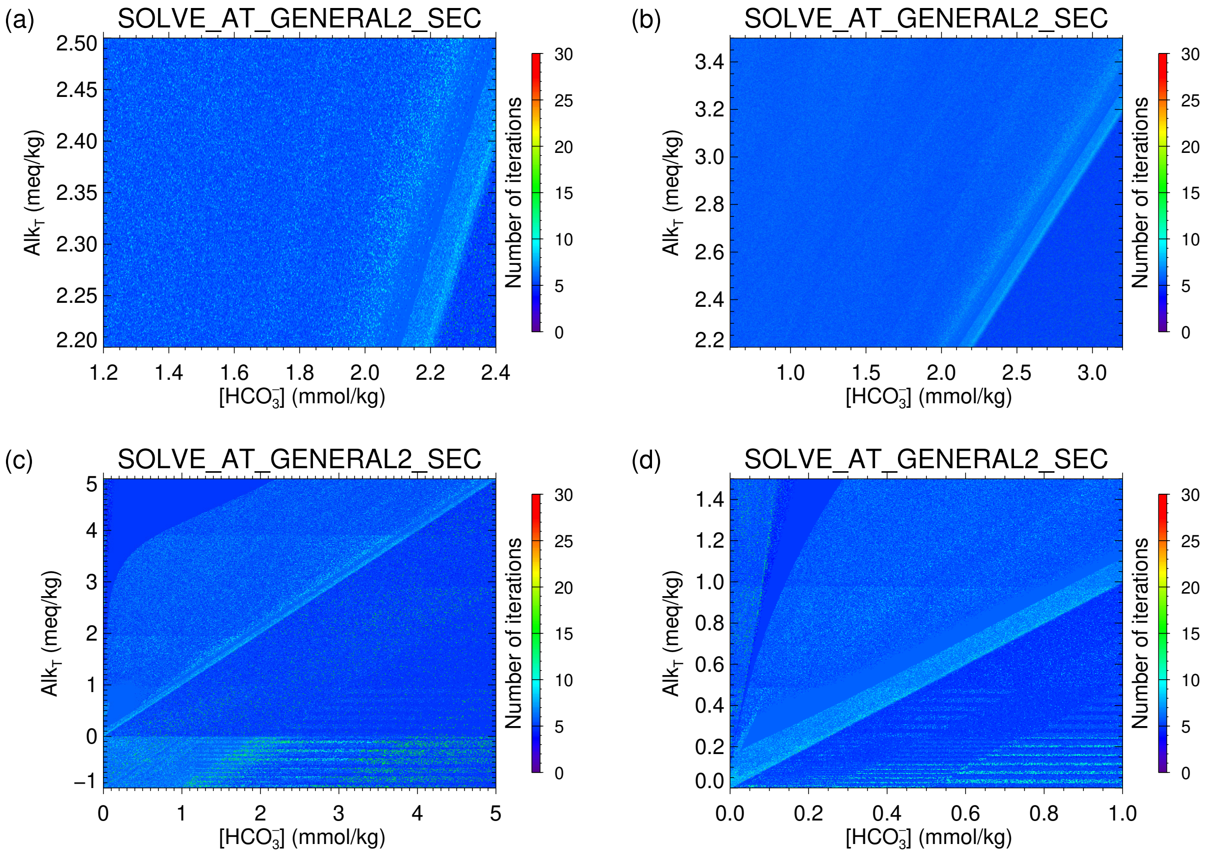

Figure S15: Number of iterations to convergence required by `solve_at_general2_sec` for the Alk_T & HCO_3^- pair: (a) SW1; (b) SW2; (c) SW3 – all with sc conditions; (d) SW4, with sb conditions.

3.4.4 Alk_T & CO_3^{2-}

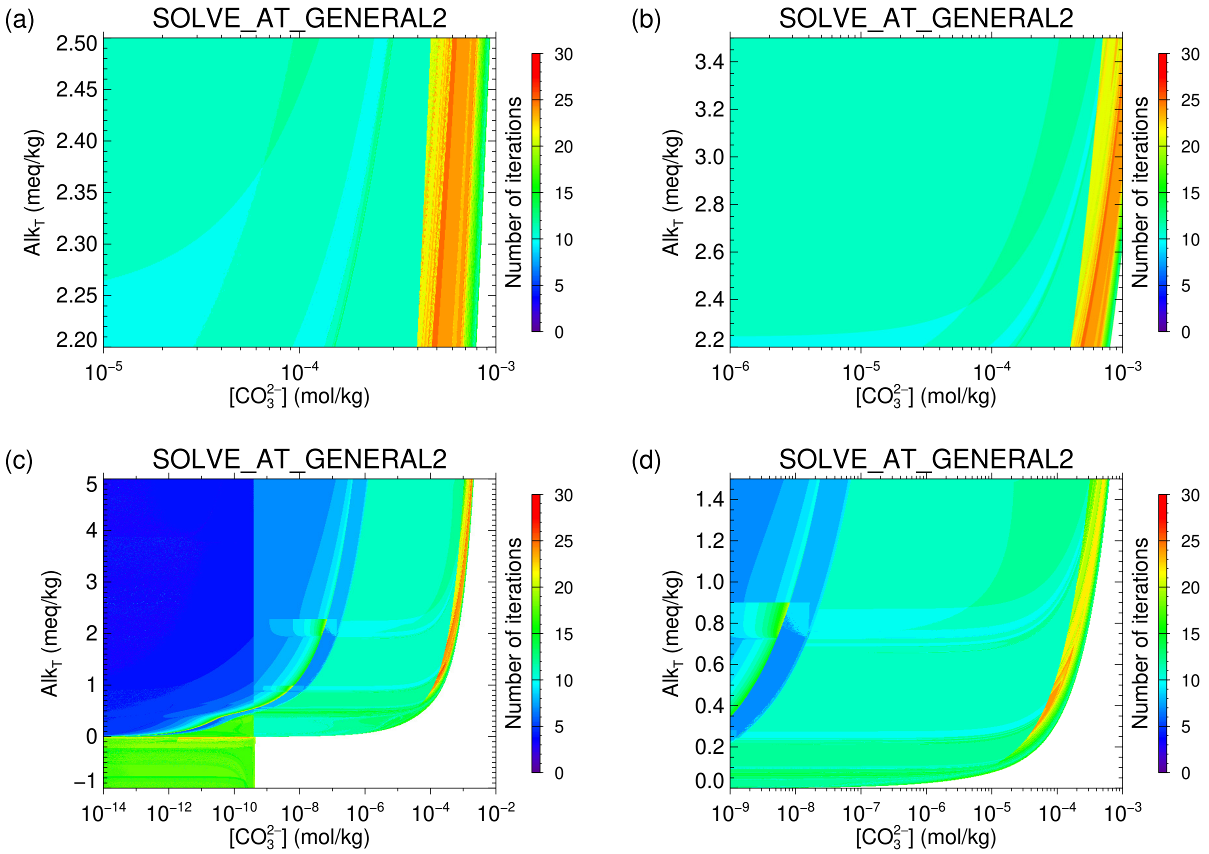

Figure S16: Number of iterations to convergence required by `solve_at_general2` for the Alk_T & CO_3^{2-} pair to determine the unique or the lower one of the two $[H^+]$ roots: (a) SW1; (b) SW2; (c) SW3 – all with sc conditions; (d) SW4, with sb conditions.

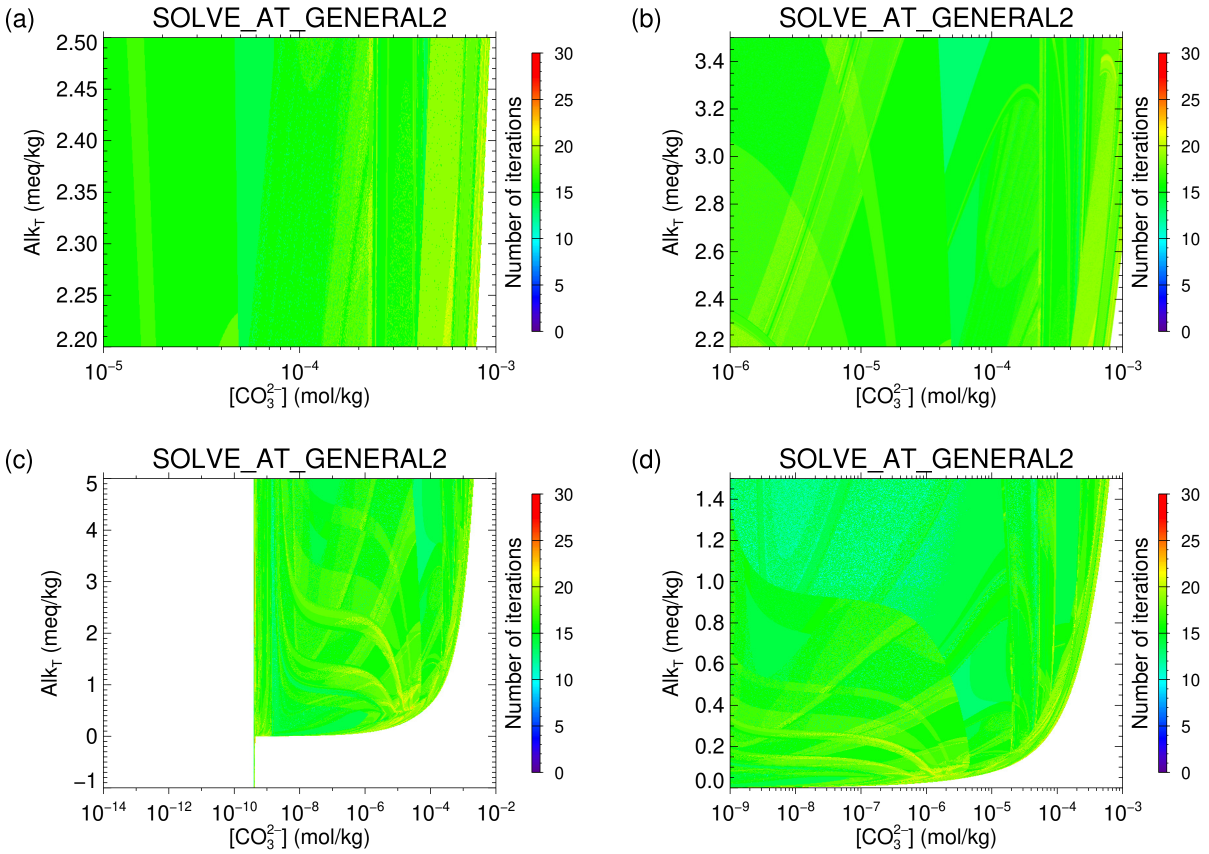

Figure S17: Number of iterations to convergence required by `solve_at_general2` for the Alk_T & CO_3^{2-} pair to determine the greater one of the two $[H^+]$ roots: (a) SW1; (b) SW2; (c) SW3 – all with sc conditions; (d) SW4, with sb conditions.

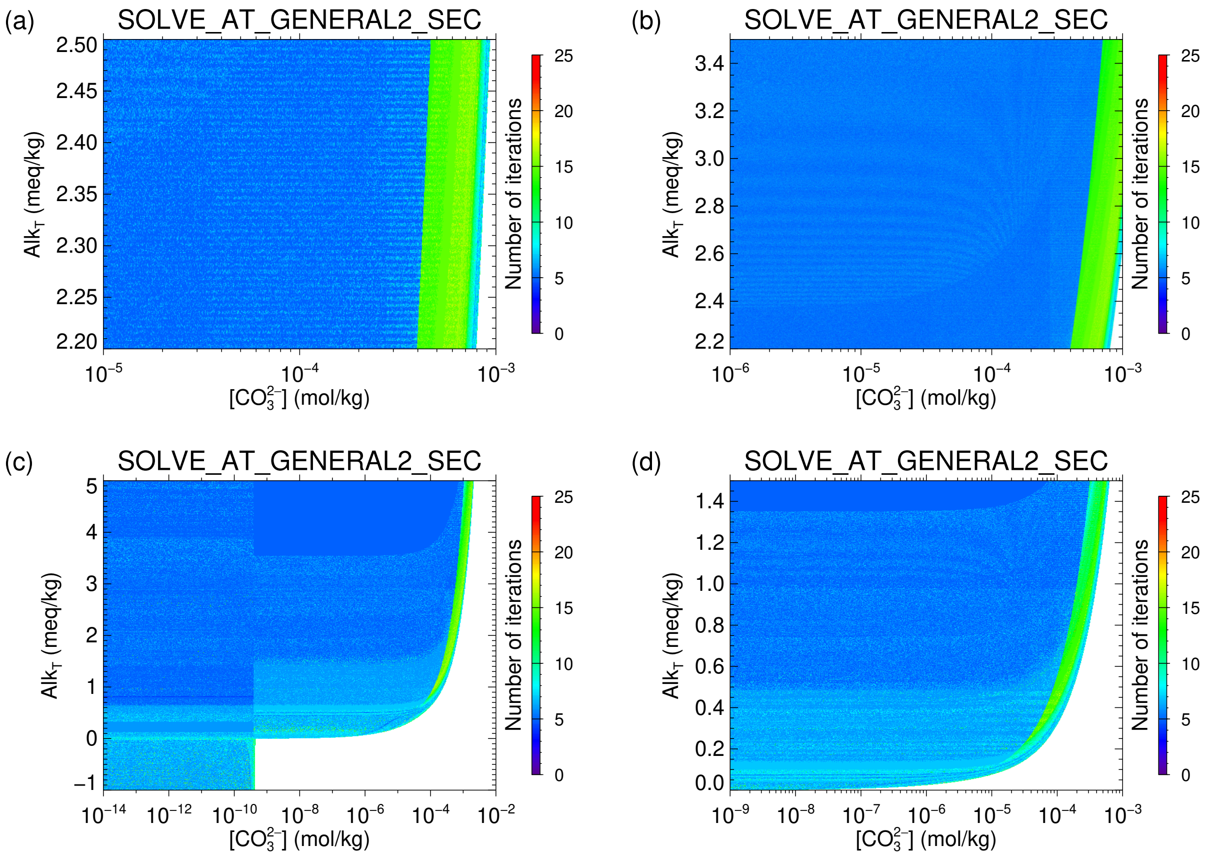

Figure S18: Number of iterations to convergence required by `solve_at_general2_sec` for the Alk_T & CO_3^{2-} pair to determine the unique or the lower one of the two $[H^+]$ roots: (a) SW1; (b) SW2; (c) SW3 – all with sc conditions; (d) SW4, with sb conditions.

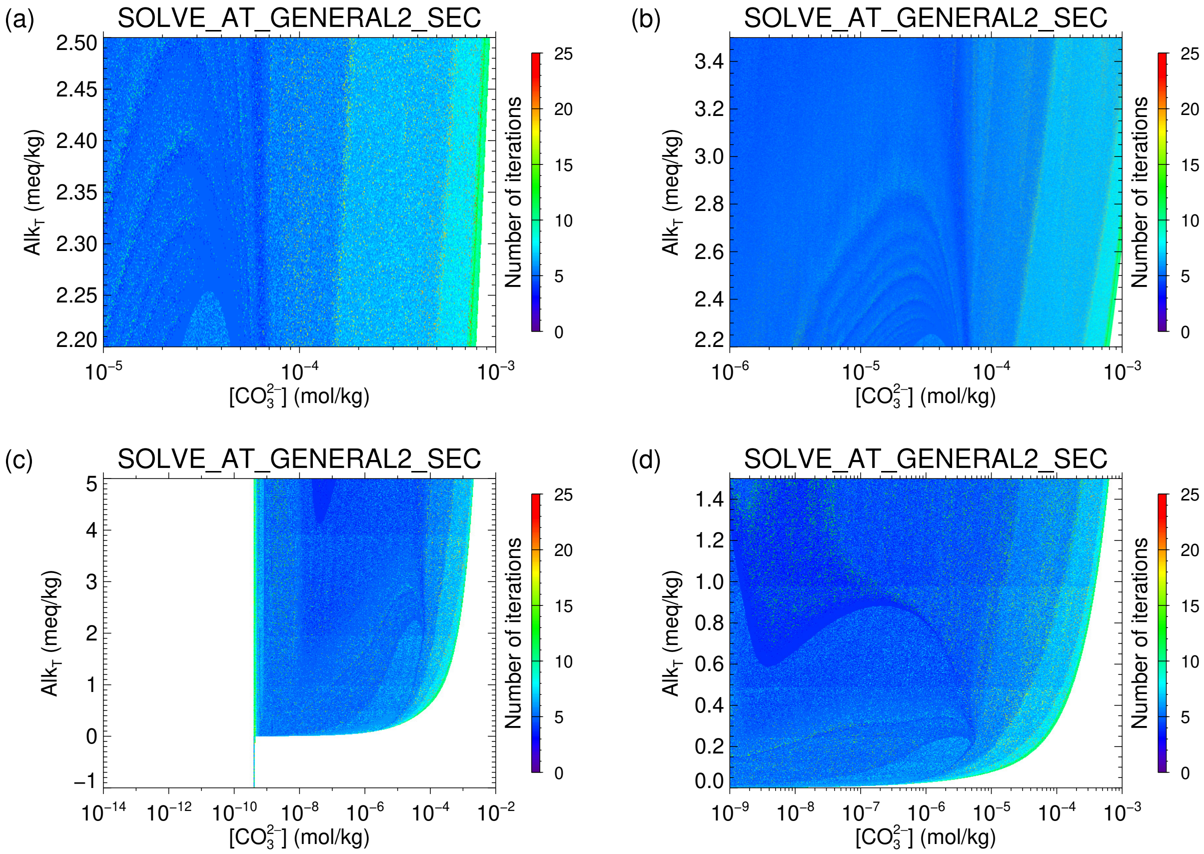

Figure S19: Number of iterations to convergence required by `solve_at_general2_sec` for the Alk_T & CO_3^{2-} pair to determine the greater of the two $[H^+]$ roots: (a) SW1; (b) SW2; (c) SW3 – all with sc conditions; (d) SW4, with sb conditions.

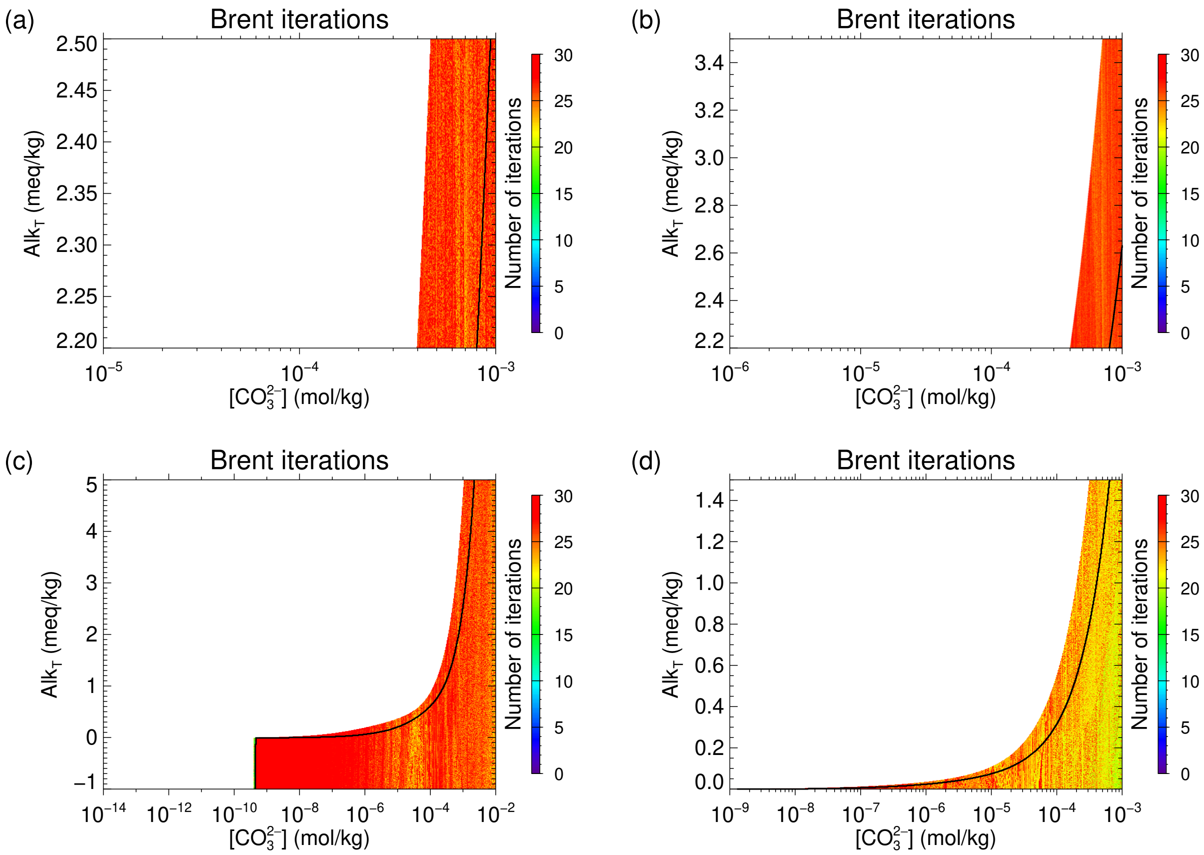

Figure S20: Number of iterations required by Brent's algorithm to solve the auxiliary minimisation problem whose solution determines the number of roots of the $\mathrm{Alk_T}$ & CO_3^{2-} pair and also provides the separation between the two roots: (a) SW1; (b) SW2; (c) SW3 – all with sc conditions; (d) SW4, with sb conditions. The white areas covers the region where the solution of the minimisation problems was not required (either because $\gamma \leq 0$ or because the $L_{\min}$ was sufficiently low so that it as clear that there were two roots). The black line in each panel traces the limit between regions with two roots (above and to the left of the line) and without roots (below and to the right of the line).