Supplementary Material to

"SolveSAPHE-r2 (v2.0.1): 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 Test Case Definitions: Additional Characteristics 2

2 Speciation calculations with SOLVESAPHE v. 1 3

3 SOLVESAPHE-r2: Additional Results and Information 8

3.1 Test case SW2: results for sw and dc conditions . . . 11
3.2 Test case SW3: results for sc, sw and dc conditions . . . 13
3.3 Test case BW4: results for sb conditions . . . 16
3.4 Test case ABW5: results for ib conditions . . . 17
3.5 Numbers of iterations . . . 18
3.5.1 $\mathrm{Alk_T}$ & C_T . . . 18
3.5.2 $\mathrm{Alk_T}$ & $\mathrm{CO_2}$ . . . 20
3.5.3 $\mathrm{Alk_T}$ & $\mathrm{HCO_3^-}$ . . . 22
3.5.4 $\mathrm{Alk_T}$ & $\mathrm{CO_3^{2-}}$ . . . 24

1 Test Case Definitions: Additional Characteristics

The ranges adopted for $\mathrm{Alk_T}$, C_T, $[\mathrm{CO_2}]$, $[\mathrm{HCO_3^-}]$ and $[\mathrm{CO_3^{2-}}]$ adopted for the different test cases can be found in the main paper on Table 1. Here, we provide the remaining characteristics required to completely define the test cases

Each one of the seawater test cases SW1, SW2 and SW3 can be used in combination with any of three following sets of environmental conditions: ‘sc’ – surface cold; ‘sw’ – surface warm; ‘dc’ – deep cold. The test case BW4 (brackish or dilute water) is only used together with the set ‘sb’ and ABW5 (anoxic brackish water) only with the set ‘ib’. The characteristics of these five sets in terms of temperature, salinity and applied pressure are reported on Table S1. In some experiments, the set of environmental conditions used may be specified by attaching its name to the tests case name (e.g., SW2-dc then stands for test case SW2 with the dc conditions). Table S2 presents the total concentrations adopted for the acid systems that contribute to non-carbonate alkalinity. The dimensions for the $C_\mathrm{T} \times \mathrm{Alk_T}$, $[\mathrm{CO_2}] \times \mathrm{Alk_T}$, $[\mathrm{HCO_3^-}] \times \mathrm{Alk_T}$ and $[\mathrm{CO_3^{2-}}] \times \mathrm{Alk_T}$ grids used in the different test case configurations are reported on Table S3.

Table S1: Temperature, salinity and applied pressure for the five typical environmental conditions.

	$T/°\mathrm{C}$	S	P/bar
sc	2	35	0
sw	25	35	0
dc	2	35	300
sb	2	3.5	0
ib	7.56	22.82	13.5

Table S2: Total concentrations of acid systems contributing to non-carbonate alkalinity.

	SW1,2,3	BW4	ABW5
$B_\mathrm{T}/\mu\mathrm{mol\,kg^{-1}}$	416*	41.6*	271*
$S_\mathrm{T}/\mu\mathrm{mol\,kg^{-1}}$	28235*	2823.5*	18410*
$\Sigma\mathrm{PO_4}/\mu\mathrm{mol\,kg^{-1}}$	0.5	0.5	100
$\Sigma\mathrm{SiO_2}/\mu\mathrm{mol\,kg^{-1}}$	5	5	600
$\Sigma\mathrm{NH_4}/\mu\mathrm{mol\,kg^{-1}}$	0	0	1500
$\Sigma\mathrm{H_2S}/\mu\mathrm{mol\,kg^{-1}}$	0	0	5100

* The total borate (B_T) and sulfate (S_T) concentrations are calculated from salinity.

Table S3: Grid-dimensions for the $C \times \mathrm{Alk_T}$ grids adopted for the different test cases, where C may stand for any of C_T, $[\mathrm{CO_2}]$, $[\mathrm{HCO_3^-}]$ or $[\mathrm{CO_3^{2-}}]$.

Test case	C	$\mathrm{Alk_T}$
SW1	600	300
SW2	1500	1300
SW3	600	600
BW4	600	600
ABW5	500	600

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).

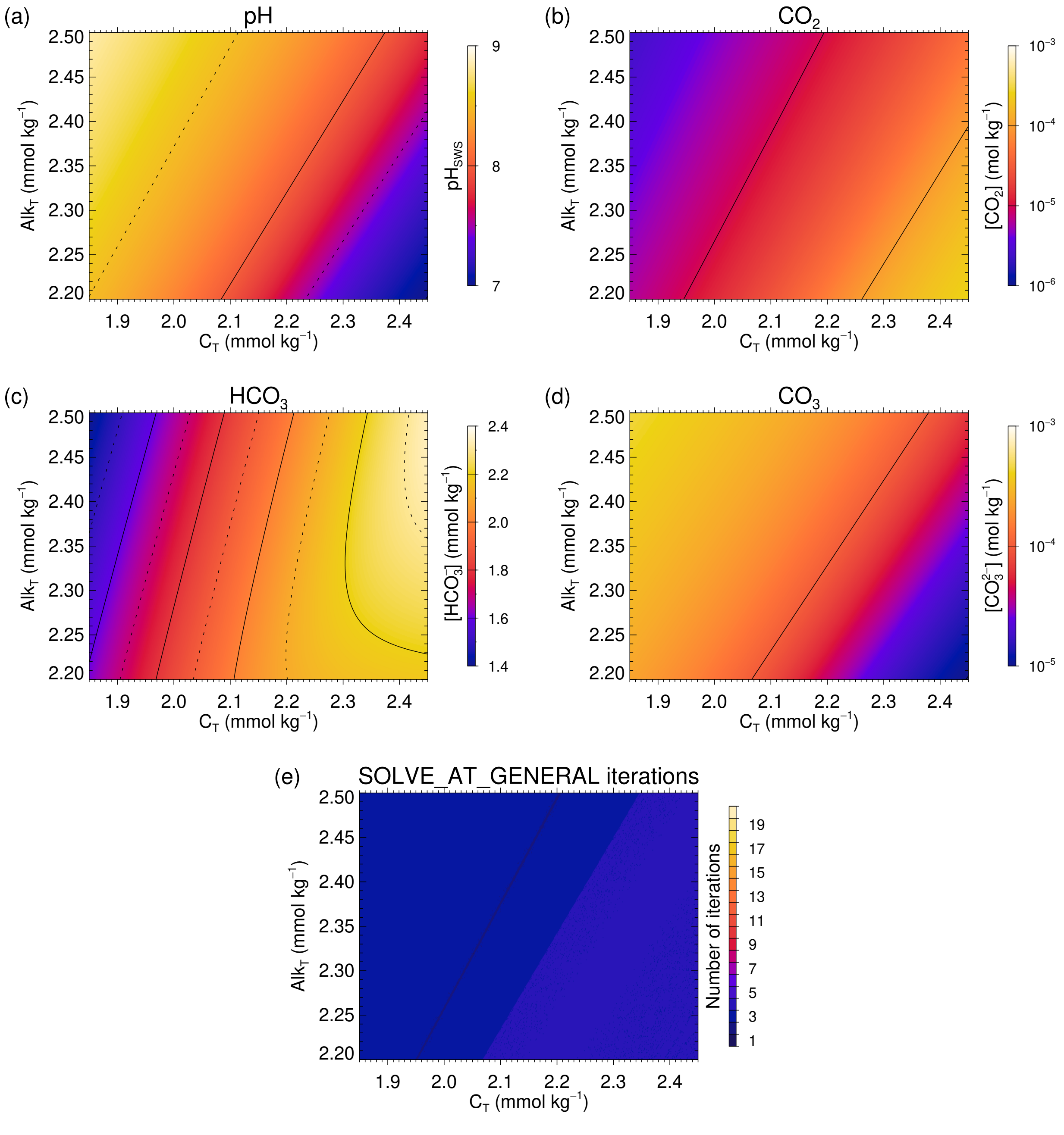

Figure S1: Test case SW1-sc: (a) pH; (b) CO_2; (c) HCO_3^-; (d) CO_3^{2-}; (e) number of iterations.

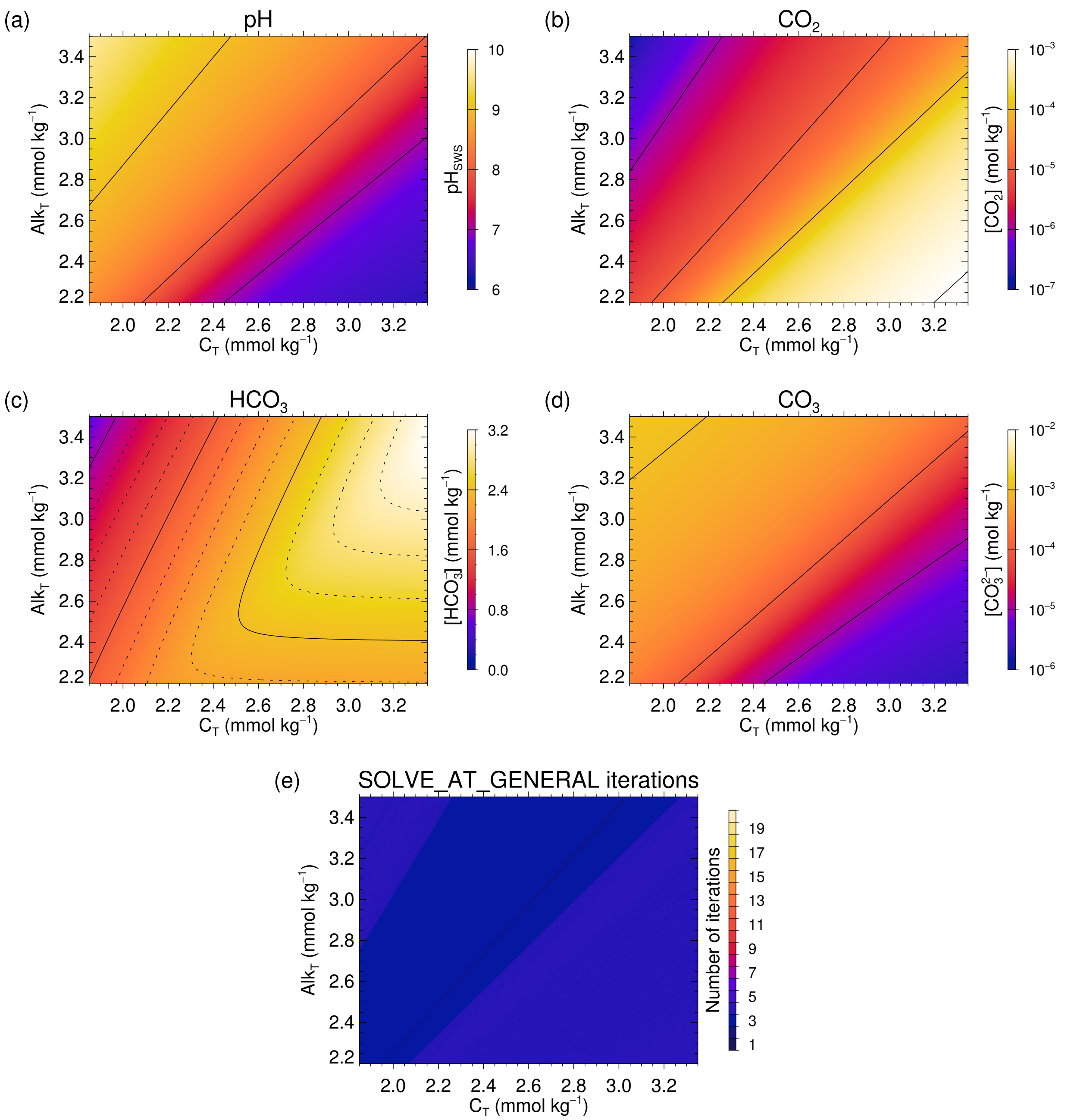

Figure S2: Test case SW2-sc: (a) pH; (b) CO_2; (c) HCO_3^-; (d) CO_3^{2-}; (e) number of iterations.

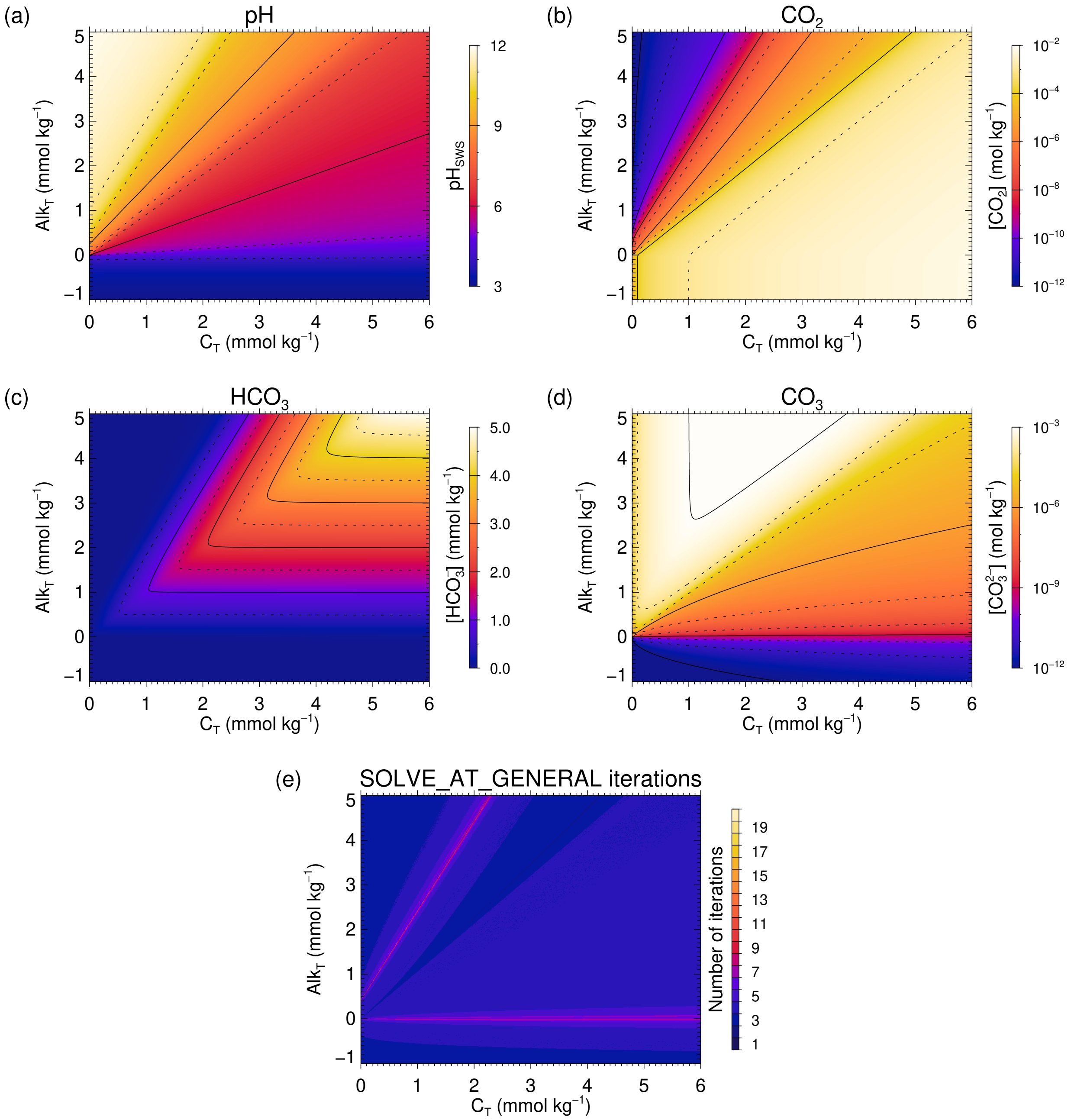

Figure S3: Test case SW3-sc: (a) pH; (b) CO_2; (c) HCO_3^-; (d) CO_3^{2-}; (e) number of iterations.

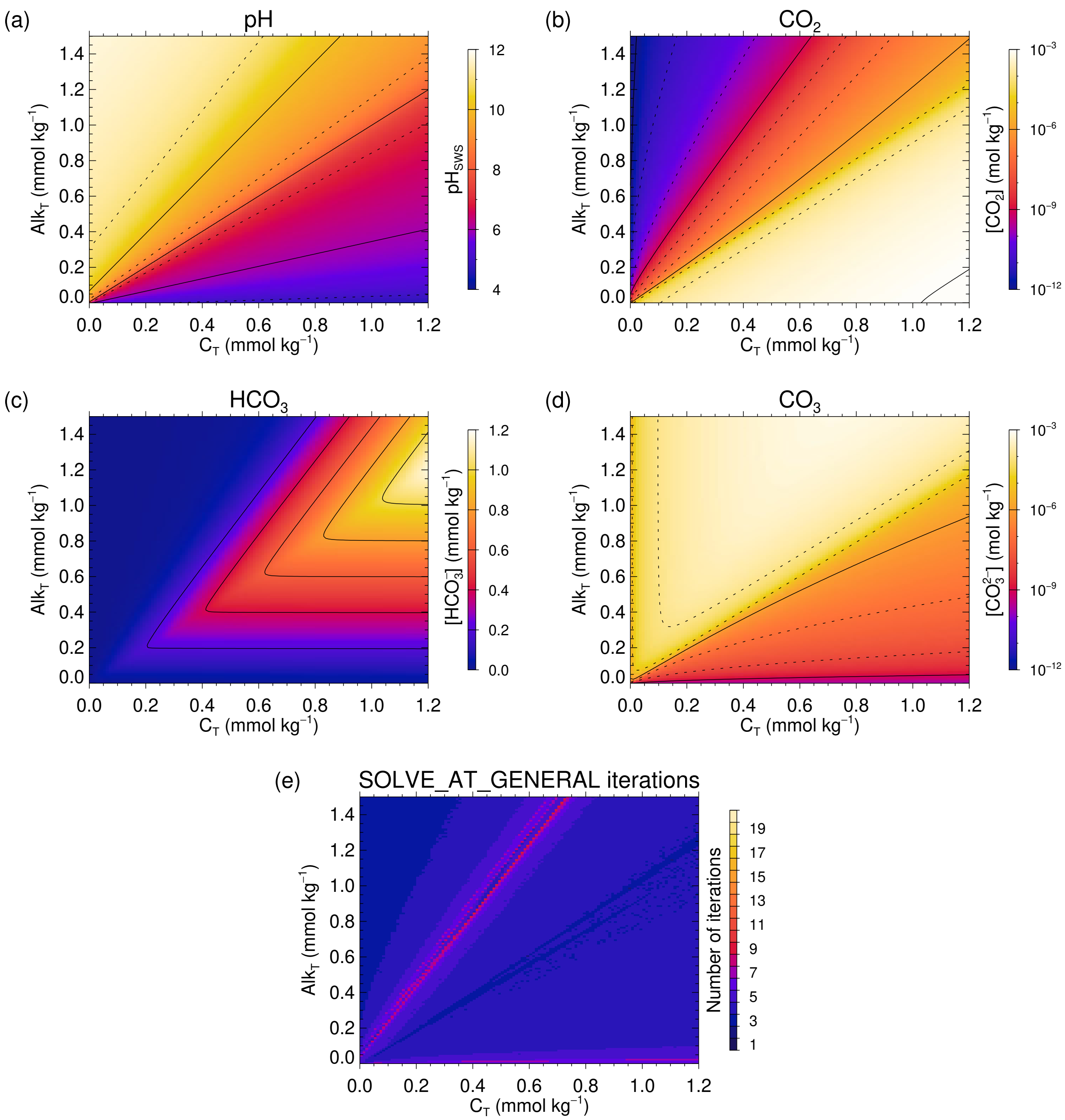

Figure S4: Test case BW4-sb: (a) pH; (b) CO_2; (c) HCO_3^-; (d) CO_3^{2-}; (e) number of iterations.

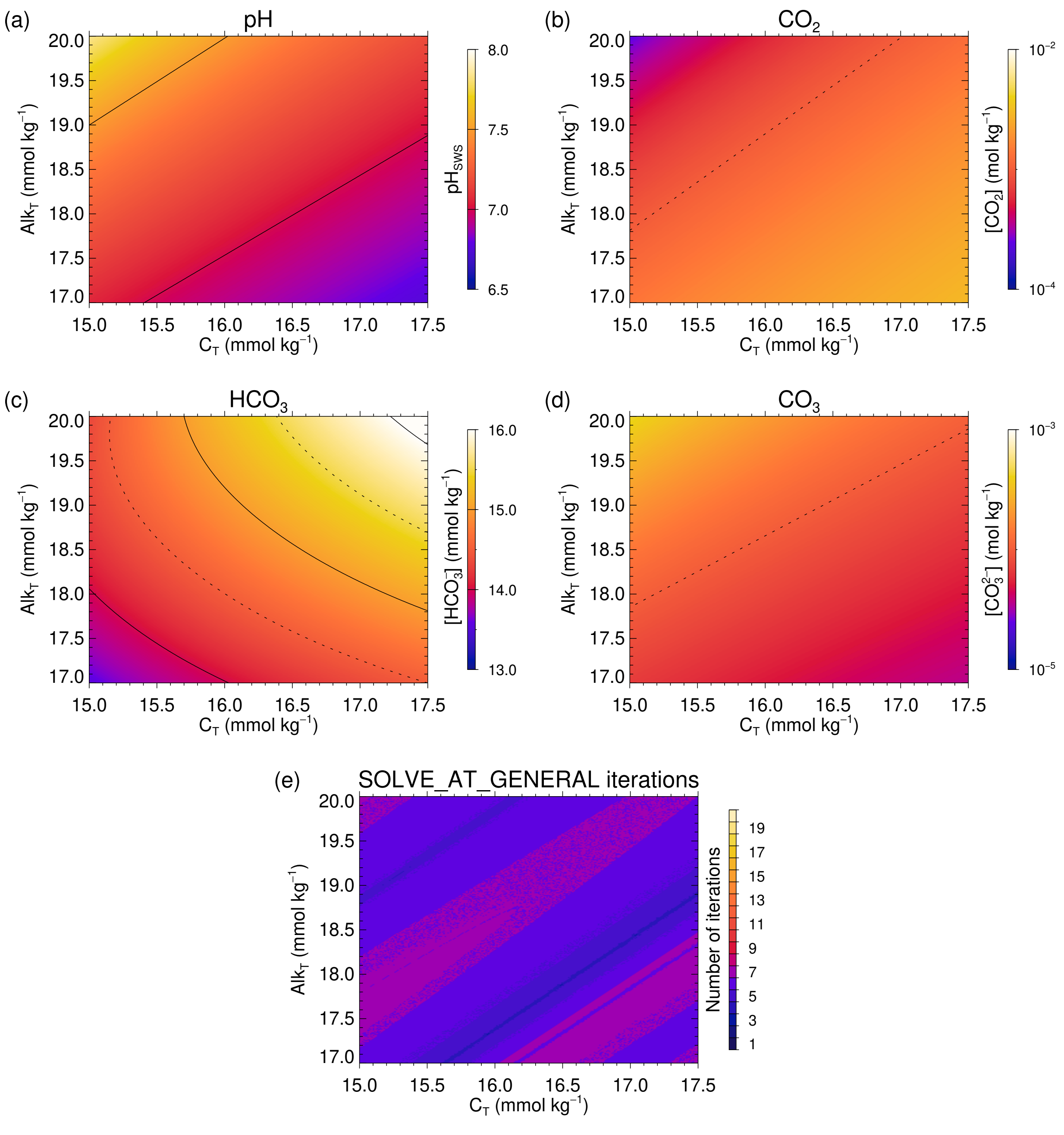

Figure S5: Test case ABW5-ib: (a) pH; (b) CO_2; (c) HCO_3^-; (d) CO_3^{2-}; (e) number of iterations.

3 SolveSAPHE-r2: Additional Results and Information

Here we present additional results from all the test cases SolveSAPHE-r2.

To illustrate the quality of the final results, the spans of equation residuals are reported in Tables S4 and S5: Table S4 shows the actual minima and maxima; Table S5 shows 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 the corresponding $K_W/[H^+] - [H^+]/s$ value, and then the absolute minimum and maximum over all the so-obtained ratios over the complete test case grid taken).

Table S4: Minimum and maximum equation residuals obtained with `solve_at_general` and `solve_at_general_sec` at convergence, for the five test cases (SW, SW2, SW3 for the sc conditions, BW4 for the sb conditions and ABW5 for ib 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).

	SW1		SW2		SW3		BW4		ABW5	
	min	max	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	−3.5E−18	6.9E−18
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	−1.4E−16	8.3E−17
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	−1.9E−12	1.8E−12
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	−4.2E−12	3.5E−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	−4.1E−11	4.5E−11
	`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	−1.0E−17	1.0E−17
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	−1.0E−17	1.0E−17
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	−1.0E−17	1.0E−17
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	−6.9E−18	3.5E−18
	−1.3E−18	1.3E−18	−1.7E−18	1.7E−18	−8.0E−15	5.3E−15	−6.5E−19	1.1E−18	−1.0E−17	1.0E−17

Table S5: 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 five test cases (SW, SW2, SW3 for the sc conditions, BW4 for the sb conditions and ABW5 for ib 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).

	SW1		SW2		SW3		BW4		ABW5	
	min	max	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	−5.3E−7	4.2E−6
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	−5.1E−6	3.6E−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	−7.0E−2	1.1E−2
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	−5.5E−10	3.0E−10
	−2.2E−4	3.2E−4	−2.8E−3	1.0E−3	−1.4E−4	3.9E−4	−3.1E−4	5.6E−5	−2.2E−3	2.1E−3
					`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	−7.2E−7	8.4E−7
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	−2.3E−6	7.9E−7
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	−1.0E−7	1.6E−6
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	−7.4E−16	4.5E−16
	−3.5E−8	9.6E−8	−3.8E−7	3.8E−7	−1.7E−8	4.7E−9	−8.3E−8	3.4E−8	−4.6E−8	1.2E−7

3.1 Test case SW2: results for sw and dc conditions

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

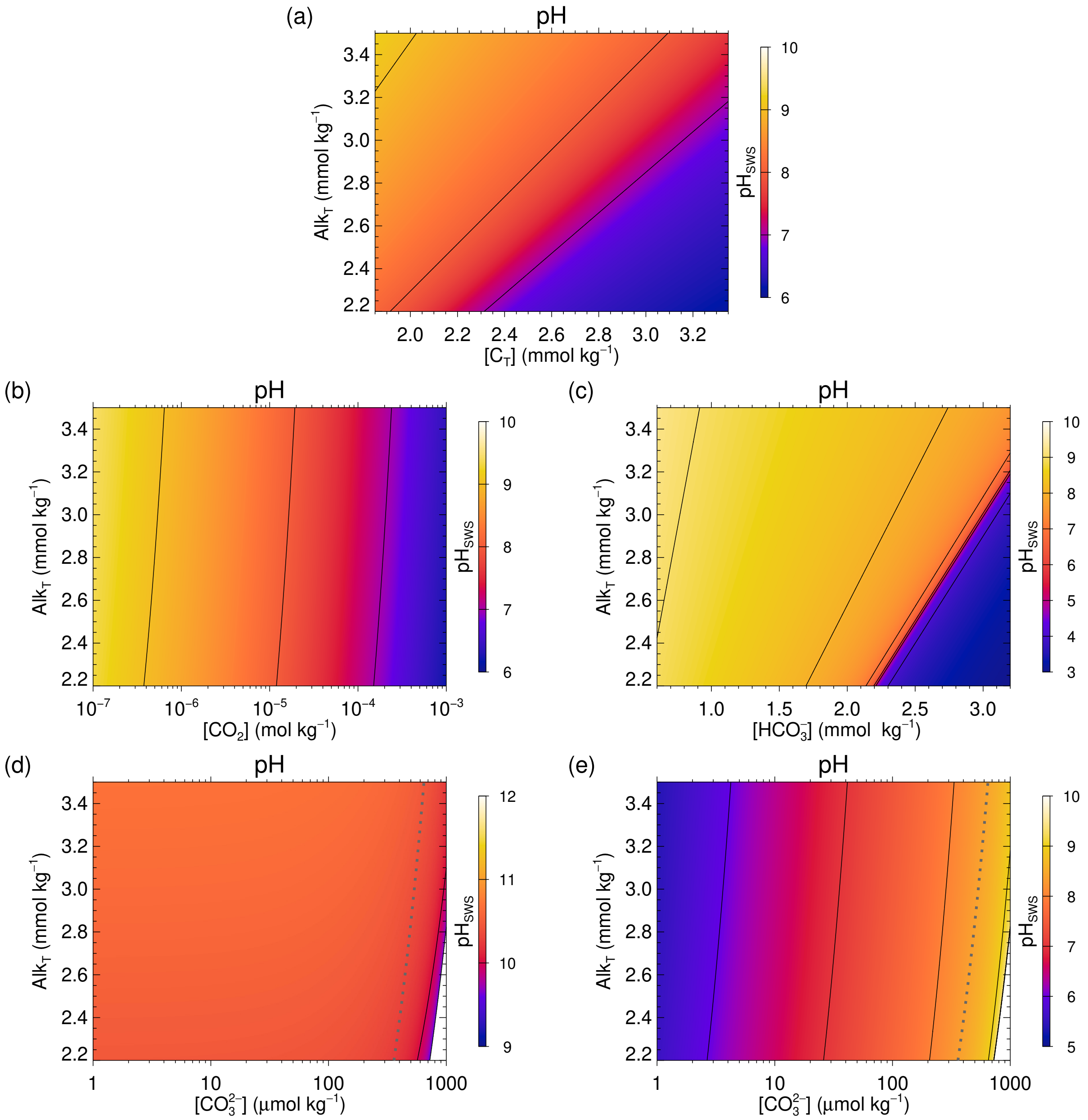

Figure S6: pH distributions for the SW2 test case under `sw` conditions ($T = 298.15\,\mathrm{K}$, $S = 35$ and $P = 0\,\mathrm{bar}$), obtained with `solve_at_general2_sec`: (a) $\mathrm{Alk_T}$ & C_T; (b) $\mathrm{Alk_T}$ & CO_2; (c) $\mathrm{Alk_T}$ & HCO_3^-; (d) the lower $[H^+]$ root (higher pH root) of $\mathrm{Alk_T}$ & CO_3^{2-}; (e) the greater $[H^+]$ root (lower pH 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 pH colour coding in the four panels.

Test case SW2: results for sw and dc conditions (continued)

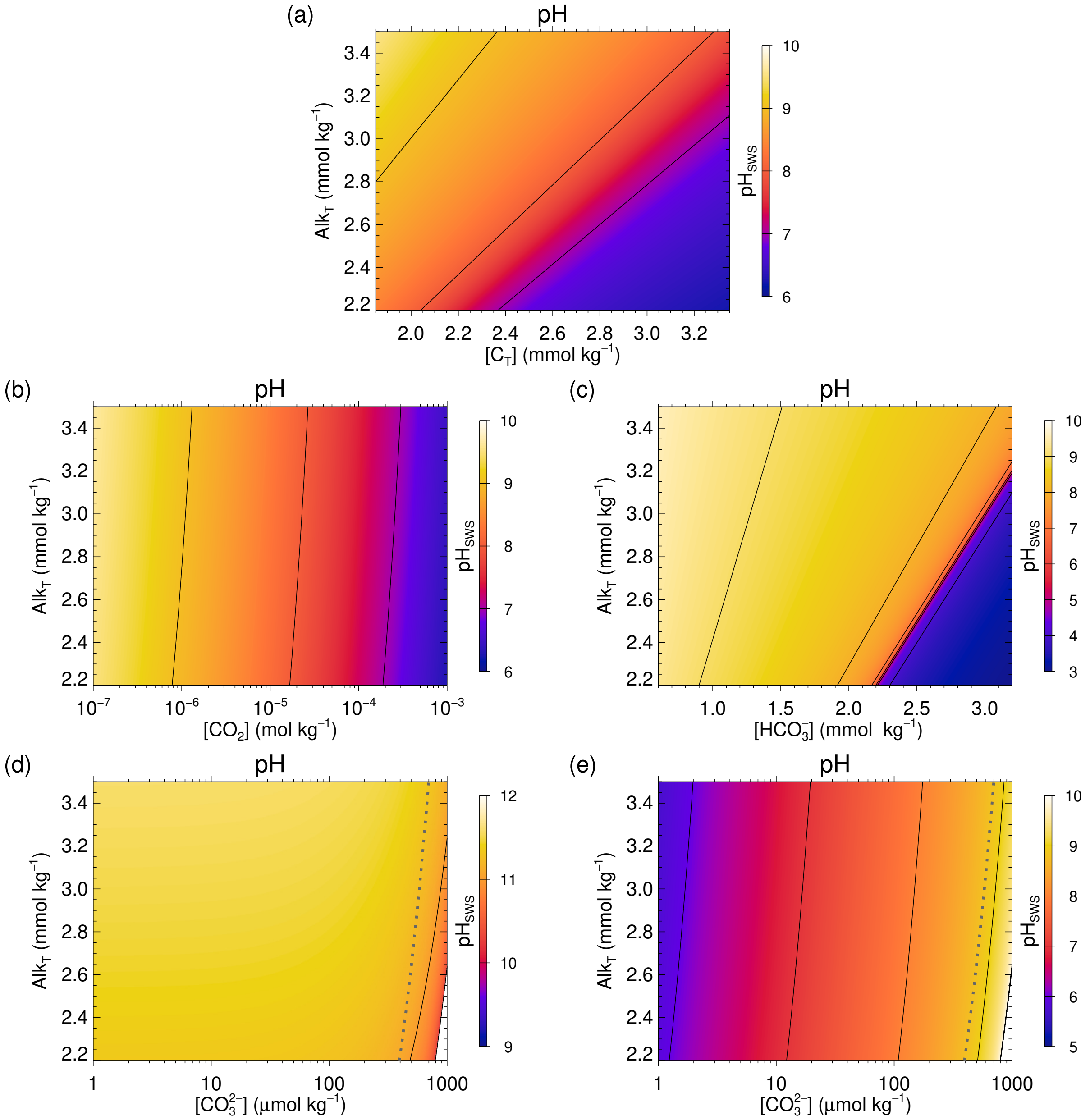

Figure S7: pH distributions for the SW2 test case under `dc` conditions ($T = 275.15$ K, $S = 35$ and $P = 300$ bar), obtained with `solve_at_general2_sec`: (a) Alk$_T$ & C_T; (b) Alk$_T$ & CO_2; (c) Alk$_T$ & HCO_3^-; (d) the lower [H^+] root (higher pH root) of Alk$_T$ & CO_3^{2-}; (e) the greater [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.

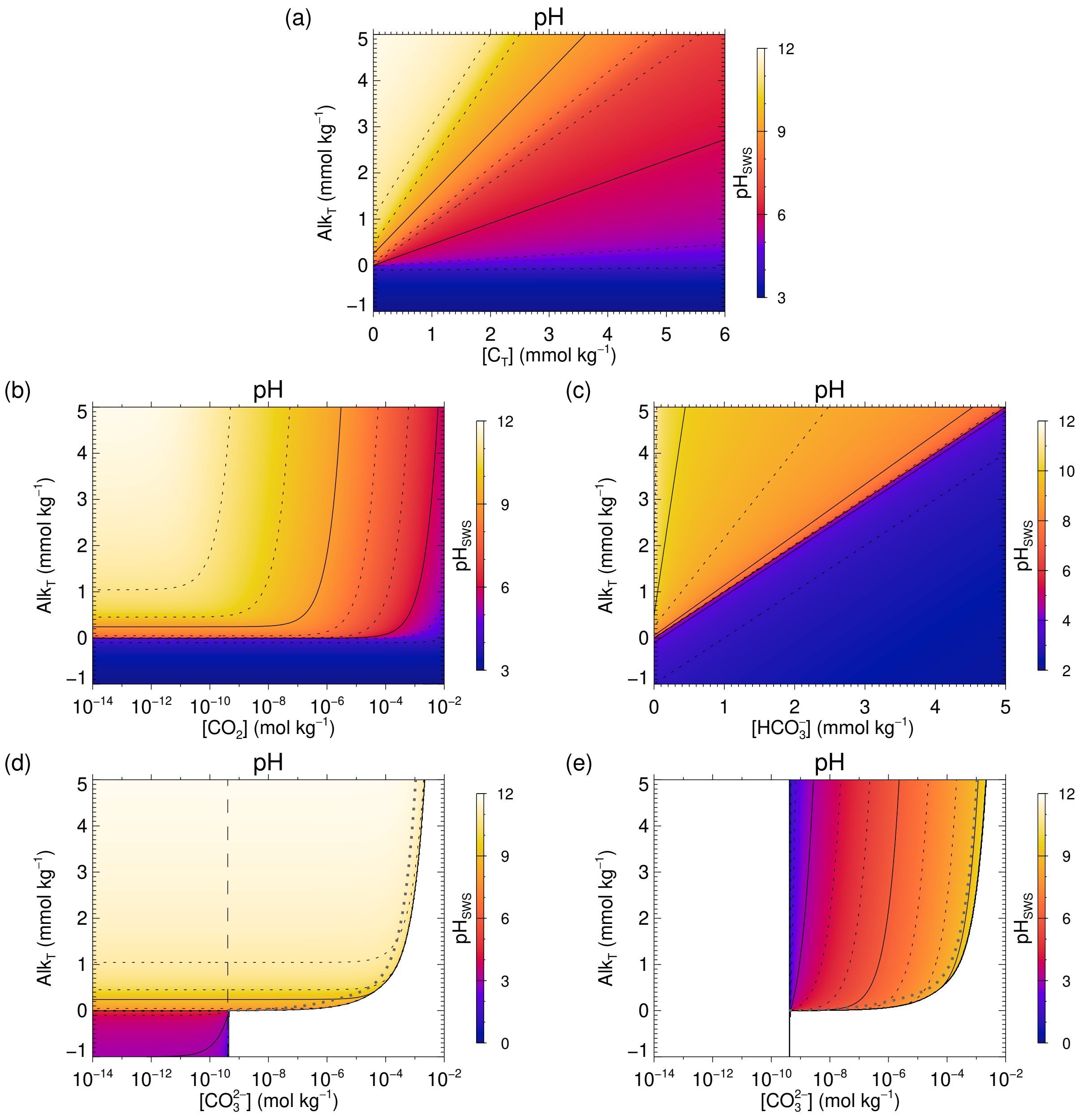

Figure S8: pH distributions for the SW3 test case under `sc` conditions ($T = 275.15\,\mathrm{K}$, $S = 35$ and $P = 0\,\mathrm{bar}$), obtained with `solve_at_general2_sec`: (a) Alk_T & C_T; (b) Alk_T & CO_2; (c) Alk_T & HCO_3^-; (d) the lower $[H^+]$ root (higher pH root) of Alk_T & CO_3^{2-}; (e) 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.

Test case SW3: results for sc, sw and dc conditions (continued)

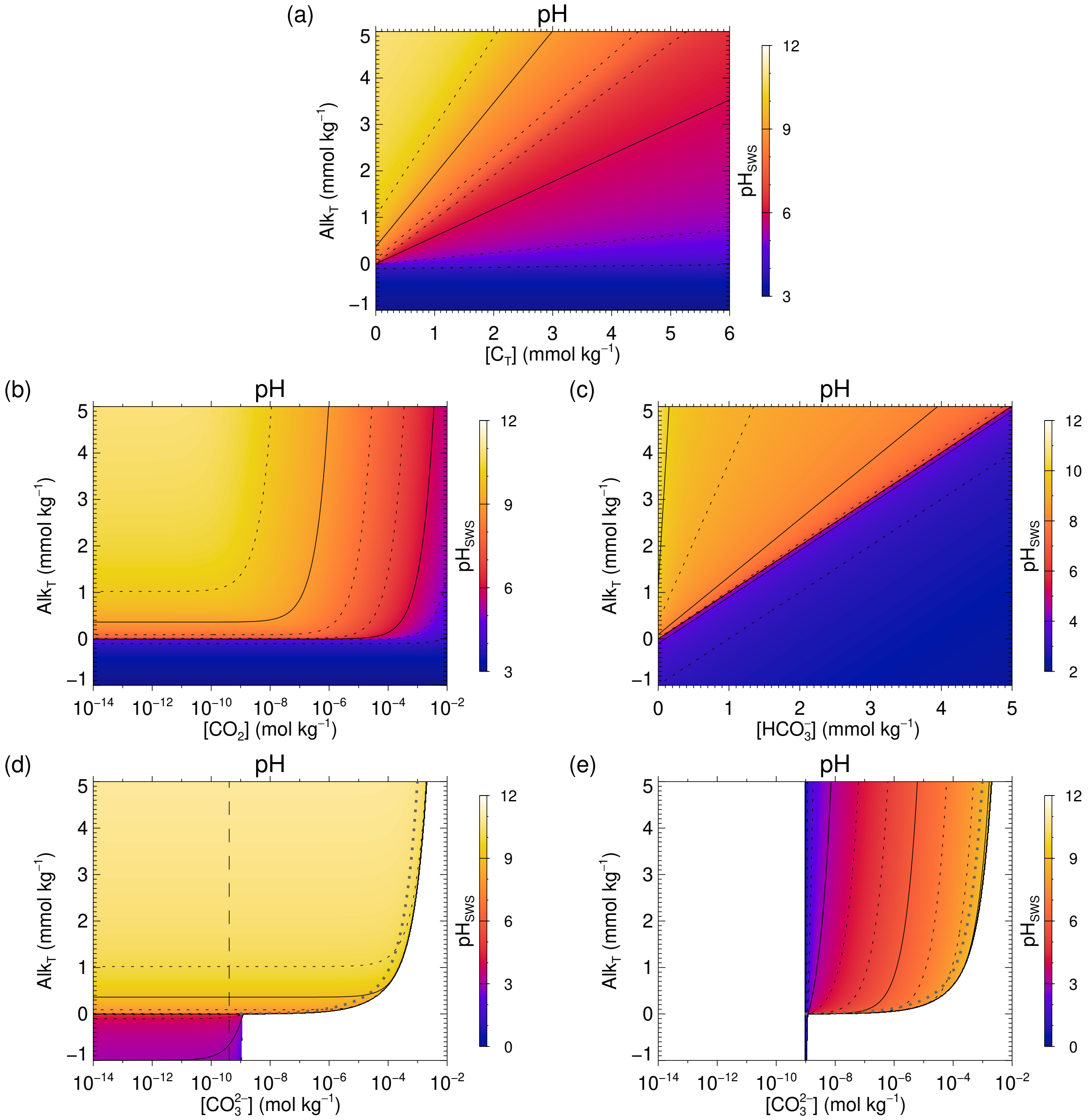

Figure S9: pH distributions for the SW3 test case under `sw` conditions ($T = 275.15\,\mathrm{K}$, $S = 35$ and $P = 0\,\mathrm{bar}$), obtained with `solve_at_general2_sec`: (a) $\mathrm{Alk_T}$ & C_T; (b) $\mathrm{Alk_T}$ & $\mathrm{CO_2}$; (c) $\mathrm{Alk_T}$ & $\mathrm{HCO_3^-}$; (d) the lower $[\mathrm{H^+}]$ 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.

Test case SW3: results for sc, sw and dc conditions (continued)

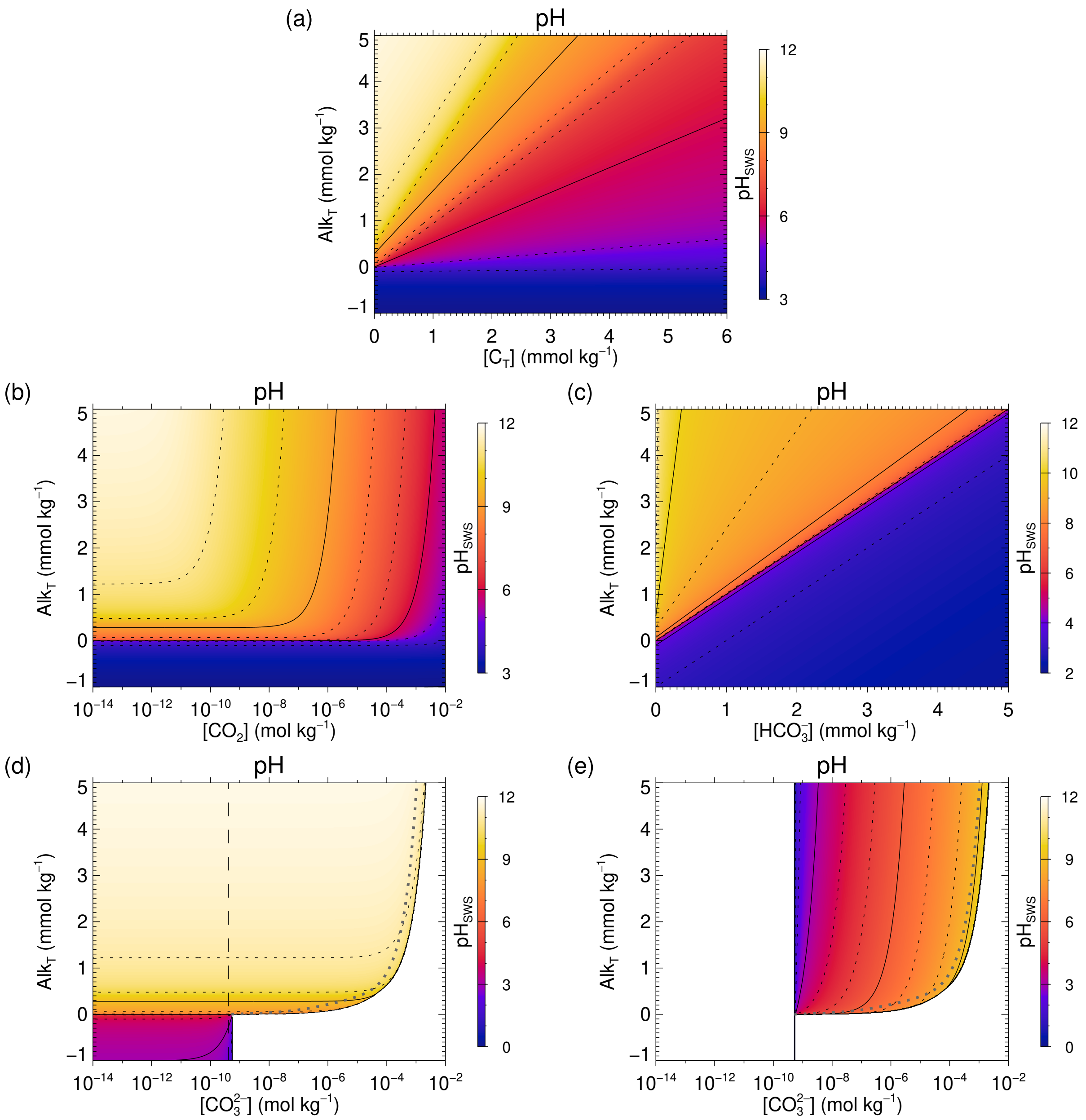

Figure S10: pH distributions for the SW3 test case under dc conditions ($T = 275.15$ K, $S = 35$ and $P = 300$ bar), obtained with `solve_at_general2_sec`: (a) Alk_T & C_T; (b) Alk_T & CO_2; (c) Alk_T & HCO_3^-; (d) the lower [H^+] root (higher pH root) of Alk_T & CO_3^{2-}; (e) the greater [H^+] root (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.

3.3 Test case BW4: results for sb conditions

In this section, we present the *p*H distributions obtained for the test case BW4, with environmental conditions sb.

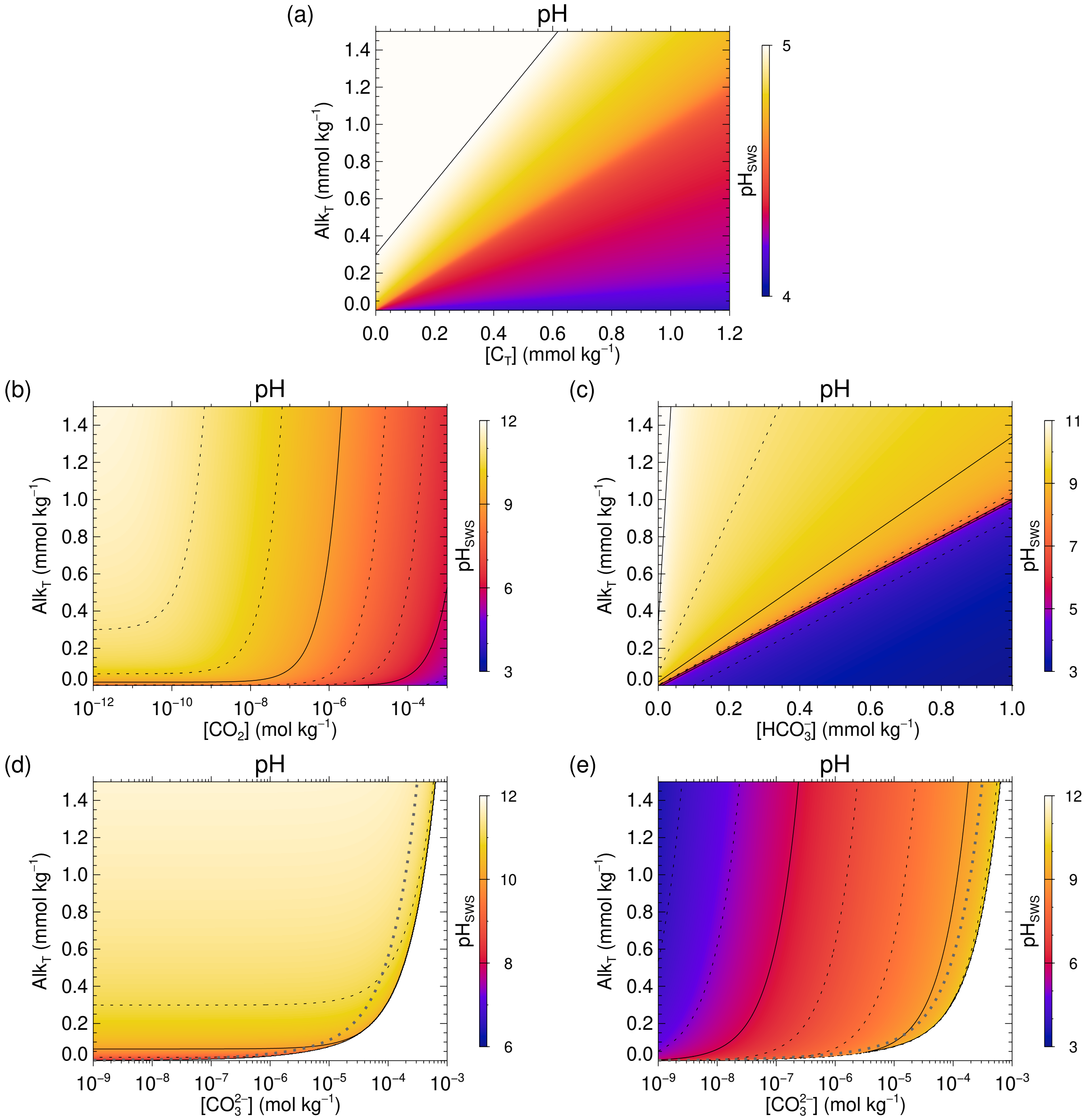

Figure S11: *p*H distributions for the BW4 test case under cold brackish surface conditions ($T = 275.15\,K$, $S = 3.5$ and $P = 0\,bar$), obtained with `solve_at_general2_sec`: (a) Alk_T & C_T; (b) Alk_T & CO_2; (c) Alk_T & HCO_3^-; (d) the lower [H^+] root (higher *p*H root) of Alk_T & CO_3^{2-}; (e) the greater [H^+] root (lower *p*H 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 *p*H colour coding in the four panels.

3.4 Test case ABW5: results for ib conditions

In this section, we present the pH distributions obtained for the test case ABW5, with environmental conditions ib.

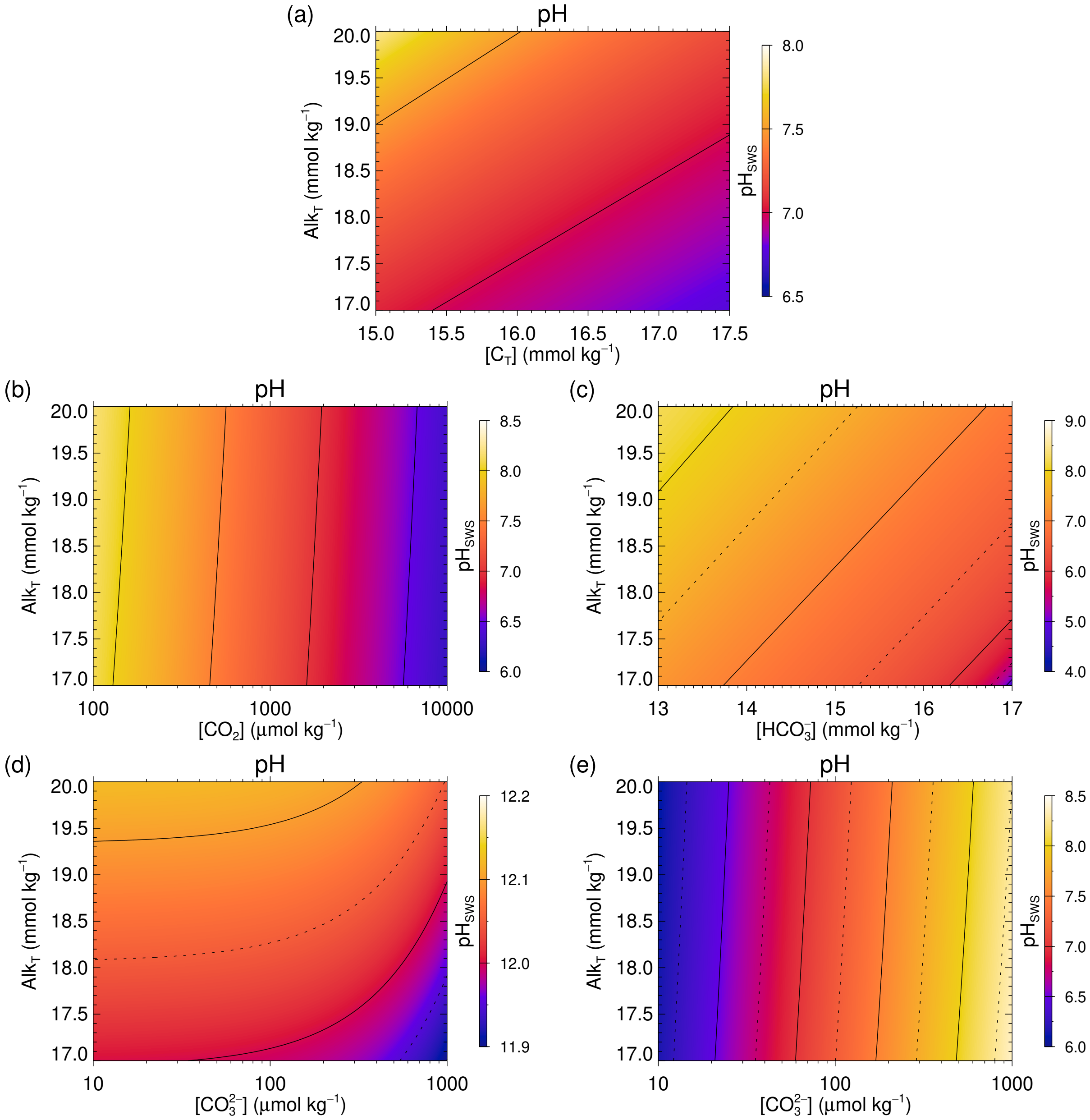

Figure S12: pH distributions for the ABW5 test case under cold brackish subsurface conditions (T = 280.71 K, S = 22.82 and P = 13.5 bar), obtained with `solve_at_general2_sec`: (a) Alk_T & C_T; (b) Alk_T & CO_2; (c) Alk_T & HCO_3^-; (d) the lower [H^+] root (higher pH root) of Alk_T & CO_3^{2-}; (e) 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.

3.5 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 $\mathrm{Alk_T}$ & 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.

3.5.1 $\mathbf{Alk_T}$ & $C_\mathbf{T}$

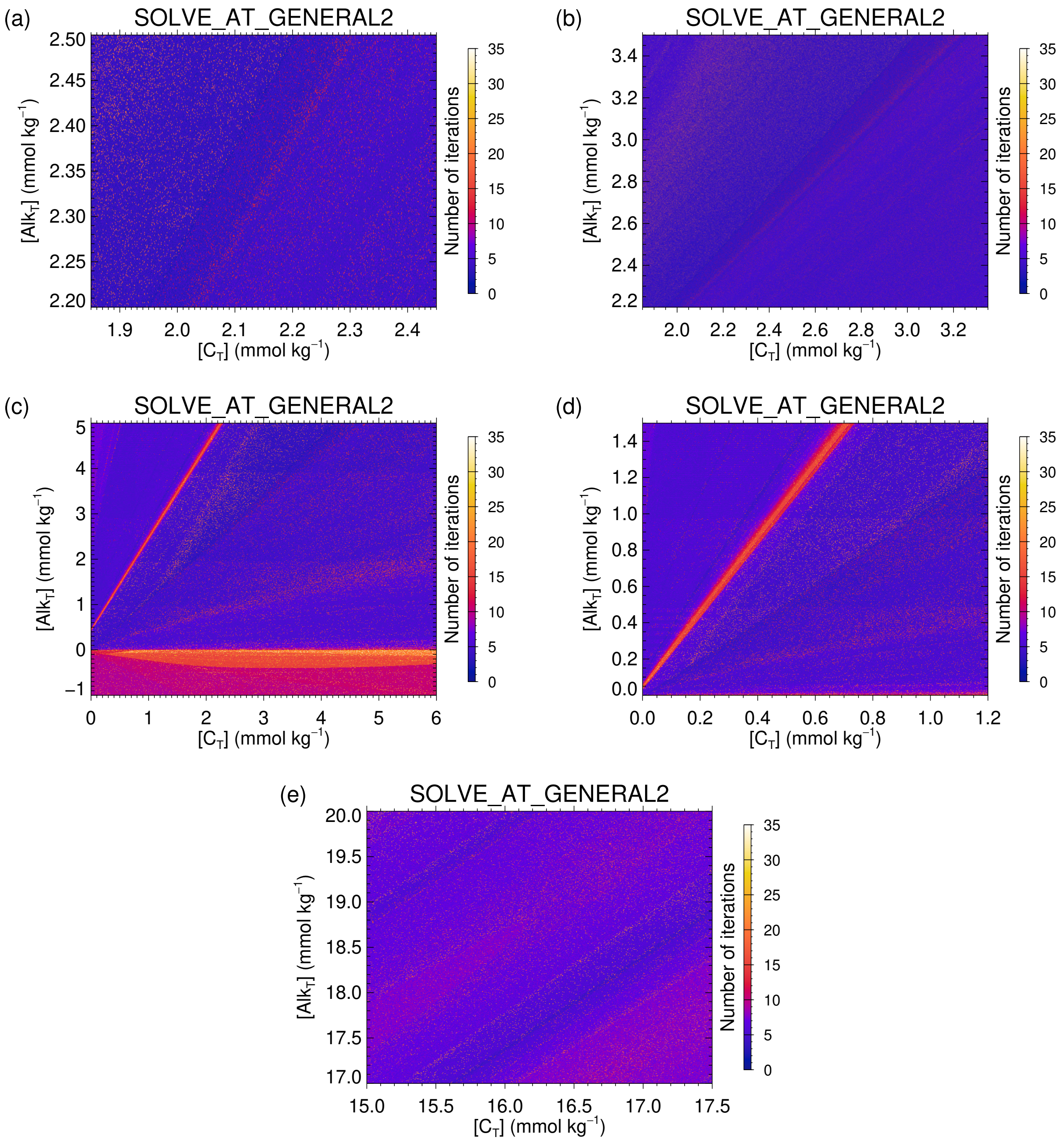

Figure S13: Number of iterations to convergence required by `solve_at_general2` for the $\mathrm{Alk_T}$ & C_T pair: (a) SW1; (b) SW2; (c) SW3 – all with sc conditions; (d) BW4, with sb conditions; (e) ABW5, with ib conditions.

Alk_T & C_T (continued)

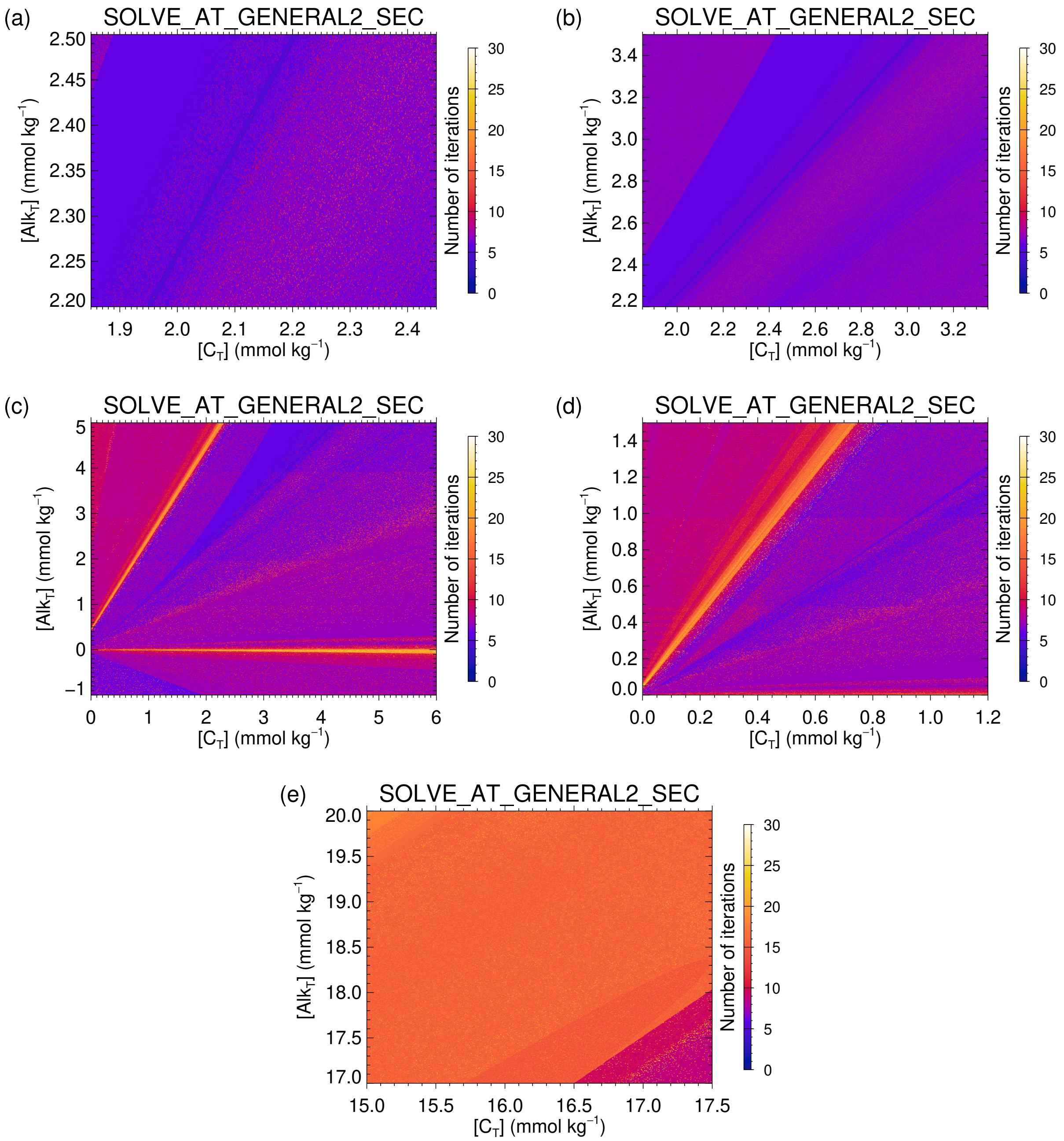

Figure S14: Number of iterations to convergence required by `solve_at_general2_sec` for the Alk_T & C_T pair: (a) SW1; (b) SW2; (c) SW3 – all with sc conditions; (d) BW4, with sb conditions; (e) ABW5, with ib conditions.

3.5.2 Alk_T & CO_2

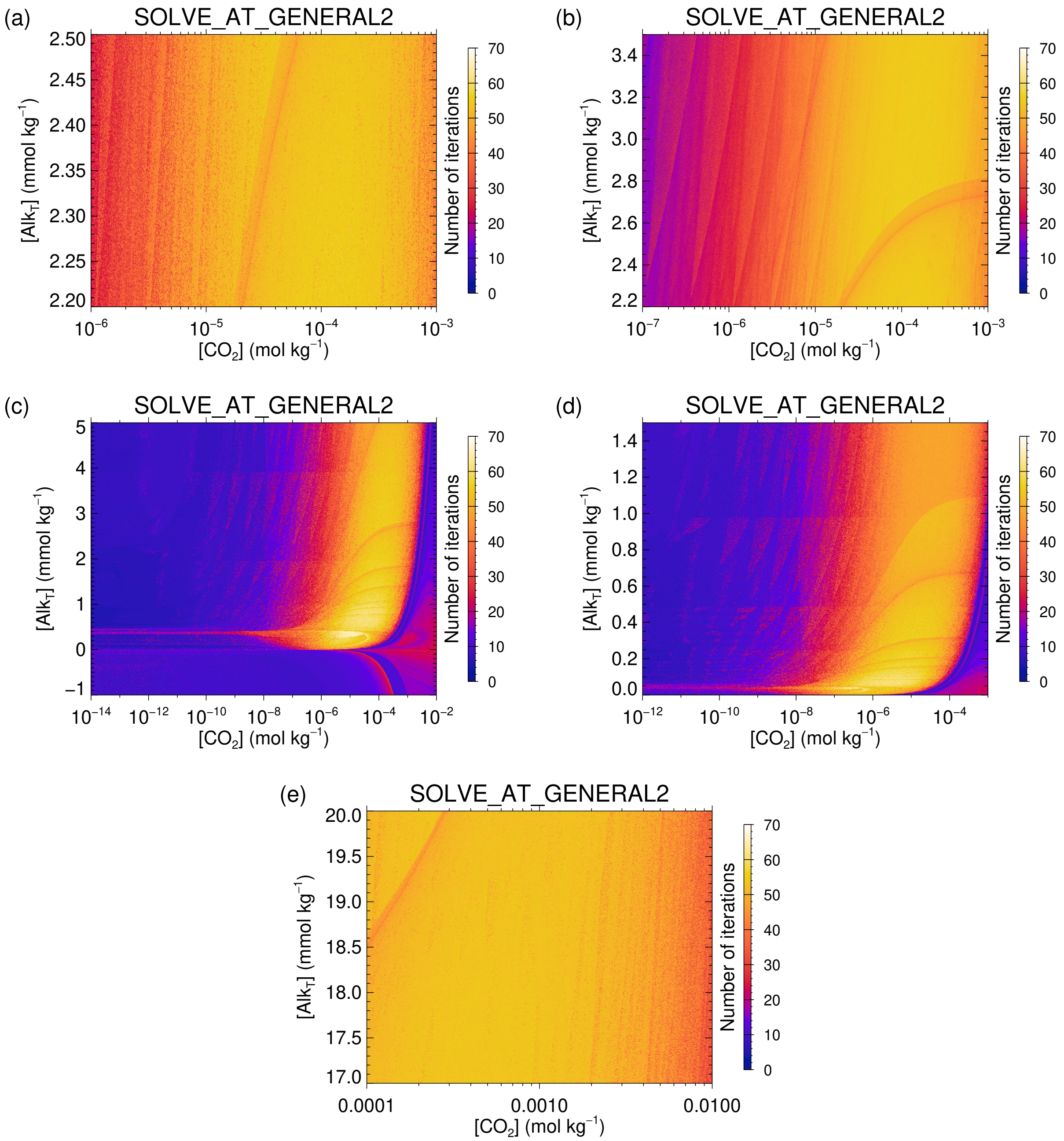

Figure S15: Number of iterations to convergence required by `solve_at_general2` for the Alk_T & CO_2 pair: (a) SW1; (b) SW2; (c) SW3 – all with sc conditions; (d) BW4, with sb conditions; (e) ABW5, with ib conditions.

Alk_T & CO_2 (continued)

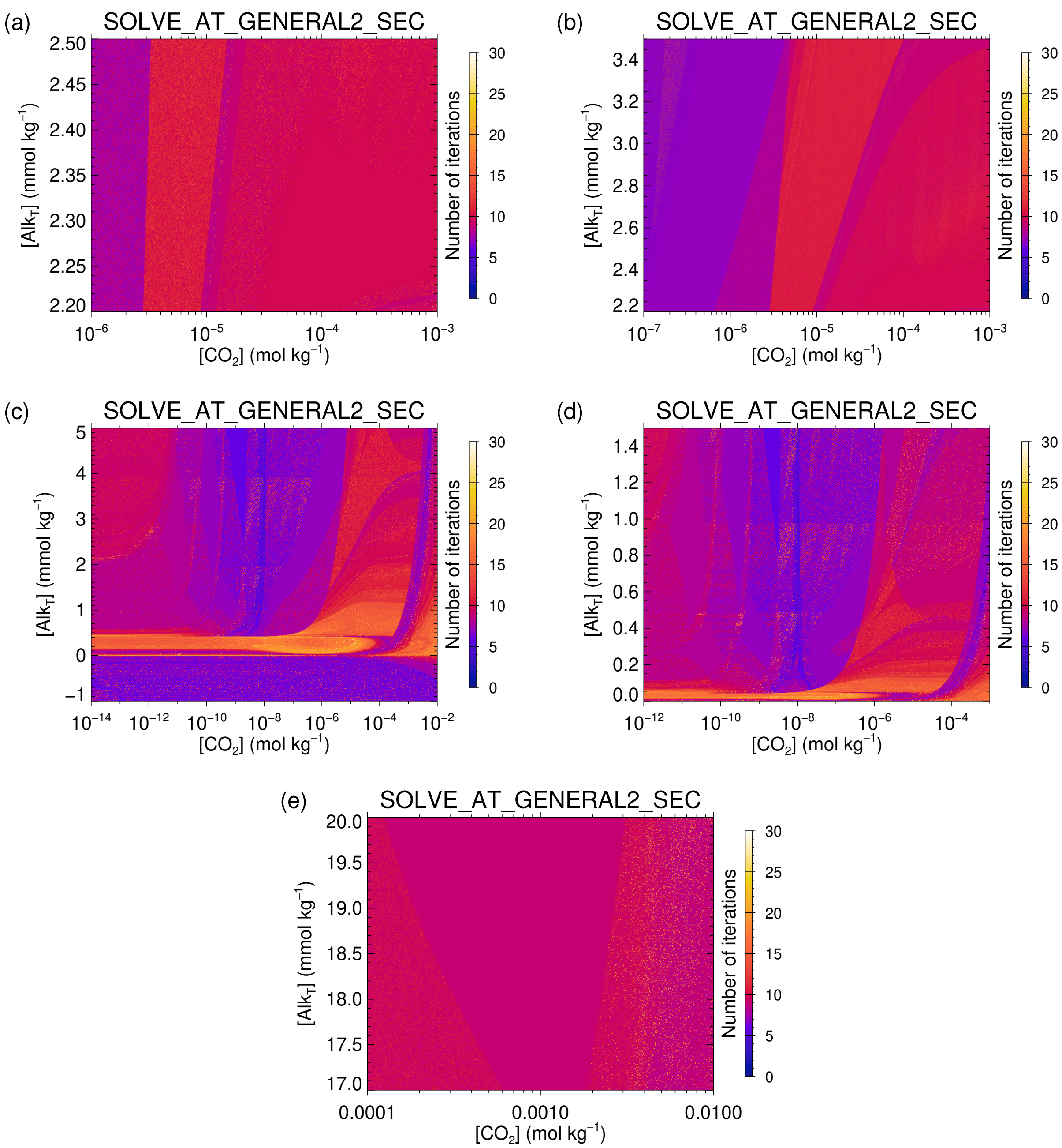

Figure S16: Number of iterations to convergence required by `solve_at_general2_sec` for the Alk_T & CO_2 pair: (a) SW1; (b) SW2; (c) SW3 – all with sc conditions; (d) BW4, with sb conditions; (e) ABW5, with ib conditions.

3.5.3 Alk_T & HCO_3^-

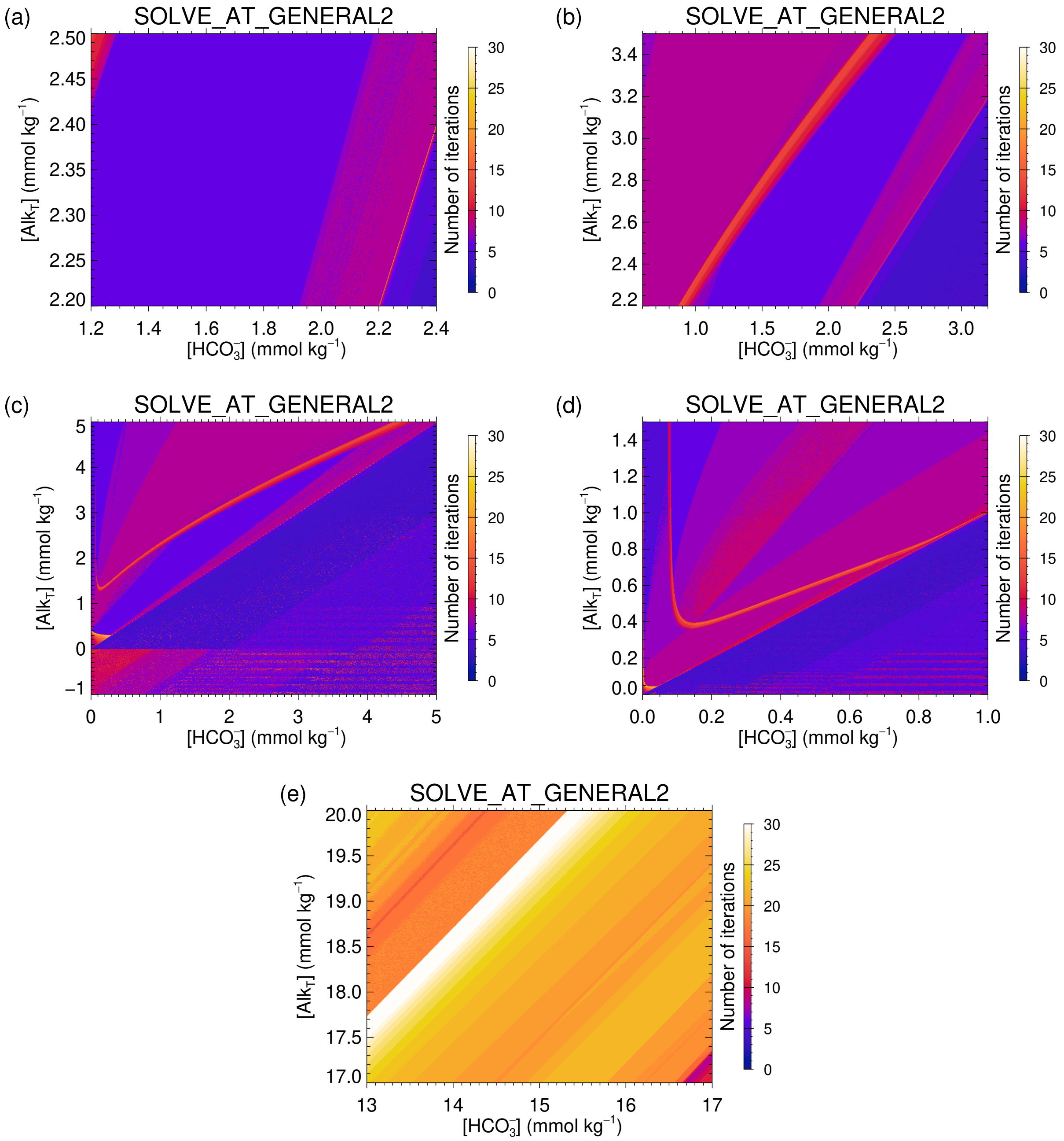

Figure S17: Number of iterations to convergence required by `solve_at_general2` for the Alk_T & HCO_3^- pair: (a) SW1; (b) SW2; (c) SW3 – all with sc conditions; (d) BW4, with sb conditions; (e) ABW5, with ib conditions.

Alk_T & HCO_3^- (continued)

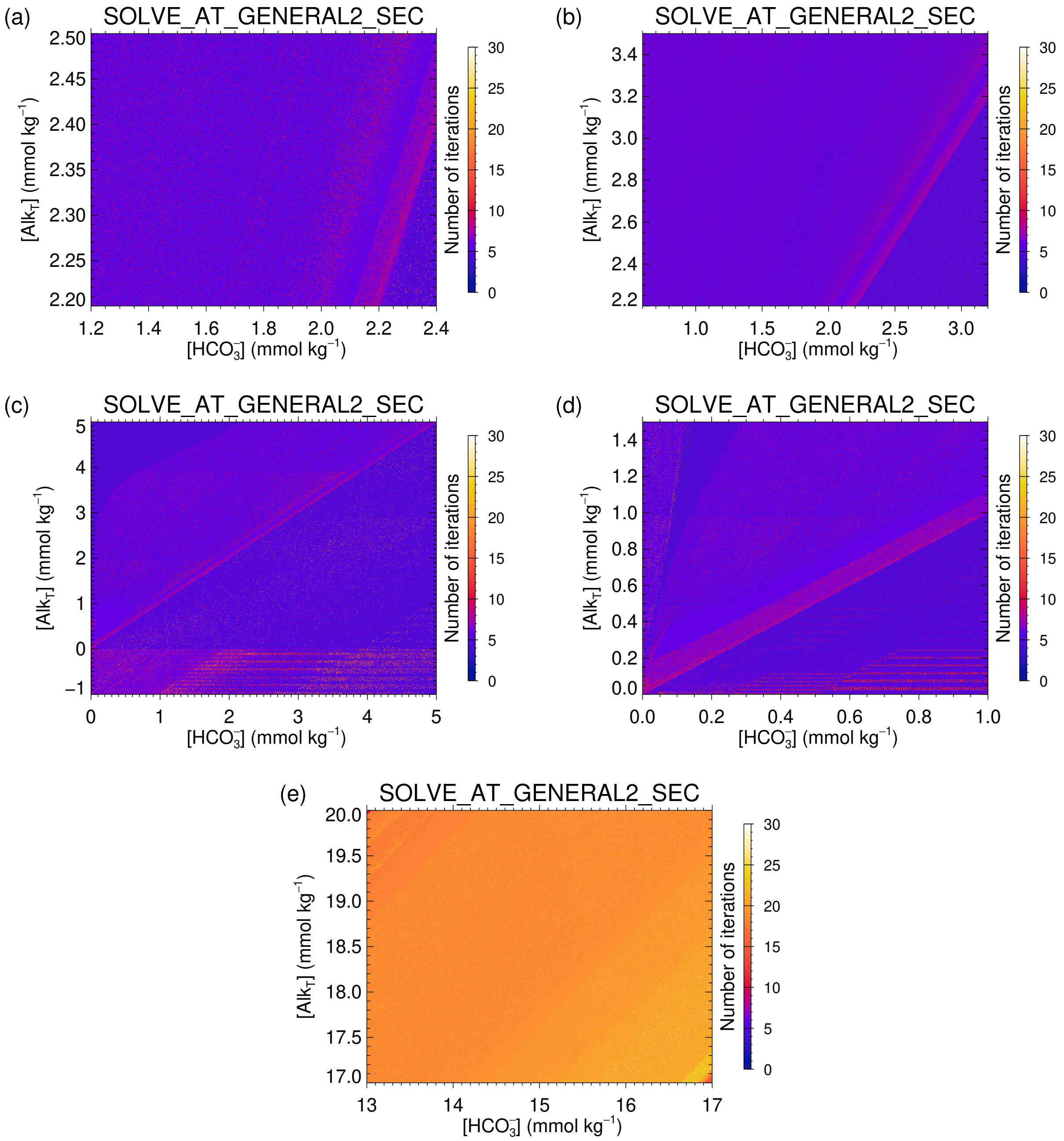

Figure S18: Number of iterations to convergence required by `solve_at_general2_sec` for the Alk_T & HCO_3^- pair: (a) SW1; (b) SW2; (c) SW3 – all with sc conditions; (d) BW4, with sb conditions; (e) ABW5, with ib conditions.

3.5.4 Alk_T & CO_3^{2-}

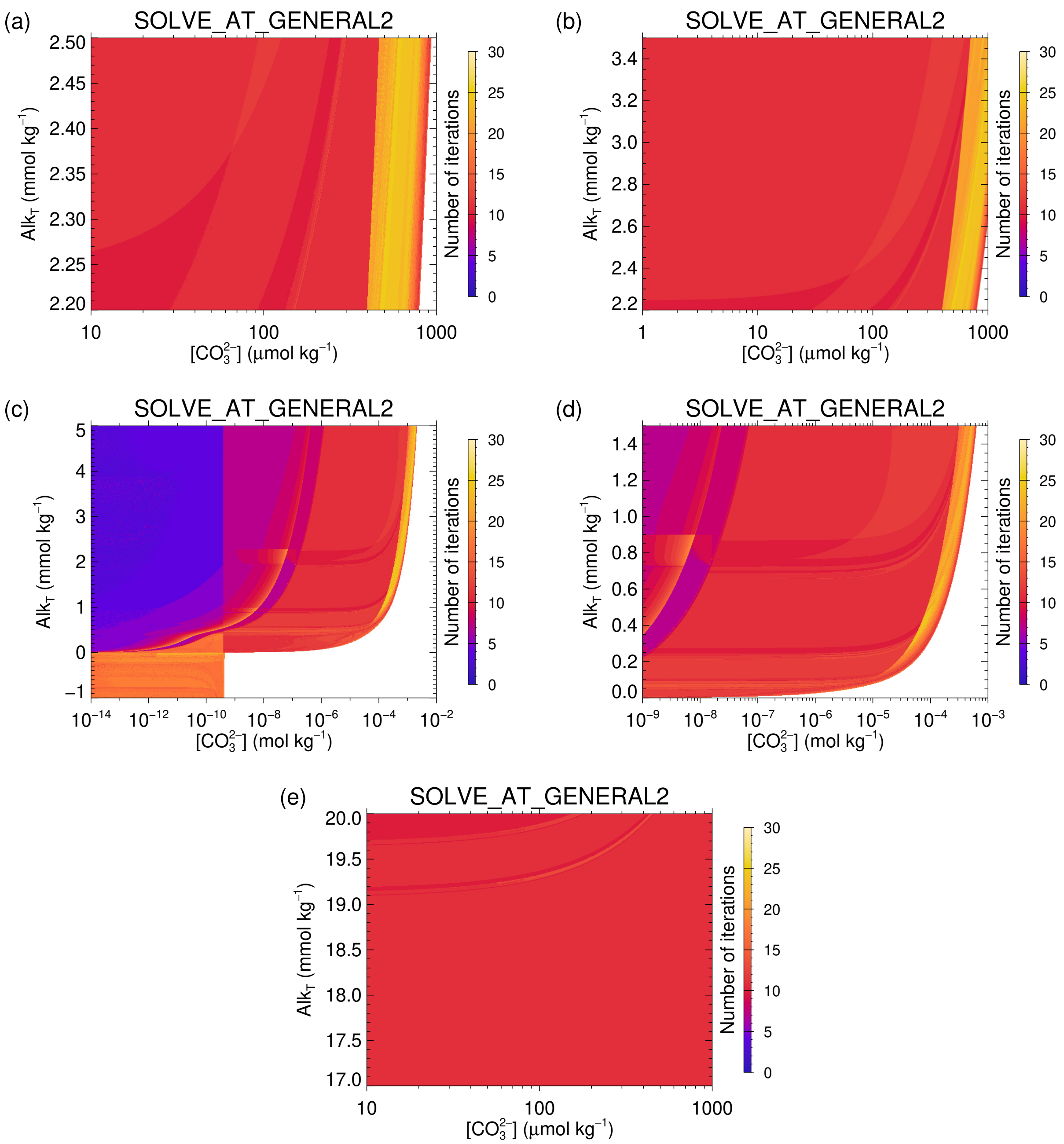

Figure S19: Number of iterations to convergence required by `solve_at_general2` for the Alk_T & CO_3^{2-} pair to determine the unique or the lower one of the two $[H^+]$ roots: (a) SW1; (b) SW2; (c) SW3 – all with sc conditions; (d) BW4, with sb conditions; (e) ABW5, with ib conditions.

Alk_T & CO_3^{2-} (continued)

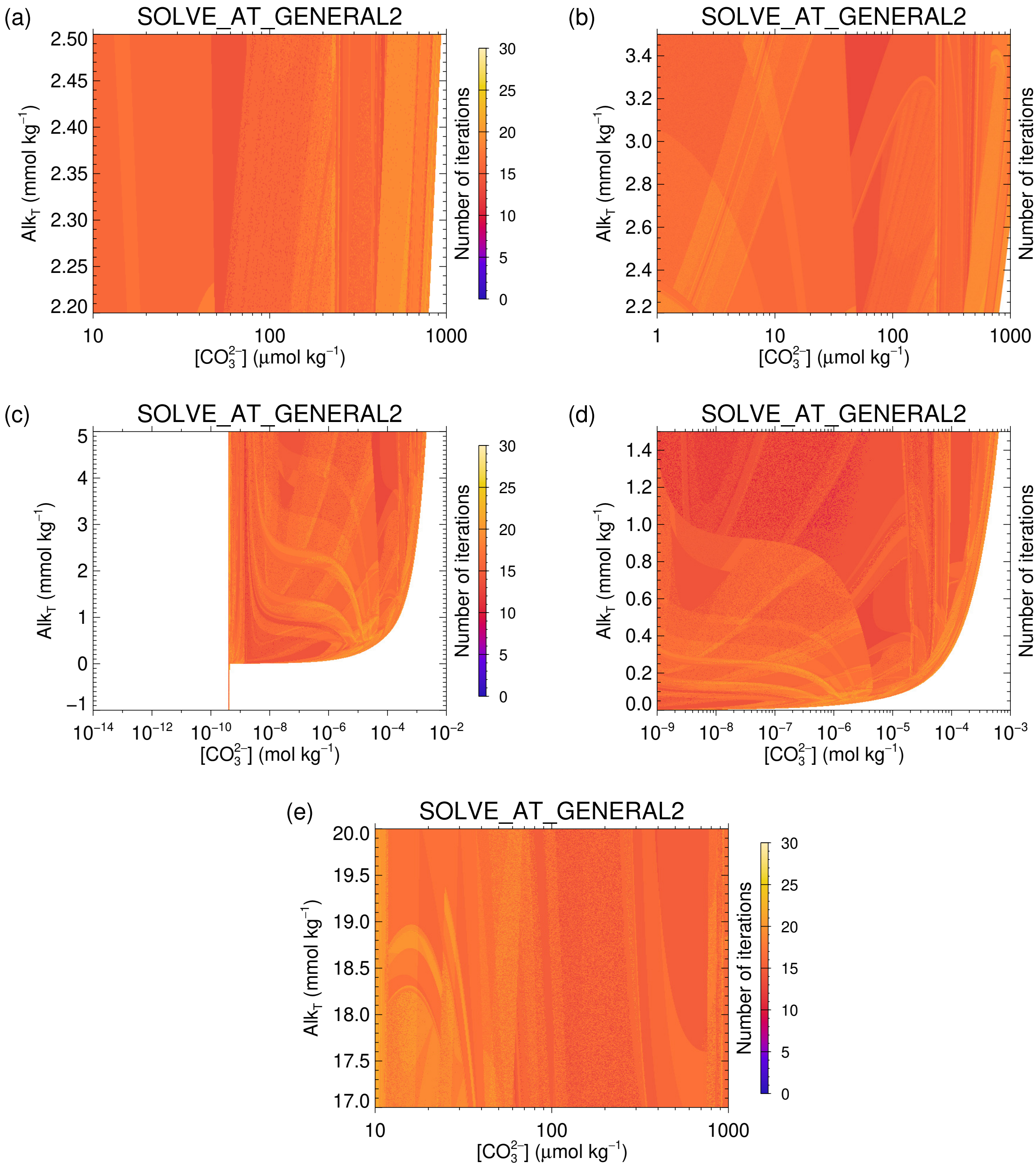

Figure S20: Number of iterations to convergence required by `solve_at_general2` for the Alk_T & CO_3^{2-} pair to determine the greater one of the two $[H^+]$ roots: (a) SW1; (b) SW2; (c) SW3 – all with sc conditions; (d) BW4, with sb conditions; (e) ABW5, with ib conditions.

$\mathrm{Alk_T}$ & $\mathrm{CO_3^{2-}}$ (continued)

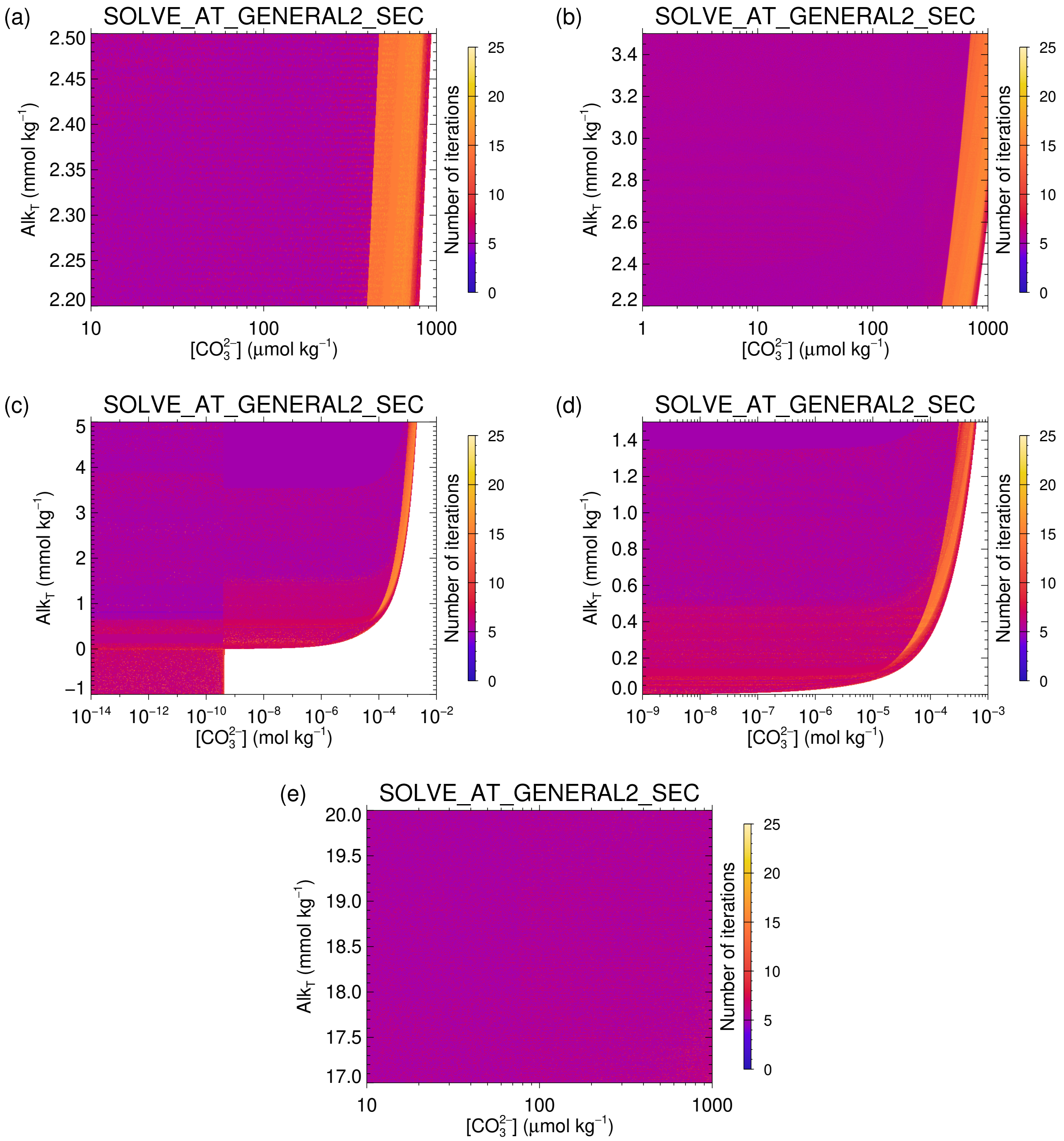

Figure S21: Number of iterations to convergence required by `solve_at_general2_sec` for the $\mathrm{Alk_T}$ & $\mathrm{CO_3^{2-}}$ pair to determine the unique or the lower one of the two $[\mathrm{H^+}]$ roots: (a) SW1; (b) SW2; (c) SW3 – all with sc conditions; (d) BW4, with sb conditions; (e) ABW5, with ib conditions.

Alk$_T$ & CO_3^{2-} (continued)

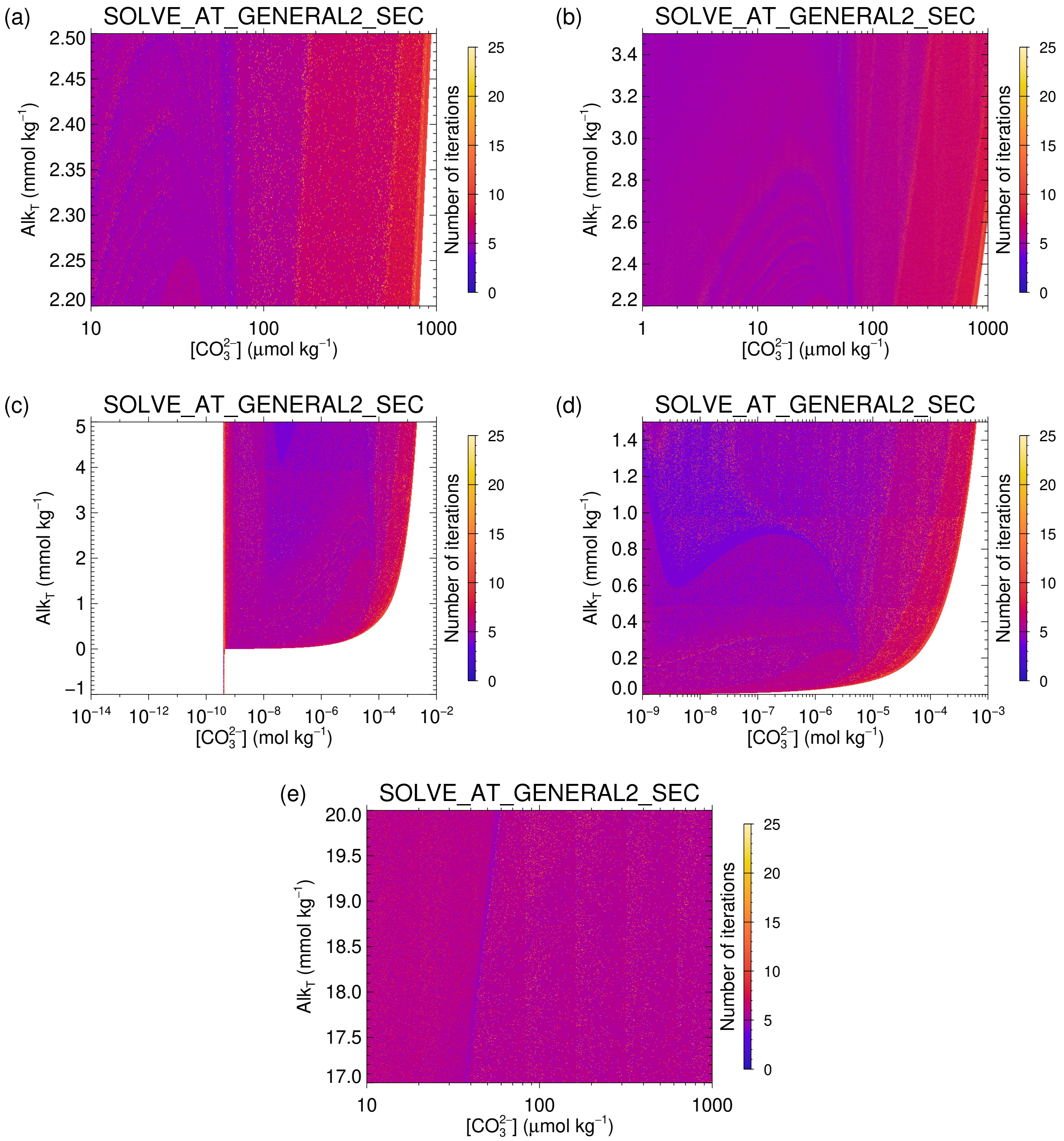

Figure S22: Number of iterations to convergence required by `solve_at_general2_sec` for the Alk$_T$ & CO_3^{2-} pair to determine the greater of the two [H^+] roots: (a) SW1; (b) SW2; (c) SW3 – all with sc conditions; (d) BW4, with sb conditions; (e) ABW5, with ib conditions.

Alk_T & CO_3^{2-} (continued)

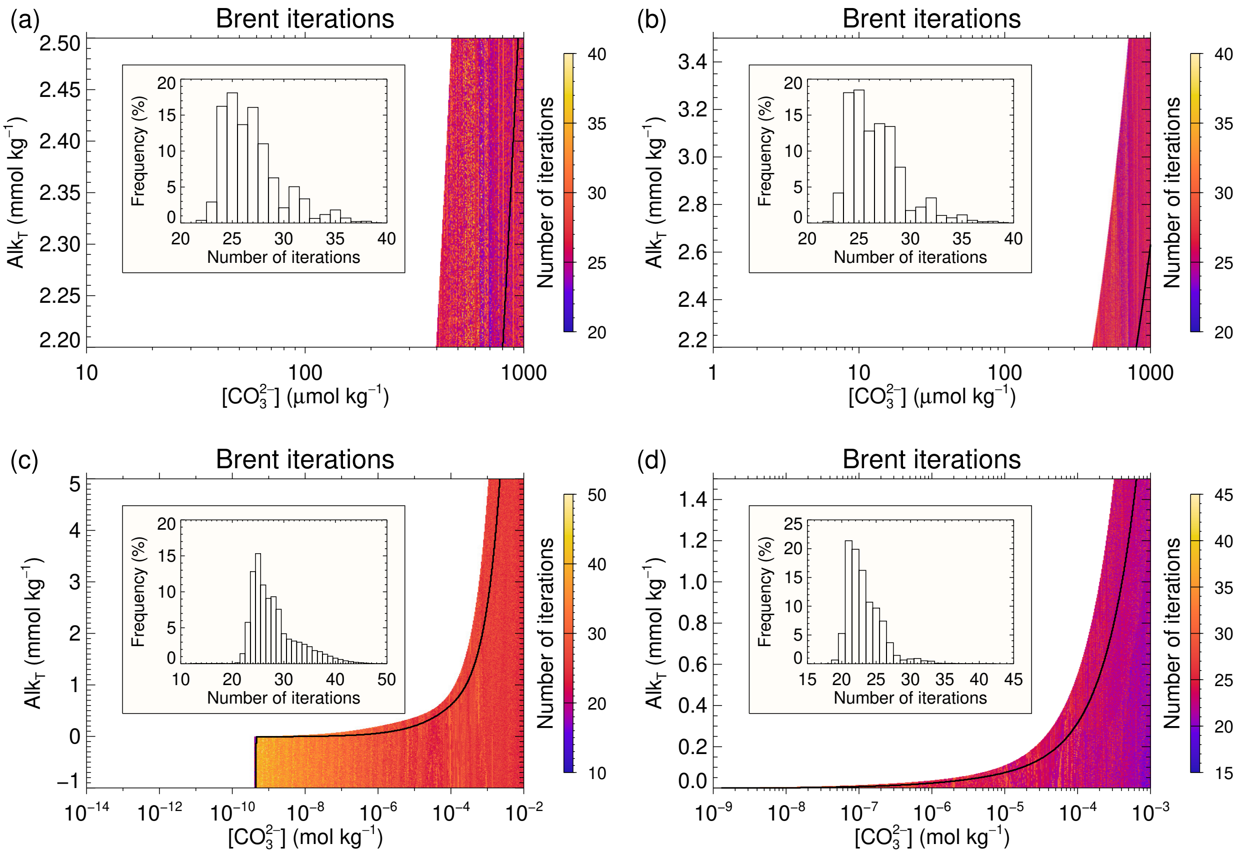

Figure S23: Number of iterations required by Brent's algorithm to solve the auxiliary minimisation problem whose solution determines the number of roots of the Alk_T & CO_3^{2-} pair and also provides the separation between the two roots: (a) SW1; (b) SW2; (c) SW3 – all with sc conditions; (d) BW4, with sb conditions. ABW5 does not require the minimisation problem to be solved. 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).