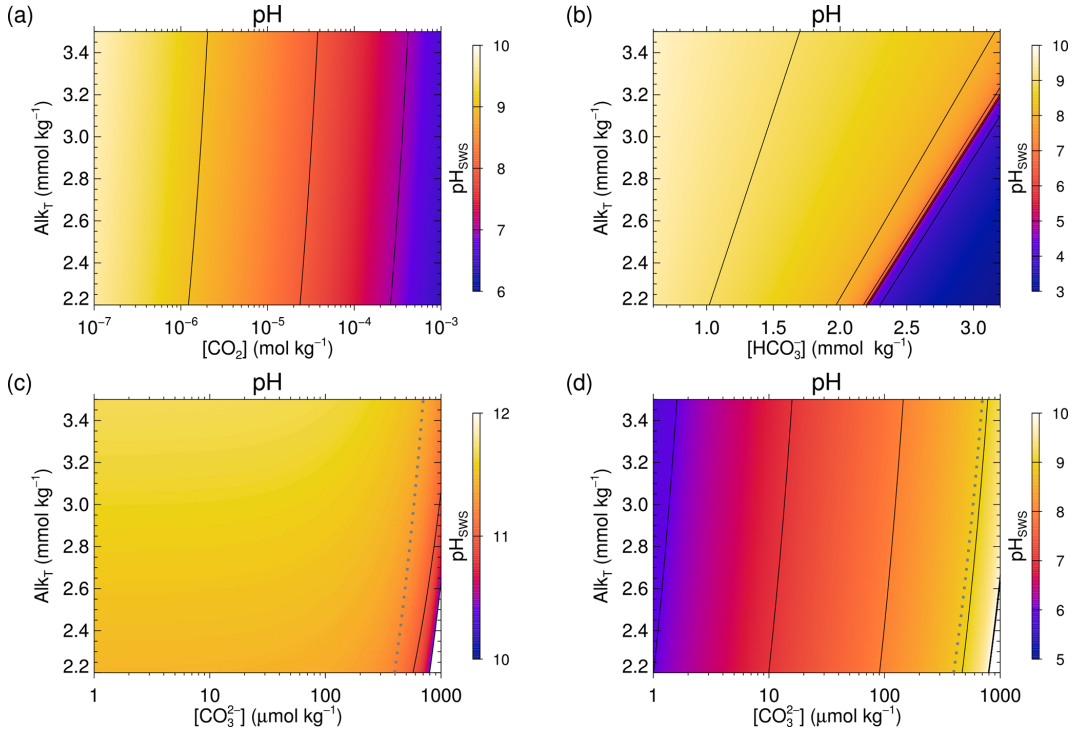

Figure 5. pH distributions for the SW2-sc test case (SW2 under cold surface conditions, where $T = 273.15\,\mathrm{K}$, $S = 35$ and $P = 0\,\mathrm{bar}$), obtained with `solve_at_general2_sec`: **(a)** $\mathrm{Alk_T}$–$\mathrm{CO_2}$; **(b)** $\mathrm{Alk_T}$–$\mathrm{HCO_3^-}$; **(c)** the lower $[\mathrm{H^+}]$ root (higher pH root) of $\mathrm{Alk_T}$–$\mathrm{CO_3^{2-}}$; **(d)** the greater $[\mathrm{H^+}]$ root (lower pH root) of $\mathrm{Alk_T}$–$\mathrm{CO_3^{2-}}$. The thick dashed grey line in panels **(c)** and **(d)** 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 text and in the Supplement. Please notice the different scales on the horizontal axes and for the pH colour coding in the four panels.

quires typically about twice as many iterations to solve the $\mathrm{Alk_T}$–C_T problem than `solve_at_general`.

All these observations are also reflected in the execution times of the two solvers. The Newton–Raphson-based solver takes more than 5 times as much time for the SW2 test case with $\mathrm{Alk_T}$–$\mathrm{CO_2}$ than with $\mathrm{Alk_T}$–C_T; for $\mathrm{Alk_T}$–$\mathrm{CO_3^{2-}}$, it takes 4 times as much (for both roots though, including the solution of the minimisation problem for part of the domain). For $\mathrm{Alk_T}$–$\mathrm{HCO_3^-}$, the difference is only 20 %. With the secant-based method, the picture is completely different: $\mathrm{Alk_T}$–$\mathrm{CO_2}$ takes only about 30 % more time than $\mathrm{Alk_T}$–C_T, $\mathrm{Alk_T}$–$\mathrm{CO_3^{2-}}$ twice as much, whereas $\mathrm{Alk_T}$–$\mathrm{HCO_3^-}$ executes even about 5 % faster. For the $\mathrm{Alk_T}$–$\mathrm{CO_2}$ pair of input data, the difference between the two 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. 2.5) results in 40 %–60 % increases of the execution times for the $\mathrm{Alk_T}$–C_T and the $\mathrm{Alk_T}$–$\mathrm{HCO_3^-}$ input pairs, compared to the standard cubic polynomial one. Similar increases are obtained with a constant uniform pH = 8 initialisation. For $\mathrm{Alk_T}$–$\mathrm{CO_2}$, and $\mathrm{Alk_T}$–$\mathrm{CO_3^{2-}}$, 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 Sect. 2.4.1, two characteristic thresholds for $\mathrm{Alk_T}$ have been made out for $\gamma > 0$: an upper one at $L_\mathrm{min} + \mathrm{Alk_{nWC}}(H_\mathrm{min})$, above which the problem always has two $[\mathrm{H^+}]$ solutions, and a lower one at $L_\mathrm{min} + \mathrm{Alk_{nWCinf}}$, below which the problem does not have any solution at all. For intermediate values of $\mathrm{Alk_T}$, it is necessary to determine H_tan and $\mathrm{Alk_{tan}}$ 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 in Fig. 8 (for SW2-sc). The most probable number of iterations is in all experiments between 21 and 25; the median number is each time 0.9 ± 0.5 higher than the most probable number, due to the skew-symmetric nature of the distribution of the number of iterates, as illustrated in the insert in Fig. 8 (see also Fig. S23 in the "Additional Results" section in the Supplement). The subsequent computation of the roots is much