Supplementary Information for Temperature effect on seawater fCO_2 revisited: theoretical basis, uncertainty analysis, and implications for parameterising carbonic acid equilibrium constants

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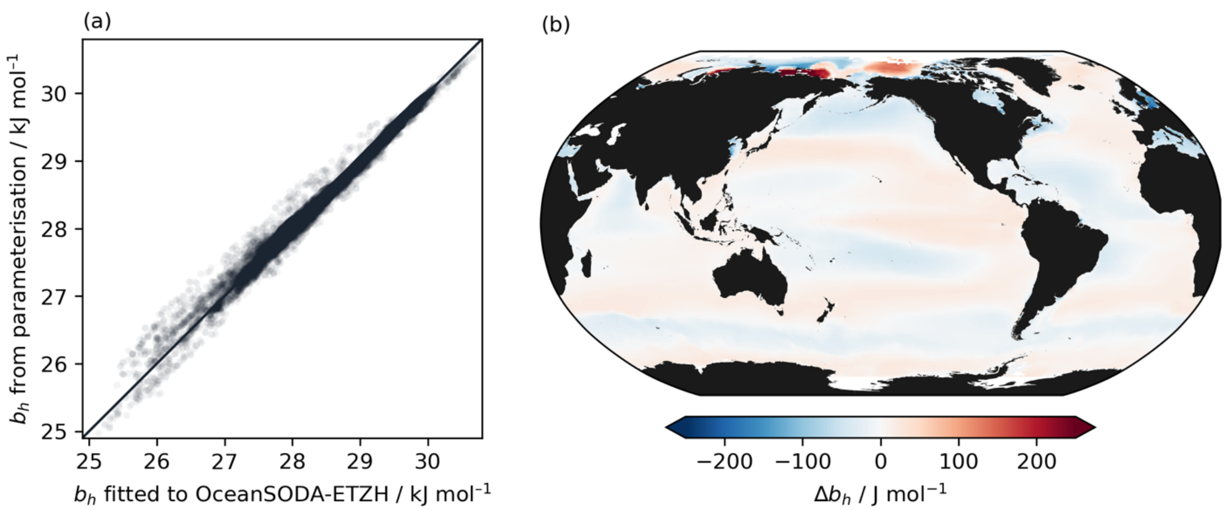
Supplementary Table 1: Best-fit coefficients for the parameterisation of b_h in Eq. (35).

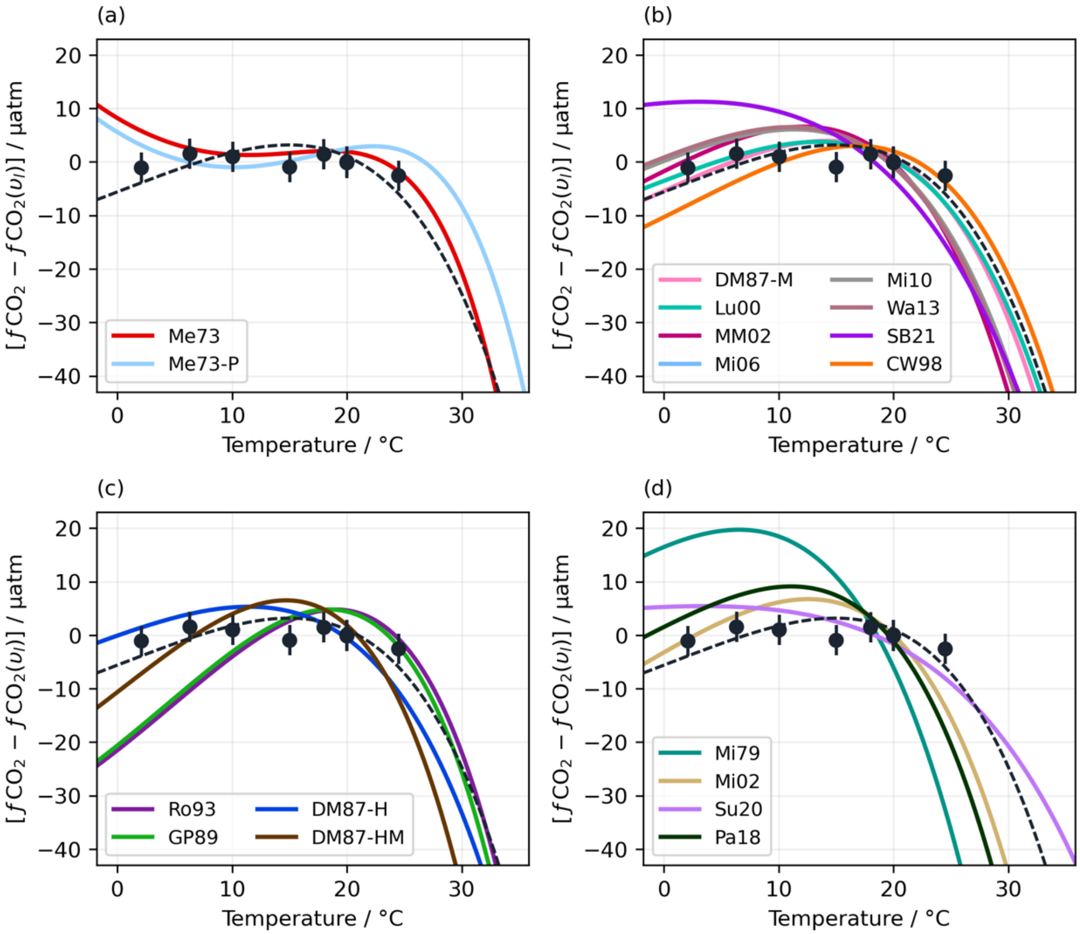
Coefficient	Value	Unit
u_0	31318.4	J mol^{-1}
u_1	139.488	J mol^{-1} °C^{-1}
u_2	−1.21088	J mol^{-1}
u_3	−4.22484	J mol^{-1} µatm^{-1}
u_4	−0.652212	J mol^{-1} °C^{-2}
u_5	−16.9522	J mol^{-1}
u_6	−0.000547593	J mol^{-1} µatm^{-2}
u_7	−3.02072	J mol^{-1} °C^{-1}
u_8	0.166973	J mol^{-1} °C^{-1} µatm^{-1}
u_9	0.309654	J mol^{-1} µatm^{-1}

Supplementary Table 2: The variance-covariance matrix for uncertainty propagation for the best-fit coefficients (Supp. Table 1) of the b_h parameterisation in Eq. (35). The main diagonal gives the variance for each coefficient while the off-diagonal values represent the covariances. The units are consistent with Supp. Table 1.

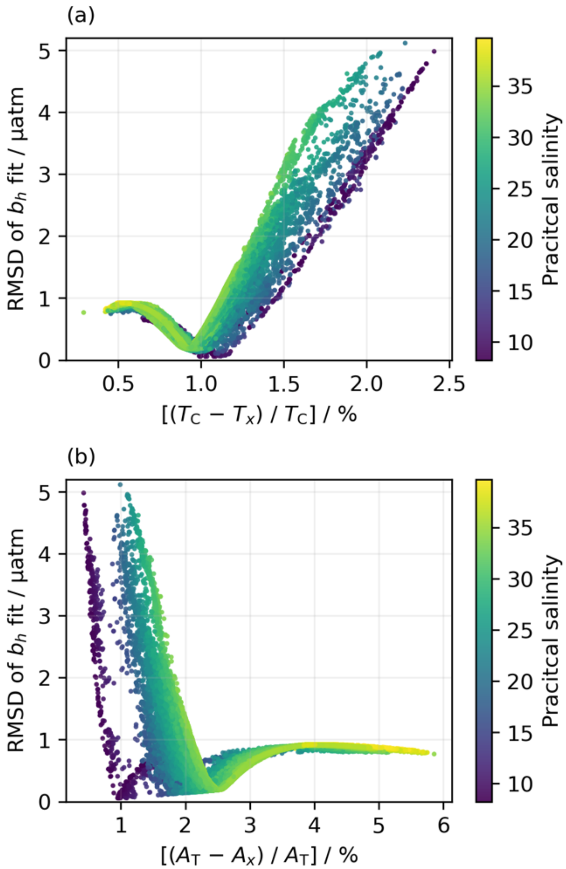
	u_0	u_1	u_2	u_3	u_4	u_5	u_6	u_7	u_8	u_9
u_0	28.8	$2.13\cdot10^{-1}$	$5.77\cdot10^{-4}$	$-8.22\cdot10^{-1}$	$3.60\cdot10^{-3}$	$-9.96\cdot10^{-2}$	$6.24\cdot10^{-5}$	$-1.36\cdot10^{-3}$	$-5.29\cdot10^{-4}$	$1.87\cdot10^{-3}$
u_1	$2.13\cdot10^{-1}$	$1.21\cdot10^{-2}$	$1.51\cdot10^{-5}$	$-5.34\cdot10^{-3}$	$6.73\cdot10^{-5}$	$-1.15\cdot10^{-3}$	$1.35\cdot10^{-6}$	$-2.40\cdot10^{-4}$	$-1.21\cdot10^{-5}$	$1.09\cdot10^{-5}$
u_2	$5.77\cdot10^{-4}$	$1.51\cdot10^{-5}$	$3.79\cdot10^{-7}$	$-1.87\cdot10^{-5}$	$3.66\cdot10^{-7}$	$-2.77\cdot10^{-6}$	$3.95\cdot10^{-9}$	$-2.73\cdot10^{-7}$	$-4.71\cdot10^{-8}$	$1.29\cdot10^{-8}$
u_3	$-8.22\cdot10^{-1}$	$-5.34\cdot10^{-3}$	$-1.87\cdot10^{-5}$	$4.05\cdot10^{-2}$	$-3.93\cdot10^{-4}$	$1.34\cdot10^{-3}$	$6.32\cdot10^{-7}$	$1.37\cdot10^{-4}$	$4.13\cdot10^{-6}$	$-5.46\cdot10^{-5}$
u_4	$3.60\cdot10^{-3}$	$6.73\cdot10^{-5}$	$3.66\cdot10^{-7}$	$-3.93\cdot10^{-4}$	$8.61\cdot10^{-6}$	$8.56\cdot10^{-6}$	$-3.99\cdot10^{-9}$	$-3.35\cdot10^{-6}$	$9.37\cdot10^{-8}$	$-2.22\cdot10^{-7}$
u_5	$-9.96\cdot10^{-2}$	$-1.15\cdot10^{-3}$	$-2.77\cdot10^{-6}$	$1.34\cdot10^{-3}$	$8.56\cdot10^{-6}$	$5.00\cdot10^{-4}$	$-4.88\cdot10^{-7}$	$3.40\cdot10^{-6}$	$3.17\cdot10^{-6}$	$-5.97\cdot10^{-6}$
u_6	$6.24\cdot10^{-5}$	$1.35\cdot10^{-6}$	$3.95\cdot10^{-9}$	$6.32\cdot10^{-7}$	$-3.99\cdot10^{-9}$	$-4.88\cdot10^{-7}$	$8.00\cdot10^{-10}$	$-2.01\cdot10^{-9}$	$-3.95\cdot10^{-9}$	$-5.58\cdot10^{-10}$
u_7	$-1.36\cdot10^{-3}$	$-2.40\cdot10^{-4}$	$-2.73\cdot10^{-7}$	$1.37\cdot10^{-4}$	$-3.35\cdot10^{-6}$	$3.40\cdot10^{-6}$	$-2.01\cdot10^{-9}$	$7.94\cdot10^{-6}$	$-6.71\cdot10^{-8}$	$-3.51\cdot10^{-8}$
u_8	$-5.29\cdot10^{-4}$	$-1.21\cdot10^{-5}$	$-4.71\cdot10^{-8}$	$4.13\cdot10^{-6}$	$9.37\cdot10^{-8}$	$3.17\cdot10^{-6}$	$-3.95\cdot10^{-9}$	$-6.71\cdot10^{-8}$	$4.47\cdot10^{-8}$	$-2.94\cdot10^{-8}$
u_9	$1.87\cdot10^{-3}$	$1.09\cdot10^{-5}$	$1.29\cdot10^{-8}$	$-5.46\cdot10^{-5}$	$-2.22\cdot10^{-7}$	$-5.97\cdot10^{-6}$	$-5.58\cdot10^{-10}$	$-3.51\cdot10^{-8}$	$-2.94\cdot10^{-8}$	$2.03\cdot10^{-7}$



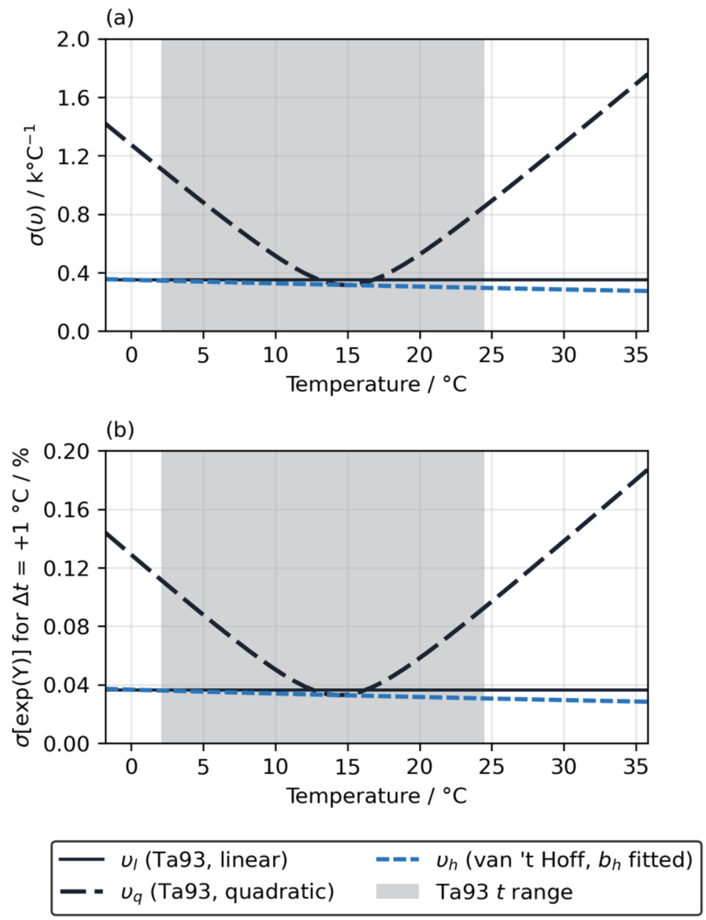
Supplementary Figure 1: Comparisons between b_h fitted to the OceanSODA-ETZH dataset and the b_h values returned from the parameterisation in Eq. (35) with the coefficients from Supp. Table 1. (a) All monthly mean data, with the ideal 1:1 relationship shown as a solid black line. (b) Spatial distribution of residuals between the parameterisation and the fitted values of b_h, averaged across all months.



Supplementary Figure 2: Variation of fCO_2 with temperature according to the measurements of Takahashi et al. (1993) (Ta93; filled circles with vertical 1σ error bars) and the different theoretical values of υ calculated from A_T and T_C for all of the carbonic acid parameterisations in PyCO2SYS, all normalised to the linear fit (υ_l) and computed under the conditions of the Takahashi et al. (1993) experiment (Sect. 2.1.2). The citations for the codes for the different carbonic acid parameterisations in the panel legends can be found in the caption of Fig. 6. With reference to Fig. 6, (a) here shows the "GEOSECS" options, (b) the "Mehrbach" options, (c) the "Synthetic" options, and (d) the others. The dark dashed line shows the best fit of Eq. (19) to the Takahashi et al. (1993) dataset (i.e., υ_h), as in Fig. 1a.



Supplementary Figure 3: Variation of the RMSD of the residuals in the b_h fit (in terms of fCO_2, as shown in Fig. 3a) with (a) the relative error in the T_x approximation (Eq. 13), and (b) the relative error in the A_x approximation (Eq. 12), both coloured by practical salinity.



Supplementary Figure 4. (a) 1σ uncertainty in υ due to experimental uncertainties in t and $f\mathrm{CO_2}$ in the Takahashi et al. (1993) dataset only and fitted with the linear (dotted line; Eq. 5) and quadratic (dashed line; Eq. 6) forms as well as the fitted van 't Hoff form (solid line; Eq. 19). The shaded area shows the range of t from the Takahashi et al. (1993) experiment, while the full t axis range matches OceanSODA-ETZH. (b) Equivalent for exp(Y) for Δt = +1 °C, i.e., identical to Fig. 4.