



Supplement of

Temperature effect on seawater $f\text{CO}_2$ revisited: theoretical basis, uncertainty analysis and implications for parameterising carbonic acid equilibrium constants

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Table S1: Best-fit coefficients for the parameterisation of b_h in Eq. (35). The ‘Value – normalised / J mol⁻¹’ column gives the coefficient values when all predictor variables are first standardised by subtracting their mean and then dividing by their standard deviation before fitting to Eq. (35); the magnitude of each normalised value thus indicates the relative importance of the corresponding coefficient to the overall fit.

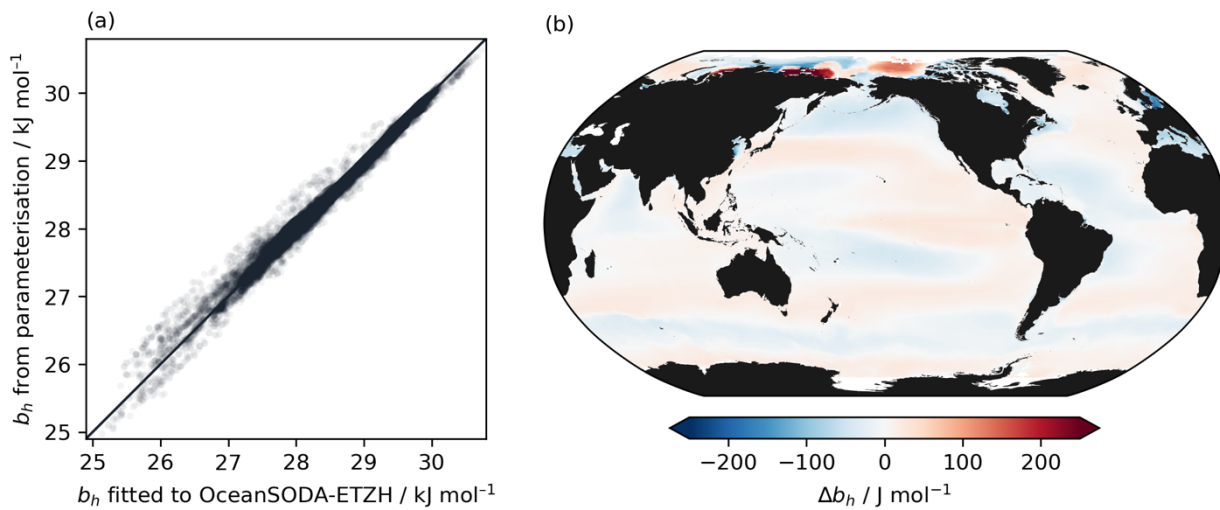
| Coefficient | Multiplier | Value | Unit | Value – normalised / J mol ⁻¹ |
|-------------|------------|--------------|---|---|
| u_0 | 1 | 31318.4 | J mol ⁻¹ | 29156.7 |
| u_1 | t | 139.488 | J mol ⁻¹ °C ⁻¹ | 1517.89 |
| u_2 | s | -4.22486 | J mol ⁻¹ | -8.05627 |
| u_3 | f | -16.9522 | J mol ⁻¹ μatm ⁻¹ | -535.804 |
| u_4 | t^2 | -1.21088 | J mol ⁻¹ °C ⁻² | -382.891 |
| u_5 | s^2 | -0.652212 | J mol ⁻¹ | -75.0765 |
| u_6 | f^2 | -0.000547593 | J mol ⁻¹ μatm ⁻² | -11.9916 |
| u_7 | ts | -3.02072 | J mol ⁻¹ °C ⁻¹ | -1155.83 |
| u_8 | tf | 0.166973 | J mol ⁻¹ °C ⁻¹ μatm ⁻¹ | 676.257 |
| u_9 | sf | 0.309654 | J mol ⁻¹ μatm ⁻¹ | 433.893 |

5

Table S2: The variance-covariance matrix for uncertainty propagation for the best-fit coefficients (Supp. Table S1) 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 the ‘Unit’ column in Supp. Table S1.

10

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



15

Figure S1: 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 S1. (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.

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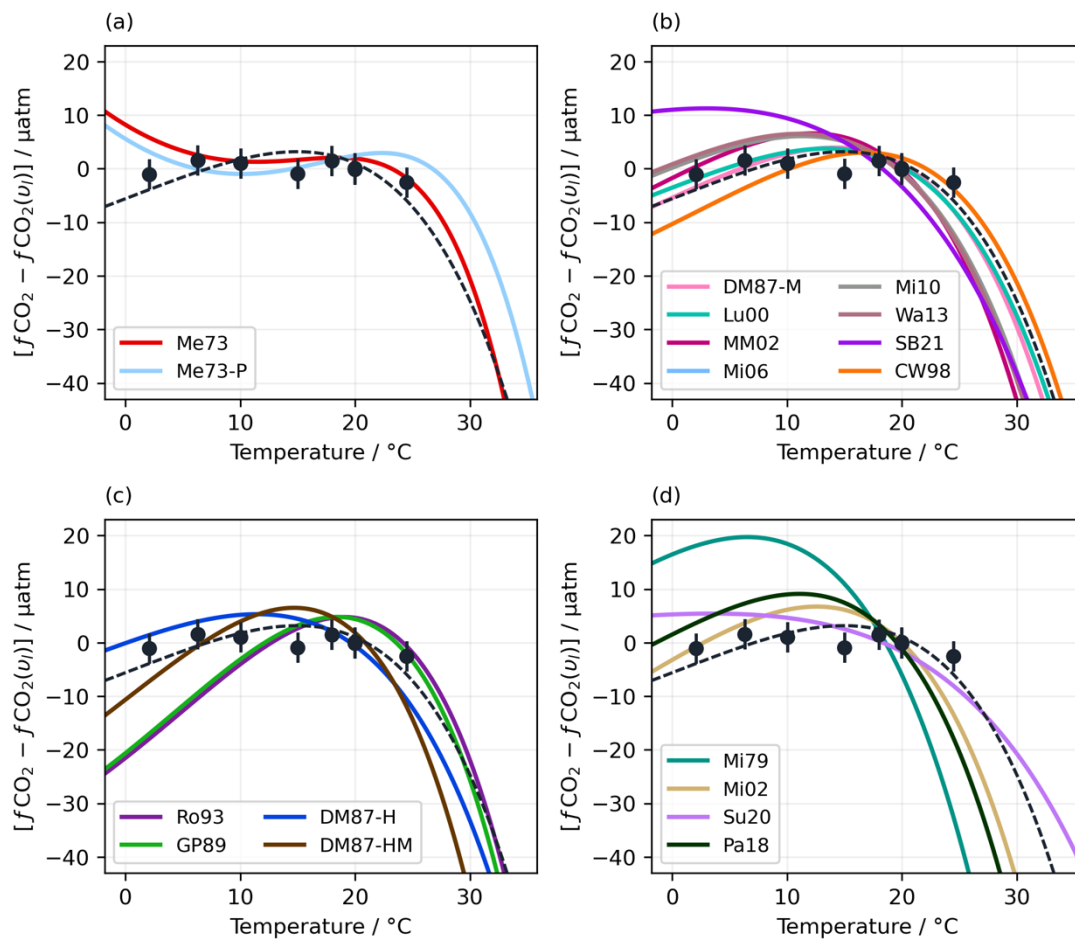


Figure S2: Variation of $f\text{CO}_2$ with temperature according to the measurements of Takahashi et al. (1993) (Ta93; filled circles with vertical 1σ error bars) and the different theoretical values of v calculated from A_T and T_C for all of the carbonic acid parameterisations in PyCO2SYS, all normalised to the linear fit (v_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., v_h), as in Fig. 1a.

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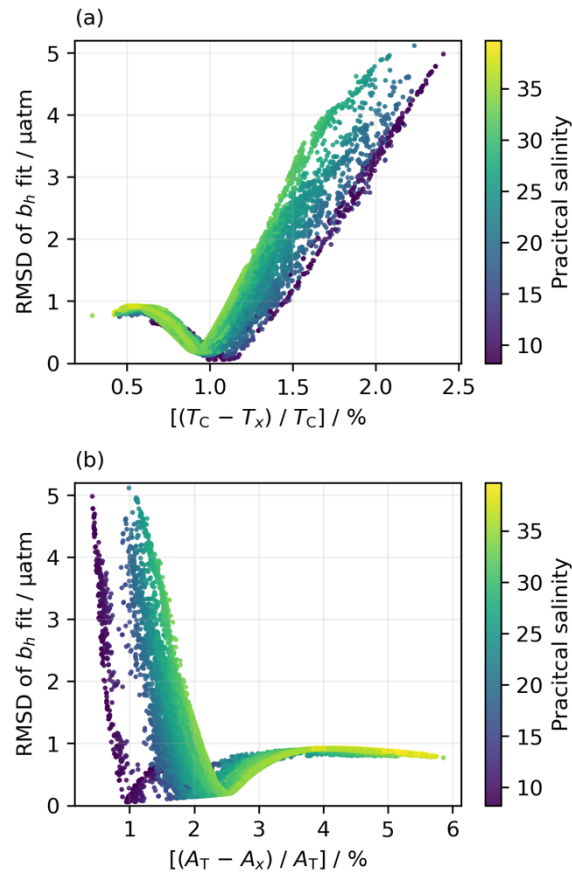
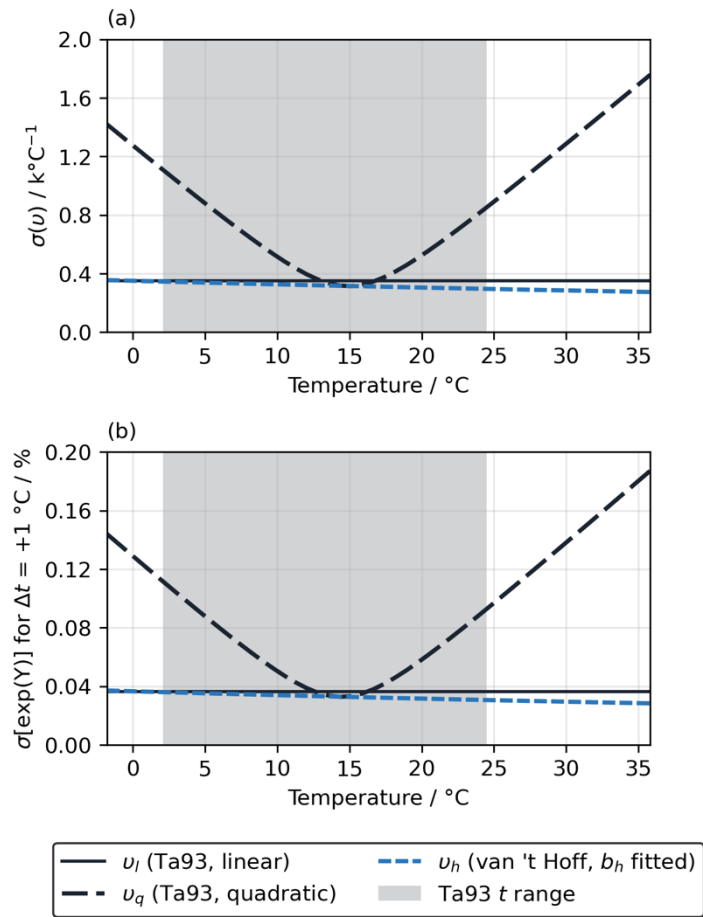


Figure S3: Variation of the RMSD of the residuals in the b_h fit (in terms of $f\text{CO}_2$, as shown in Fig. 3a) with (a) the relative inaccuracy of the T_x approximation (Eq. 13), and (b) the relative inaccuracy of the A_x approximation (Eq. 12), both coloured by practical salinity.



35 Figure S4. (a) 1σ uncertainty in ν due to experimental uncertainties in t and $f\text{CO}_2$ 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 $\Delta t = +1 \text{ } ^\circ\text{C}$, i.e., identical to Fig. 4.