Supporting Information for "Solubility of high-magnesium calcite in seawater and its implementation in (Py)CO2SYS"

Ben A. Cala[1,2], Mariette Wolthers[2], Olivier Sulpis[3], Jonathan D. Sharp[4,5], and Matthew P. Humphreys[1]

[1]NIOZ Royal Netherlands Institute for Sea Research, Department of Ocean Systems (OCS), Texel, The Netherlands
[2]Utrecht University, Department of Earth Sciences, Princetonlaan 8A, 3584 CB Utrecht, The Netherlands
[3]CEREGE, Aix Marseille Univ, CNRS, IRD, INRAE, Aix-en-Provence, France
[4]Cooperative Institute for Climate, Ocean, and Ecosystem Studies, University of Washington, Seattle, WA, USA
[5]Pacific Marine Environmental Laboratory, National Oceanic and Atmospheric Administration, Seattle, WA, USA

1 Supplementary tables

1.1 Covariance matrices for fits in Step 1

$$C_1 = \begin{pmatrix} 1.20391634 \times 10^3 & -5.11353090 \times 10^2 & 5.83413492 \times 10^1 & -1.41587358 \\ -5.11353090 \times 10^2 & 2.21673624 \times 10^2 & -2.60550579 \times 10^1 & 6.59579812 \\ 5.83413492 \times 10^1 & -2.60550579 \times 10^1 & 3.20983818 & -8.80628638 \times 10^{-2} \\ -1.41587358 & 6.59579812 & -8.80628638 \times 10^{-2} & 2.98592668 \times 10^{-3} \end{pmatrix}$$

$$C_2 = \begin{pmatrix} 4.09223066 \times 10^1 & -2.58508253 \times 10^1 & 3.67589589 & -1.14692454 \times 10^{-1} \\ -2.58508253 \times 10^1 & 1.65810318 \times 10^1 & -2.42196869 & 7.91296519 \times 10^{-2} \\ 3.67589589 & -2.42196869 & 3.77428062 \times 10^{-1} & -1.38175276 \times 10^{-2} \\ -1.14692454 \times 10^{-1} & 7.91296519 \times 10^{-2} & -1.38175276 \times 10^{-2} & 6.41341854 \times 10^{-4} \end{pmatrix}$$

$$C_3 = \begin{pmatrix} 2.52838523 \times 10^2 & -7.74403145 \times 10^1 & 5.67477025 & -6.97252538 \times 10^{-2} \\ -7.74403145 \times 10^1 & 2.46594265 \times 10^1 & -1.90081440 & 2.45539683 \times 10^{-2} \\ 5.67477025 & -1.90081440 & 1.59290388 \times 10^{-1} & -2.28508317 \times 10^{-3} \\ -6.97252538 \times 10^{-2} & 2.45539683 \times 10^{-2} & -2.28508317 \times 10^{-3} & 4.61360590 \times 10^{-5} \end{pmatrix}$$

1.2 Check values for implementation

Table S1: Check values for the three categories and three temperature options in different conditions. Check values are given for the parameterised activity coefficients, the equilibrium constants after every step for the implementation and Ω_{MC}. For the calculation of Ω_{MC}, TA = $2300\,\mu\mathrm{mol\,kg^{-1}}$ and DIC = $2150\,\mu\mathrm{mol\,kg^{-1}}$.

Options		Conditions				Check values							
Category	Temp option	x	T (°C)	S	p (dbar)	$\gamma^t_{\mathrm{Ca}^{2+}}$	$\gamma^t_{\mathrm{Mg}^{2+}}$	$\gamma^t_{\mathrm{CO}_3^{2-}}$	$pK(x)$	$pK(x,T)$	$pK^*(x,T,S)$	$pK^*(x,T,S,p)$	Ω_{MC}
1	ideal mix	0.05	10	36	1000	0.192896019	0.213887269	0.047121622	8.407981378	8.32977638	6.290562958	6.211965149	2.0994321
		0.1	5	32	2000	0.198505198	0.221003942	0.05345501	8.050631588	7.941360511	5.971783623	5.805685406	0.781424255
		0.15	20	38	4000	0.187587461	0.20490464	0.042024957	7.615740781	7.580419702	5.482882983	5.226739216	0.267666127
		0.2	0	35	5000	0.191635517	0.221772672	0.051516265	7.278907919	7.121245669	5.128352449	4.707309122	0.073211303
	calcite-like	0.05	10	36	1000	0.192896019	0.213887269	0.047121622	8.407981378	8.338629074	6.299415653	6.220817844	2.142666244
		0.1	5	32	2000	0.198505198	0.221003942	0.05345501	8.050631588	7.965025202	5.995448313	5.829350096	0.825185481
		0.15	20	38	4000	0.187587461	0.20490464	0.042024957	7.615740781	7.589207512	5.491670793	5.235527026	0.273137434
		0.2	0	35	5000	0.191635517	0.221772672	0.051516265	7.278907919	7.180497222	5.187604002	4.766560675	0.083913085
	van't Hoff	0.05	10	36	1000	0.192896019	0.213887269	0.047121622	8.407981378	8.285109151	6.24589573	6.167297921	1.894238262
		0.1	5	32	2000	0.198505198	0.221003942	0.05345501	8.050631588	7.876519248	5.90694236	5.740844142	0.673047358
		0.15	20	38	4000	0.187587461	0.20490464	0.042024957	7.615740781	7.570198986	5.472662267	5.2165185	0.2614404
		0.2	0	35	5000	0.191635517	0.221772672	0.051516265	7.278907919	7.035200386	5.042307165	4.621263838	0.060052744
2	ideal mix	0.05	10	36	1000	0.192896019	0.213887269	0.047121622	8.325242861	8.247037863	6.207824441	6.129226632	1.735255046
		0.1	5	32	2000	0.198505198	0.221003942	0.05345501	8.301545228	8.192274152	6.222697263	6.056599046	1.392517071
		0.15	20	38	4000	0.187587461	0.20490464	0.042024957	8.237936921	8.202615842	6.105079123	5.848935356	1.121474892
		0.2	0	35	5000	0.191635517	0.221772672	0.051516265	8.14951298	7.99185073	5.99895751	5.577914183	0.543479538
	calcite-like	0.05	10	36	1000	0.192896019	0.213887269	0.047121622	8.325242861	8.255890557	6.216677136	6.138079327	1.770989599
		0.1	5	32	2000	0.198505198	0.221003942	0.05345501	8.301545228	8.215938842	6.246361954	6.080263736	1.470500641
		0.15	20	38	4000	0.187587461	0.20490464	0.042024957	8.237936921	8.211403652	6.113866933	5.857723167	1.144398724
		0.2	0	35	5000	0.191635517	0.221772672	0.051516265	8.14951298	8.051102283	6.058209063	5.637165736	0.622923551
	van't Hoff	0.05	10	36	1000	0.192896019	0.213887269	0.047121622	8.325242861	8.202370634	6.163157213	6.084559404	1.565655067
		0.1	5	32	2000	0.198505198	0.221003942	0.05345501	8.301545228	8.127432888	6.157856	5.991757783	1.199386798
		0.15	20	38	4000	0.187587461	0.20490464	0.042024957	8.237936921	8.192395126	6.094858407	5.838714641	1.095390169
		0.2	0	35	5000	0.191635517	0.221772672	0.051516265	8.14951298	7.905805446	5.912912226	5.491868899	0.445797793
3	ideal mix	0.05	10	36	1000	0.192896019	0.213887269	0.047121622	8.487873394	8.409668396	6.370454974	6.291857165	2.523445034
		0.1	5	32	2000	0.198505198	0.221003942	0.05345501	8.439216411	8.329945335	6.360368447	6.194270229	1.911928781
		0.15	20	38	4000	0.187587461	0.20490464	0.042024957	8.364183249	8.328862169	6.23132545	5.975181684	1.499808748
		0.2	0	35	5000	0.191635517	0.221772672	0.051516265	8.270626474	8.112964224	6.120071004	5.699027677	0.718284826
	calcite-like	0.05	10	36	1000	0.192896019	0.213887269	0.047121622	8.487873394	8.41852109	6.379307669	6.30070986	2.575410986
		0.1	5	32	2000	0.198505198	0.221003942	0.05345501	8.439216411	8.353610025	6.384033137	6.21793492	2.019000382
		0.15	20	38	4000	0.187587461	0.20490464	0.042024957	8.364183249	8.337649979	6.24011326	5.983969494	1.530466023
		0.2	0	35	5000	0.191635517	0.221772672	0.051516265	8.270626474	8.172215777	6.179322557	5.75827923	0.823281289
	van't Hoff	0.05	10	36	1000	0.192896019	0.213887269	0.047121622	8.487873394	8.365001168	6.325787746	6.247189937	2.276809113
		0.1	5	32	2000	0.198505198	0.221003942	0.05345501	8.439216411	8.265104071	6.295527183	6.129428966	1.646760523
		0.15	20	38	4000	0.187587461	0.20490464	0.042024957	8.364183249	8.318641453	6.221104734	5.964960968	1.464924244
		0.2	0	35	5000	0.191635517	0.221772672	0.051516265	8.270626474	8.026918941	6.034025721	5.612982393	0.589184629

2 Supplementary figures

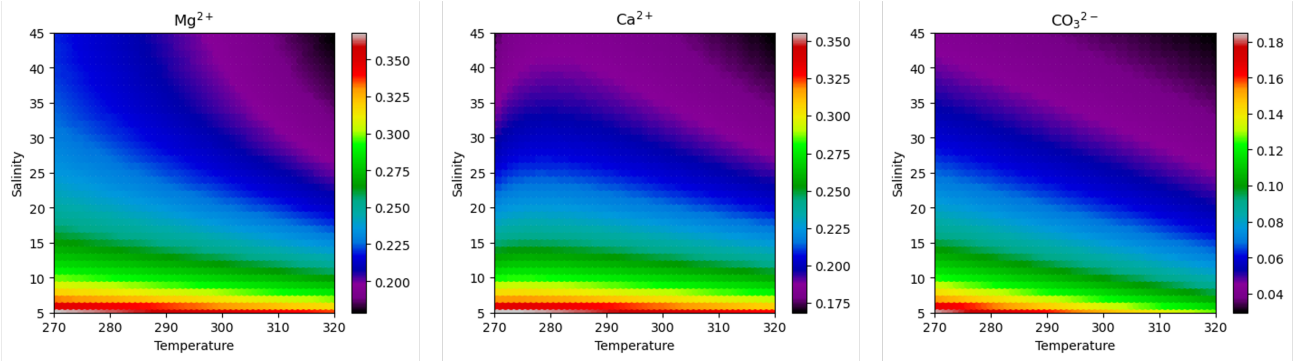

Figure S1: The activity coefficients calculated with Pytzer for the most relevant temperature and salinity ranges.

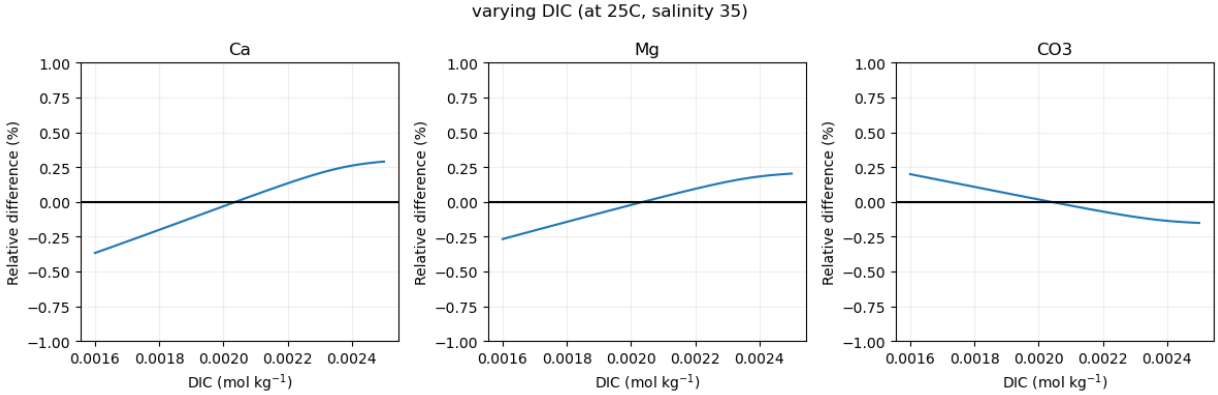

Figure S2: The relative change in the activity coefficients when varying DIC.

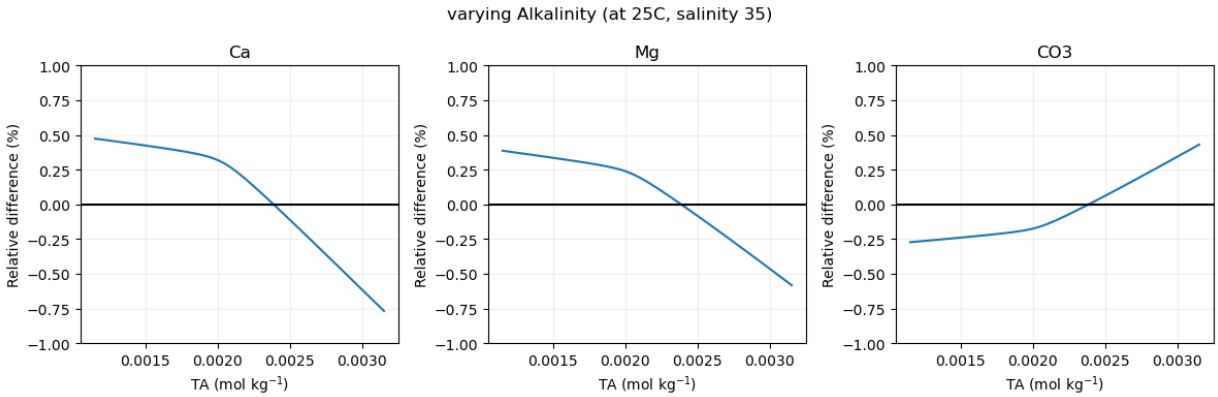

Figure S3: The relative change in the activity coefficients when varying TA.

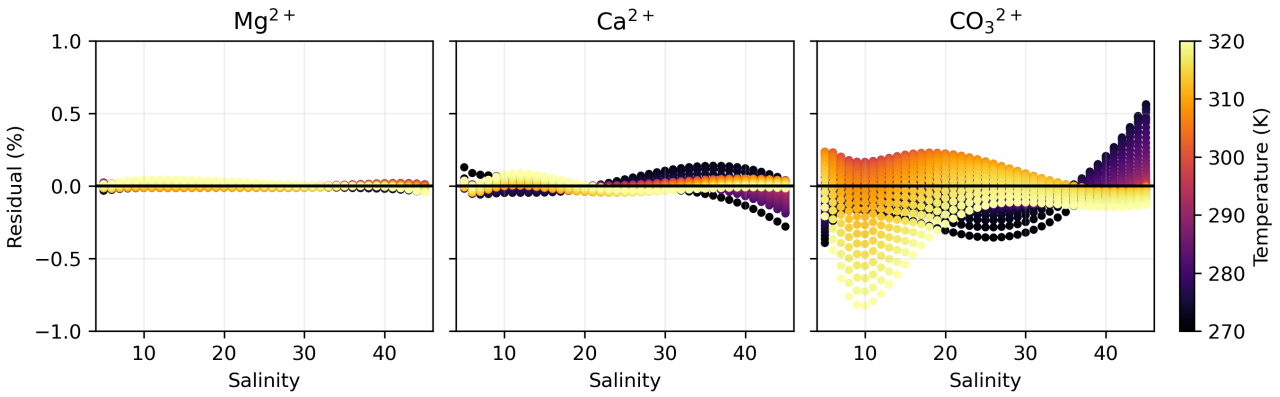

Figure S4: Residuals (calculated - parameterised) in % for the total activity coefficients a) $\gamma^t_{Mg^{2+}}$, b) $\gamma^t_{Ca^{2+}}$ and c) $\gamma^t_{CO_3^{2-}}$

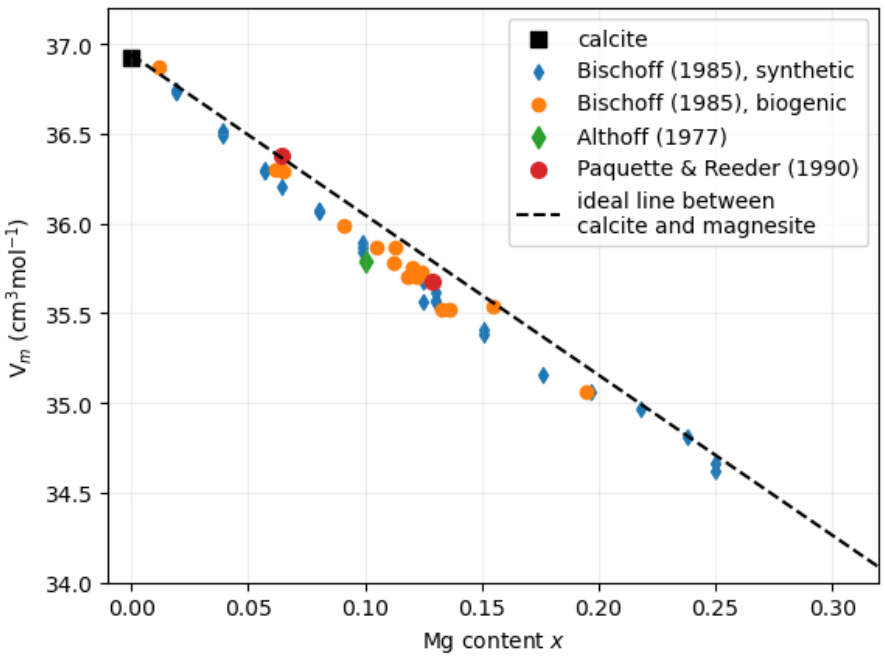

Figure S5: Molar volume V_m plotted against Mg content. Measurements for synthetic samples are shown as diamonds, biogenic samples as circles. The ideal line between calcite and magnesite is shown as a dashed line.

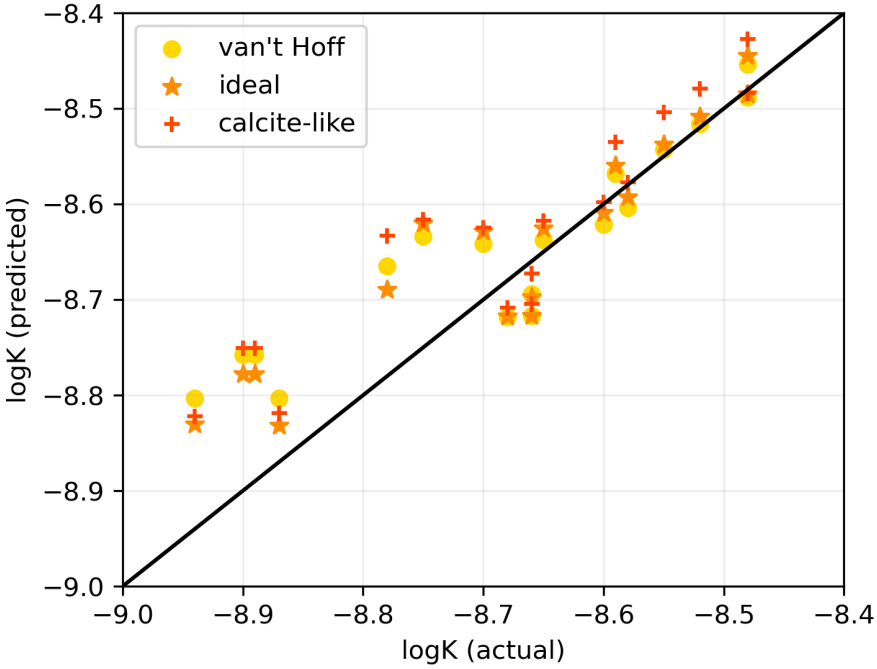

Figure S6: Comparison of the two options to calculate the temperature dependence of $\log_{10} K$ against actual measurements (Bertram et al., 1991).

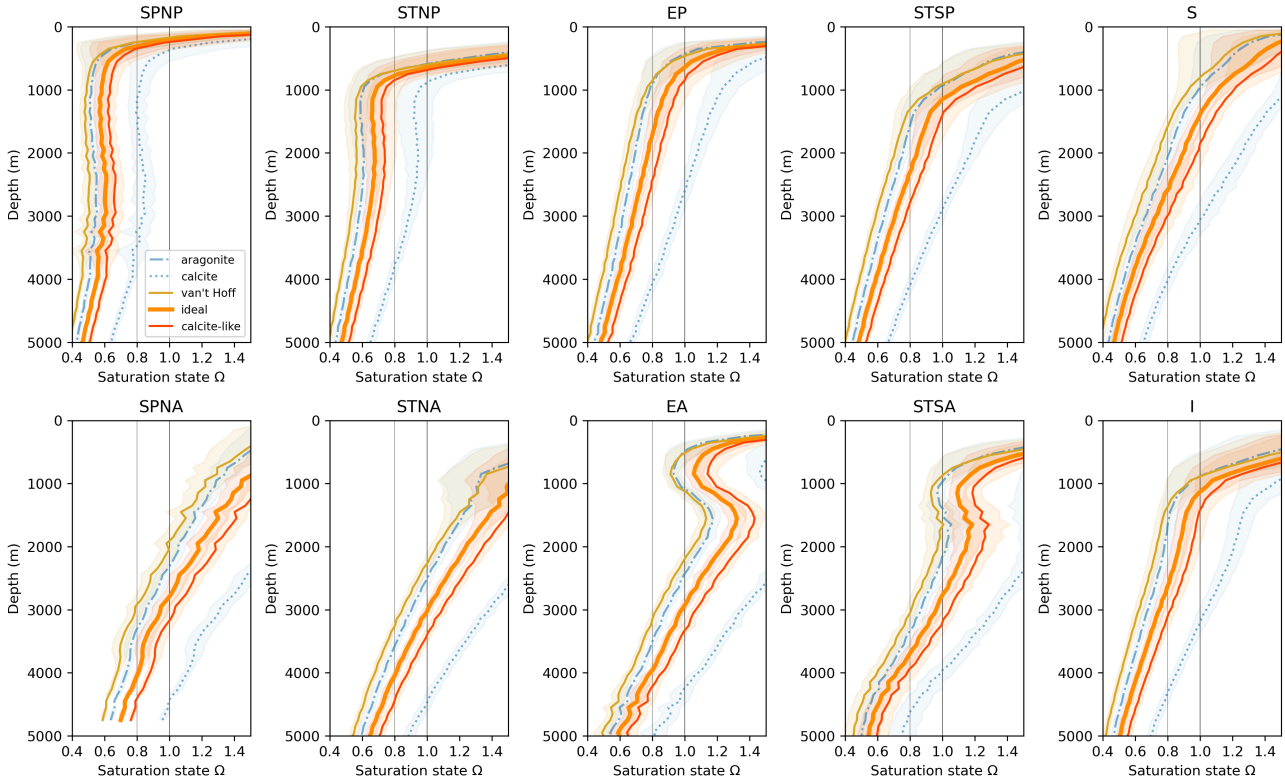

Figure S7: Saturation states with depth for the different implementations of temperature dependence of 14 Mg% (Category 2) in ten ocean biomes, calculated from GLODAPv2.2023 data (Lauvset et al., 2024). The line and envelope show the average saturation state in that ocean biome and its standard deviation. Biomes follow Fay and McKinley (2014).

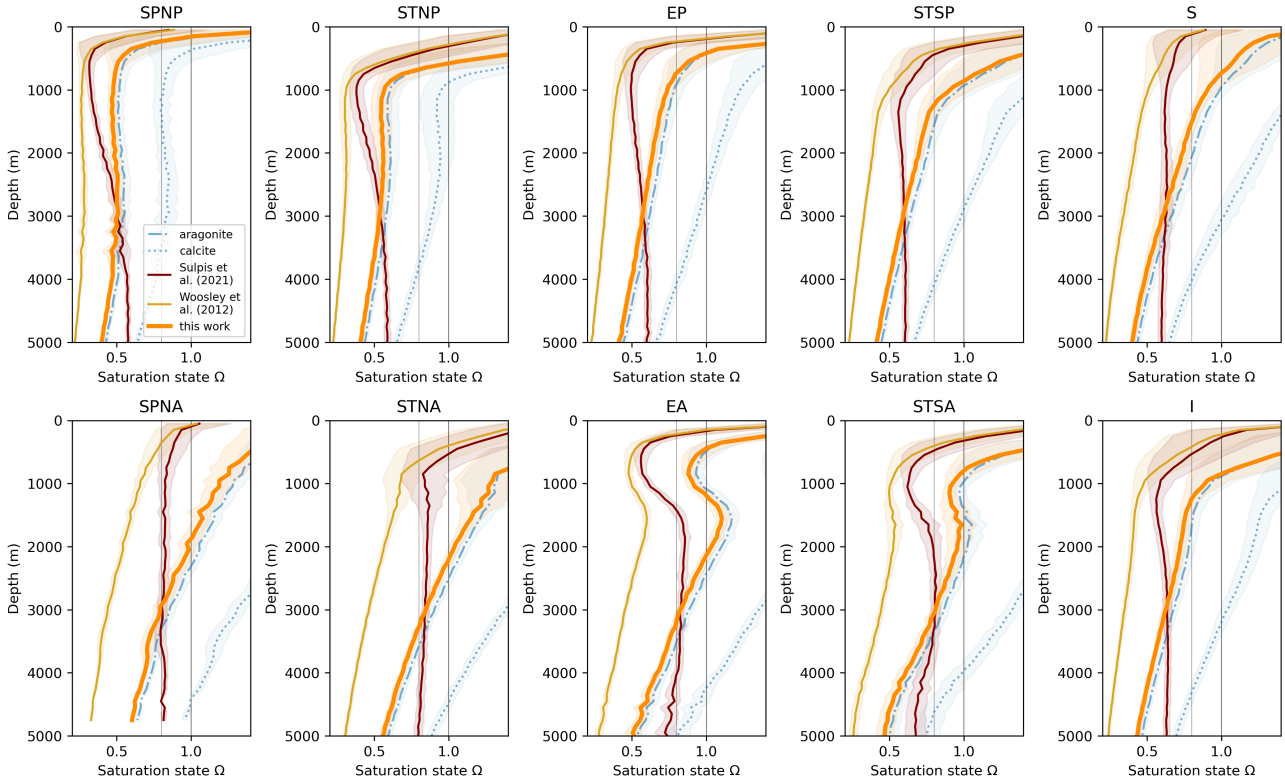

Figure S8: Ichthyocarbonate (fish-produced Mg calcite) saturation states calculated in comparison with calculations from previous studies, using the measurement for K^*_{sp} by Woosley et al. (2012). The line and envelope show the average saturation state in that ocean biome and its standard deviation. Biomes follow Fay and McKinley (2014).

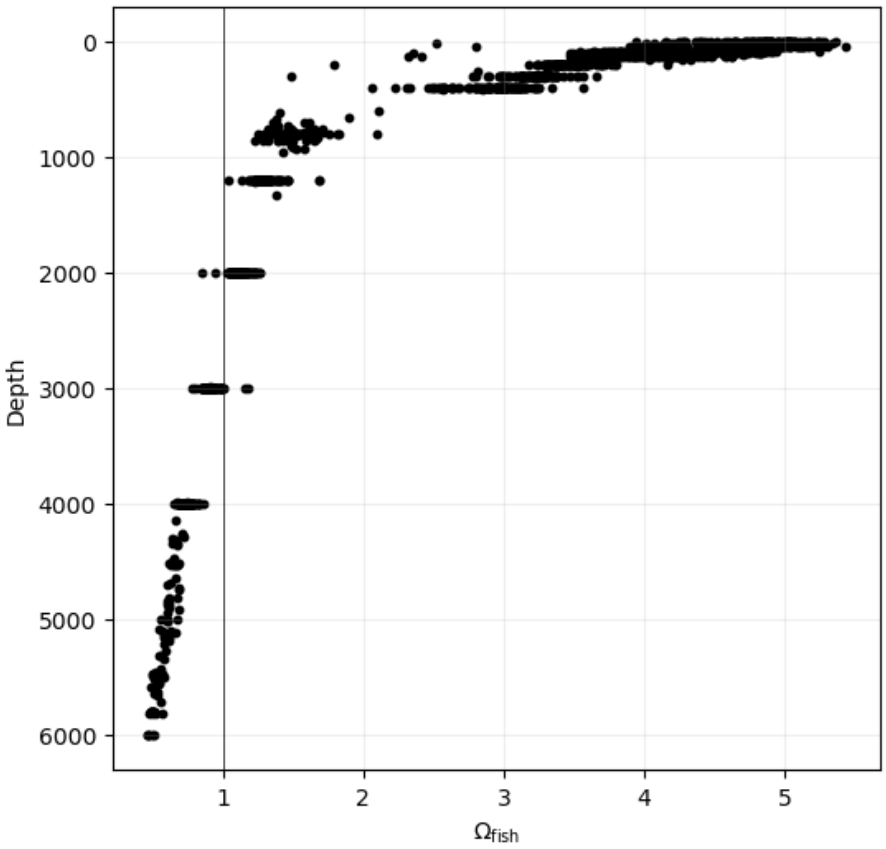

Figure S9: Ichthyocarbonate (fish-produced Mg calcite) saturation state at the Bermuda Atlantic Time Series (BATS) location using the discrete bottle samples collected during the BATS Validation (BVAL) cruises from April 1991 through July 2024 (Bates et al., 2025)

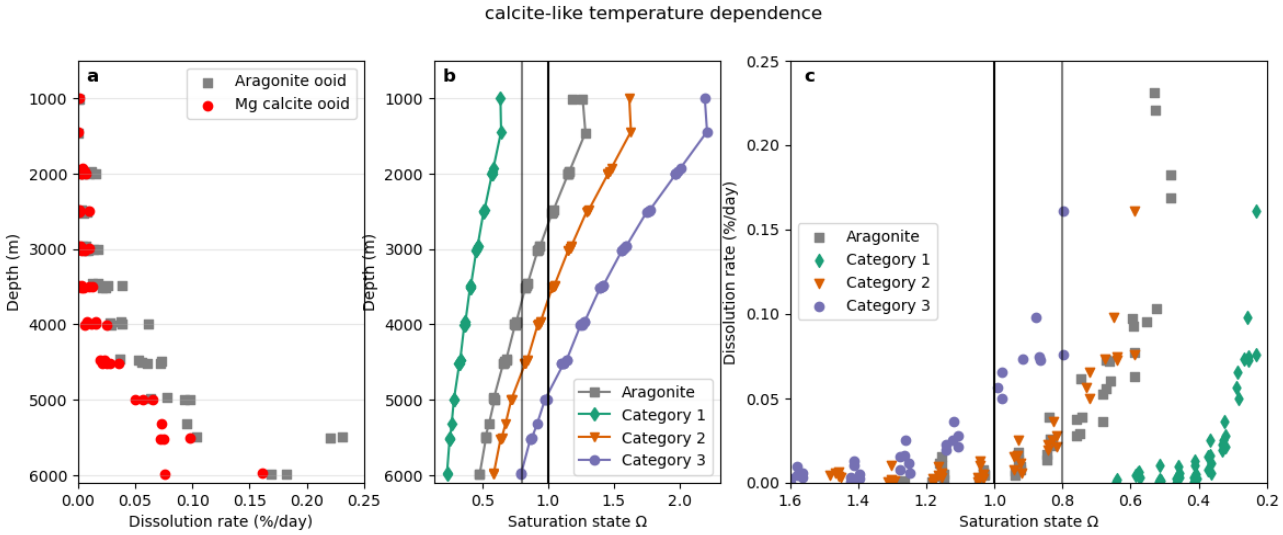

Figure S10: Subplot (a) shows the combined dissolution rate measurements from three stations by Milliman (1977) against depth. In (b) the saturation state for aragonite and all three solubility categories with $x = 0.12$ is plotted against depth (calcite-like temperature option) and (c) shows the measured dissolution rate against the calculated Ω.

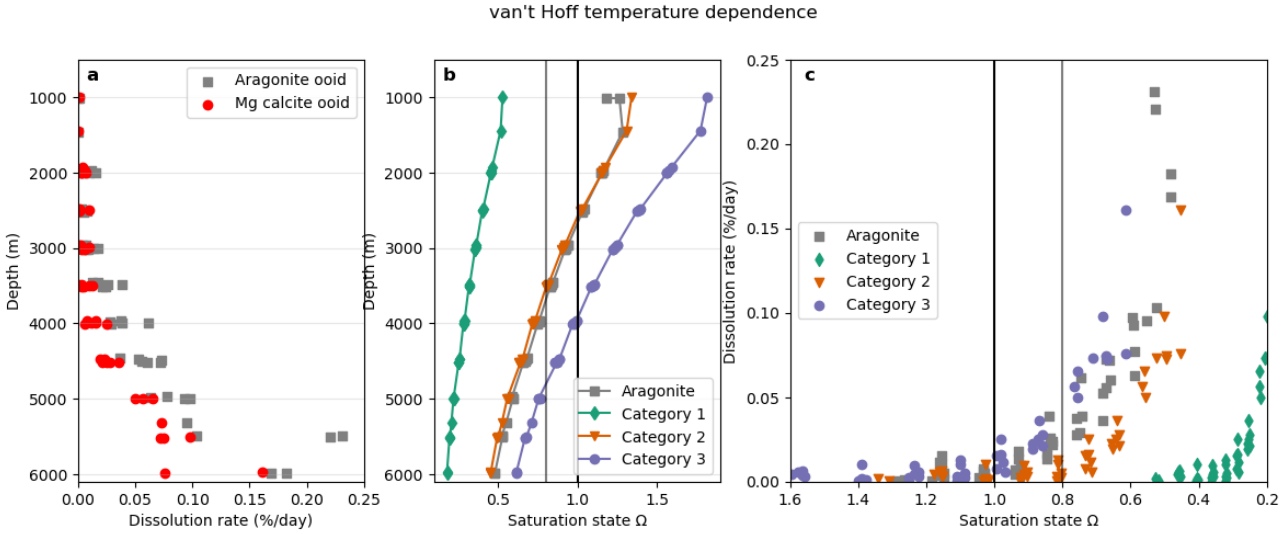

Figure S11: Subplot (a) shows the combined dissolution rate measurements from three stations by Milliman (1977) against depth. In (b) the saturation state for aragonite and all three solubility categories with $x = 0.12$ is plotted against depth (van't Hoff temperature option) and (c) shows the measured dissolution rate against the calculated Ω.

References

N. Bates, R. J. Johnson, M. W. Lomas, C. A. Carlson, D. Smith, P. J. Lethaby, D. Lomas, C. Medley, R. May, E. Davey, E. Stuart, R. Garley, and L. Derbyshire. Discrete bottle samples collected during BATS Validation (BVAL) cruises from April 1991 through July 2024, Aug. 2025.

M. A. Bertram, F. T. Mackenzie, F. C. Bishop, and W. D. Bischoff. Influence of temperature on the stability of magnesian calcite. *American Mineralogist*, 76(11-12):1889–1896, 1991.

A. R. Fay and G. A. McKinley. Global open-ocean biomes: Mean and temporal variability. *Earth System Science Data*, 6(2):273–284, Aug. 2014. ISSN 1866-3508. doi: 10.5194/essd-6-273-2014.

S. K. Lauvset, N. Lange, T. Tanhua, H. C. Bittig, A. Olsen, A. Kozyr, M. Álvarez, K. Azetsu-Scott, P. J. Brown, B. R. Carter, L. Cotrim Da Cunha, M. Hoppema, M. P. Humphreys, M. Ishii, E. Jeansson, A. Murata, J. D. Müller, F. F. Pérez, C. Schirnick, R. Steinfeldt, T. Suzuki, A. Ulfsbo, A. Velo, R. J. Woosley, and R. M. Key. The annual update GLODAPv2.2023: The global interior ocean biogeochemical data product. *Earth Syst. Sci. Data*, 16(4):2047–2072, Apr. 2024. ISSN 1866-3516. doi: 10.5194/essd-16-2047-2024.

J. D. Milliman. Dissolution of calcium carbonate in the Sargasso Sea (northwest Atlantic). In N. R. Andersen and A. Malahoff, editors, *The Fate of Fossil Fuel CO2 in the Oceans*, pages 641–653. Plenum Press, 1977. doi: 10.1007/978-1-4899-5016-1.

R. J. Woosley, F. J. Millero, and M. Grosell. The solubility of fish-produced high magnesium calcite in seawater. *Journal of Geophysical Research: Oceans*, 117(C4), 2012. ISSN 2156-2202. doi: 10.1029/2011JC007599.