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Supplementary Materials for

Thermal stress reduces pocilloporid coral resilience to ocean acidification by impairing control over calcifying fluid chemistry

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Figure S1: Comparison between boron derived carbonate parameters of the calcifying fluid based different K_D formulations and independent measurements. Comparison of carbonate parameters calculated from boron proxies with different K_D ((10) ‘M17’, (33) ‘H16’, (8) ‘new eq’) and independent measurements for *S. pistillata* (**A**, **B**, **C**) and *P. damicornis* (**D**, **E**). Carbonate ion concentration of the calcifying fluid ($[CO_3^{2-}]_{cf}$), dissolved inorganic carbon of the calcifying fluid (DIC_{cf}), saturation state of aragonite of the calcifying fluid (Ω_{cf}). **A** and **E**: $[CO_3^{2-}]_{cf}$; **B**: DIC_{cf} ; **C** and **D**: Ω_{cf} . For *S. pistillata* (**A**, **B**, **C**). The data reported here are from the control treatment ($pCO_2 \sim 400$ ppm). The carbonate parameters are in the range of independent LIX microelectrode measurements from (32). For *P. damicornis*, independent measurements based on Raman spectroscopy (61) are consistent with data from ‘M17’ using $[Ca]_{cf} = [Ca]_{sw}$. Recalculating $[CO_3^{2-}]_{cf}$ with the K_D definition from (34) (‘A17’, **E**) and data from (61) yields values that are greater than in ‘A17’, but similar to estimates of $[CO_3^{2-}]_{cf}$ from (9). Independent measurements of $[CO_3^{2-}]_{cf}$ (e.g., via LIX microelectrode) do not presently exist for *P. damicornis* but would help refine the B/Ca proxy of $[CO_3^{2-}]_{cf}$ and identify optimal K_D formulation. Error bars represent 1 standard deviation from the mean.

Figure S2: Analytical $\delta^{11}B$ comparison between the University of Cambridge and the Alfred Wagner Institute. Two-independent measurements of $\delta^{11}B$ for *S. pistillata* carried out at the University of Cambridge (‘Uni. Cambridge’) and at the Alfred Wagner Institute (‘AWI’). Regression comparing results from the two labs are not significantly different from the 1:1 line ($p > 0.05$; Welch-t test). These results cross-validate the $\delta^{11}B$ analytical procedures of both laboratories and show that the reported $\delta^{11}B$ values are reproducible by independent laboratories at the 95% confidence level. Error bars represent 2 standard deviation from the mean.

Figure S3: B/Ca and $\delta^{11}B$ measured in this study. Analytical results relative to treatment seawater pH (pH_{sw}) (blue squares: 28°C, red triangles: 31°C). A and B: show B/Ca for *P.*

damicornis and *S. pistillata*, respectively. C and D show $\delta^{11}\text{B}$ for *P. damicornis* and *S. pistillata*, respectively. Error bars represent 1 standard error, envelopes represent 95% confidence interval of the linear regressions.

Materials and methods

Measurement of calcifying fluid pH with proton-sensitive LIX microelectrodes

Microelectrode measurements of coral calcifying fluid pH were conducted by Louise Cameron, Claire Reymond, and Justin Ries at the MAREE marine experimental facility at the Leibniz Center for Tropical Marine Research (Bremen, Germany) (7).

Calcifying fluid pH was measured using pH-sensitive liquid ion-exchanger (LIX) microelectrodes produced at the Max Planck Institute for Marine Microbiology (MPIMM) using the technique described in (76). Briefly, green soda lime glass microcapillary tubes (*Schott* model 8516) were held in a heated coil and pulled to a target tip diameter of ca. 10 µm, yielding final diameters of 8 – 20 µm. These were then silanized to obtain a hydrophobic surface that allowed the adhesion of the LIX membrane. The microcapillary tubes were filled with ca. 300 µm of degassed, filtered electrolyte (300 mM KCl, 50 mM sodium phosphate adjusted to pH 7.0) using a plastic syringe with a 0.1-mm tip. The microcapillary tubes were then backfilled with LIX containing a polyvinyl chloride (PVC) epoxy to prevent leakage of electrolyte by submerging the tips of the microcapillary tubes in LIX and apply suction to the other end of the tube until the PVC-containing LIX was drawn into the tip of the microcapillary by 100 – 200 µm. Microcapillary tubes were encased in a Pasteur pipette for shielding, with the pulled tip of the microcapillary tube protruding ca. 2 cm beyond this casing. This casing was filled with a 0.3 M KCl solution and connected to the reference electrode with an Ag/AgCl wire to minimize electrical noise. Microelectrodes were left for 24 hours after construction to allow for stabilization of the LIX membranes.

All microelectrode equipment (millivolt meter, National Instruments DAQ Pad 6020E, laptop, cables, micromanipulator, VT80 Micos motor arm, lab stands, Zeiss Stemi SV6 binocular microscope) was set up adjacent to the experimental tanks to minimize transport stress for the corals. Two reservoirs of seawater, sourced from the corresponding experimental treatment tanks, were established next to the microelectrode system. These reservoirs were bubbled with the corresponding treatment gases and maintained at the corresponding treatment temperature using aquarium heaters or chillers. The seawater was circulated between the two reservoirs through two 5.4 L flow-through chambers (30 x 12 x 15 cm). All pH microelectrode measurements were performed within these smaller flow-through chambers. All corals were transferred to flow-through chambers filled with treatment seawater and light levels were maintained at 150 lux. All corals were acclimated to the microelectrode chamber until polyp

extension was observed prior to measurements (minimum of 10 minutes). Measurements of calcifying fluid pH were performed on three replicate individuals per treatment. One measurement was obtained for each coral specimen.

The proton-sensitive LIX microelectrodes were used to measure both seawater and calcifying fluid pH. Before and after measurement of calcifying fluid pH, all microelectrodes were calibrated at the treatment temperature with pH 7 and 9 NBS buffers (for slope of the calibration) and a Dickson seawater CRM (for intercept of the calibration; with pH calculated from the certified values). The vertical position of the microelectrode was controlled to one-micron precision using a motorized micromanipulator. The microelectrodes were slowly inserted through the coral tissue into the upper portion of the coral calyx, between septal ridges and proximal to the thecal wall, until the skeleton was reached. A vertical pH profile was then obtained by moving the microelectrode out of the calyx into the adjacent seawater. This profile was obtained in 1 μm steps for the first 20 μm , followed by 5 μm steps out into the surrounding seawater.

The calibration and microelectrode pH data were processed by parsing scatterplots of the data into three zones, which were annotated at the time of data collection. The calibration data were parsed as pH 7 buffer, pH 9 buffer, and Dickson CRM. The microelectrode pH data were parsed as calcifying fluid, tissue, and seawater. Notes recorded during the original measurements were used to assist in identifying boundaries of adjacent zones. Measured mV within each zone of the calcifying fluid measurements were converted to pH using the calibration regression produced for each microelectrode.

Calcification rate measurements

Calcification rates were obtained using the buoyant weight technique (77) by Louise Cameron, Claire Reymond, and Justin Ries at the MAREE marine experimental facility at the Leibniz Center for Tropical Marine Research (Bremen, Germany) (7).

Coral fragments were hung by their stands from a hook suspended from a bottom loading scale (Mettler Toledo, precision = 0.01 g). All measurements took place within a seawater bath of constant temperature and salinity. Fragments were weighed three times to obtain a mean weight, and a standard of known weight was measured every 5 samples to ensure that the scale was functioning properly (i.e. no instrumental drift). Buoyant weights were obtained during the first three days of the experimental period, and the last three days. Immediately after the final weight was taken, corals were removed from their treatment tanks

and their tissue was removed using a gas duster. Corals skeletons were soaked twice in 90% ethanol to remove any salts, and were then dried in ambient air (20 °C) for two days. Dry skeletons were then weighed using the same scale. The relationship between the dry and buoyant weight of coral skeletons was empirically defined by plotting the dry weight against their final buoyant weight (Figure S1). This relationship can be defined for the species in this experiment using the following algorithms:

- 1) *Stylophora pistillata*: Dry weight (g) = 1.919 x Buoyant Weight + 7.677
- 2) *Pocillopora damicornis*: Dry weight (g) = 1.662 x Buoyant Weight + 8.777

where the precision of the buoyant weight of coral specimens as an estimator of their dry weight is equivalent to the standard error of the regression (*Stylophora pistillata*: 0.060 g; *Pocillopora damicornis*: 0.053 g). These empirically derived relationships were then used to calculate dry weight at the start of the experimental period, and net calcification was calculated as:

$$[\text{dry weight (end)} - \text{dry weight (start)}] / [\text{dry weight (start)}].$$

Geochemical analyses

Sample preparation

Cleaning was performed following (83). Insoluble particles were removed after separation of clay from the sample. Due to high organic matter content, a double oxidative step was performed using H₂O₂. A weak acid leach was also performed using 0.001N HCl. Pristine carbonates were then dissolved in 1N double-distilled HCl.

Boron isotopes

B isotopes variations are expressed in conventional delta (δ) notation (eq. S1) and are reported versus the NIST SRM 951 (84).

$$\delta^{11}\text{B} (\text{\textperthousand}) = 1000 \times \left(\frac{{}^{11}\text{B}/{}^{10}\text{B}_{\text{Sample}}}{{}^{11}\text{B}/{}^{10}\text{B}_{\text{NIST 951-a}}} - 1 \right) \quad (\text{S1})$$

B(OH)₃ is enriched in ¹¹B compared to B(OH)₄⁻ with a constant offset between the two chemical species given by the fraction factor (α). This fractionation factor (α) between B(OH)₃ and B(OH)₄⁻ of 27.2 ± 0.6 ‰ has been empirically determined by (82) in seawater and confirmed by an independent method by (85).

Boron purification was achieved via microdistillation (78, 86, 87, 88, 89). The recovered distillate was diluted with 0.5% HF to a final B concentration matching the liquid

standards to avoid matrix effects. Boron isotopic measurements were carried out on a Thermo Scientific ®Neptune Plus MC-ICP-MS at the University of Cambridge configured with $10^{13} \Omega$ resistance (91).

Seawater samples were prepared using column chemistry and analyzed at the Pôle Spectrométrie Océan (PSO), Plouzané. pH of the samples was elevated to 8-9. Five mL of Amberlite IRA-743 (Rohm and Hass®, Philadelphia, PA, USA) was cleaned and conditioned using 2% HNO₃ followed by MQ water buffered at pH 9. 200µL of seawater was loaded onto the resin. The matrix was then eluted using 2ml of MQ water pH 9, 1ml NaNO₃ (0.6N, pH9), and 5ml MQ water of pH 9. Boron was then recovered using 2.5 mL of 2% HNO₃. Na and S was removed to avoid matrix effects. A few seawater samples were also prepared using microdistillation to allow for comparison between methods.

Data quality was controlled by analyzing external standards, the NEP internal coral standard (Porites sp., $\delta^{11}\text{B} = 26.12 \pm 0.92 \text{ ‰}$, 2SD, n=33; (35, 80), Table S3) from University of Western Australia/Australian National University and the JCp-1 (Porites sp., $\delta^{11}\text{B} = 24.37 \pm 0.32 \text{ ‰}$, 2SD, n=57 (80), Table S3) from the Geological Survey of Japan. The certified boron isotope liquid standard ERM® AE121 ($\delta^{11}\text{B} = 19.88 \pm 0.3\text{‰}$, certified) was used to monitor reproducibility and drift during each session.

Samples measured for boron isotopes typically ranged from 10 ppb B (~5 ng B) to 20 ppb B samples (~10 ng B). Sensitivity was 8 mV/ppb B (e.g., 80 mV for 10ppb B) in wet plasma at 50µl/min sample aspiration rate. Procedural boron blanks ranged from 15pg B to 65 pg B and the acid blank during analyses was measured at 1mV on the ^{11}B , indicating a blank contribution of <1% of the sample signal with no memory effect within and across sessions. External reproducibility was ensured by the measurements of carbonate standard sublimated at the same time as the samples. Results for the isotopic composition of the NEP is $\delta^{11}\text{B}_{\text{NEP}} = 25.71 \pm 0.79 \text{ ‰}$ (2 SD, n=22, over 8 analytical sessions with each number representing an *ab-initio* processed sample). Our results are within error of published values of $25.80 \pm 0.89 \text{ ‰}$ (35). Results for JCp-1 is $\delta^{11}\text{B}_{\text{JCp-1}} = 24.06 \pm 0.19 \text{ ‰}$ (2 SD, n=6, over 6 analytical sessions with each number representing an *ab initio* processed sample), within error of published values of $24.37 \pm 0.32 \text{ ‰}$ (80) and $24.42 \pm 0.28 \text{ ‰}$ (35).

Boron isotope ($\delta^{11}\text{B}$) analyses of *S. pistillata* specimens were also performed independently at AWI (Bremerhaven, Germany). Coral samples were washed at least six times in MilliQ water and two times in methanol, and subsequently oxidized in buffered 1% H₂O₂ to

remove organic material. Samples were then leached in 0.001 N HNO₃ to remove any adsorbed contaminants, and finally dissolved 1 N HNO₃. Boron in the dissolved samples was separated from the matrix using the microdistillation technique. Boron isotope analyses were performed at AWI with a Nu Plasma II MC-ICP-MS equipped with a customized detector array including six secondary electron multipliers (SEM), where high-mass IC5 was used for ¹¹B and IC0 for ¹⁰B. The standard-sample-bracketing technique was used to correct for the instrumental mass bias and drift using the boron reference material NBS 951. Boron concentrations of samples and standards were matched to within $\pm 5\%$ to ensure that plasma conditions and the background contribution to the signal are similar between samples and standards. Each micro-distilled sample was analyzed in triplicate where at least two measurements were used for averaging the $\delta^{11}\text{B}_{\text{C}_\text{C}}$. Error is specified as 2σ (2 standard errors) of the mean derived from the replicates, accounting for $\sim 95\%$ of the data. The long-term instrumental uncertainty is monitored by frequent analysis of a control standard (AE121) that was run six times with each batch of samples. If the 2σ from sample replicates was smaller than the long-term instrumental uncertainty of ± 0.30 , the latter was reported as the measurement uncertainty. More detailed information on sample separation and analytical procedures is available in (90).

Unpaired t-tests with Welch's correction showed that values of seawater $\delta^{11}\text{B}$ measured by both were not significantly different amongst treatments ($p>0.05$; Table S6).

Table S1

Species	pCO _{2sw}	T	pH _{sw}	[CO ₃ ²⁻] - M17	NS*	S**	DIC - M17	NS*	S**	[CO ₃ ²⁻] - H16	NS*	S**	DIC - H16	NS*	S**	[CO ₃ ²⁻] - newEq	NS*	S**	DIC - newEq	NS*	S**
	(ppm)	(°C)	(total scale)	(μmol/kg)			(μmol/kg)			(μmol/kg)			(μmol/kg)			(μmol/kg)			(μmol/kg)		
<i>P. damicornis</i>	466	28	8.14	520	16	49	4457	114	160	325	18	49	2793	143	240	347	20	28	2971	158	96
<i>P. damicornis</i>	466	28	8.14	620	17	45	3894	93	130	404	20	46	2531	115	168	429	21	23	2704	121	78
<i>P. damicornis</i>	466	28	8.14	875	27	51	4692	129	159	706	37	67	3788	176	214	726	35	35	3893	164	91
<i>P. damicornis</i>	466	28	8.14	897	27	45	4244	105	134	718	33	60	3385	145	170	736	34	30	3483	142	81
<i>P. damicornis</i>	466	28	8.14	975	48	46	4231	112	144	812	60	61	3510	152	172	823	58	31	3565	148	80
<i>P. damicornis</i>	466	28	8.14	465	44	52	4509	126	172	278	39	49	2698	189	269	293	44	27	2825	248	102
<i>P. damicornis</i>	499	31	8.09	757	34	44	3832	104	127	558	41	54	2837	135	162	586	39	27	2967	132	74
<i>P. damicornis</i>	499	31	8.09	788	24	43	3831	101	129	594	30	55	2878	128	159	618	30	27	3002	129	73
<i>P. damicornis</i>	499	31	8.09	708	23	50	4132	115	141	518	30	56	3007	150	195	544	29	31	3173	146	80
<i>P. damicornis</i>	499	31	8.09	809	25	47	4126	109	137	628	33	59	3195	156	180	651	32	30	3320	143	82
<i>P. damicornis</i>	499	31	8.09	456	16	46	4002	107	157	270	16	45	2383	121	219	287	20	23	2517	153	91
<i>P. damicornis</i>	499	31	8.09	183	10	51	3455	106	410	81	7	30	1530	97	277	nd	nd	nd	nd	nd	nd
<i>P. damicornis</i>	925	28	7.90	262	11	57	4310	124	314	128	9	39	2106	123	321	nd	nd	nd	nd	nd	nd
<i>P. damicornis</i>	925	28	7.90	421	12	42	3808	85	146	224	11	37	2022	85	185	228	15	20	2069	114	88
<i>P. damicornis</i>	925	28	7.90	799	27	50	4363	109	146	605	34	58	3317	146	193	630	32	29	3438	144	83
<i>P. damicornis</i>	925	28	7.90	735	21	48	4386	103	146	538	27	58	3202	144	195	565	26	31	3368	141	85
<i>P. damicornis</i>	925	28	7.90	653	19	45	4283	103	147	447	23	53	2933	128	210	474	22	28	3121	135	86
<i>P. damicornis</i>	925	28	7.90	538	13	37	3481	72	118	315	14	38	2030	78	144	336	16	20	2170	86	70
<i>P. damicornis</i>	885	31	7.97	387	10	31	2814	52	101	182	8	25	1324	51	107	nd	nd	nd	nd	nd	nd
<i>P. damicornis</i>	885	31	7.97	356	14	51	4143	109	200	194	13	43	2261	118	264	nd	nd	nd	nd	nd	nd
<i>P. damicornis</i>	885	31	7.97	533	15	41	3549	74	122	321	16	40	2139	92	156	343	18	21	2285	102	75
<i>P. damicornis</i>	885	31	7.97	217	9	50	3425	82	269	94	6	27	1477	79	223	nd	nd	nd	nd	nd	nd
<i>P. damicornis</i>	885	31	7.97	668	20	55	4753	134	163	493	28	65	3507	176	253	521	27	34	3702	176	97
<i>P. damicornis</i>	2807	28	7.49	864	31	50	4661	125	153	694	38	70	3743	160	201	714	37	34	3868	160	90
<i>P. damicornis</i>	2807	28	7.49	845	24	53	4612	121	155	667	32	67	3654	161	211	690	31	32	3777	148	86
<i>P. damicornis</i>	2807	28	7.49	782	25	56	5124	144	175	615	32	74	4021	193	253	640	31	39	4173	195	101
<i>P. damicornis</i>	2807	28	7.49	811	23	46	4334	102	143	621	30	60	3313	135	186	644	27	30	3451	139	84
<i>P. damicornis</i>	3194	31	7.55	734	45	49	4308	111	143	546	49	59	3208	167	200	574	50	31	3357	156	85
<i>P. damicornis</i>	3194	31	7.55	559	17	49	4268	111	150	366	21	53	2795	140	224	392	22	29	2989	147	90
<i>P. damicornis</i>	3194	31	7.55	74	7	39	2266	105	633	25	3	16	766	51	224	nd	nd	nd	nd	nd	nd
<i>P. damicornis</i>	3194	31	7.55	113	8	44	2781	96	484	42	4	19	1018	64	243	nd	nd	nd	nd	nd	nd
<i>P. damicornis</i>	3194	31	7.55	14	4	nd	955	176	nd	7	1	11	507	55	353	nd	nd	nd	nd	nd	nd
<i>P. damicornis</i>	3194	31	7.55	511	16	48	4056	102	152	317	17	46	2516	122	212	339	19	26	2693	134	87
<i>S. pistillata</i>	466	28	8.14	889	33	50	4465	119	149	715	43	64	3580	163	196	732	40	32	3678	156	87
<i>S. pistillata</i>	466	28	8.14	919	36	51	4620	127	154	752	43	67	3787	169	196	770	42	33	3876	165	89
<i>S. pistillata</i>	466	28	8.14	912	35	50	4578	119	149	743	43	63	3735	171	197	763	42	35	3826	160	92
<i>S. pistillata</i>	466	28	8.14	659	26	42	4026	99	132	446	29	51	2729	125	179	474	31	25	2890	127	79
<i>S. pistillata</i>	466	28	8.14	1050	43	53	4822	142	157	920	56	73	4219	192	192	927	53	36	4243	184	97
<i>S. pistillata</i>	466	28	8.14	1049	38	50	4275	110	141	902	49	63	3674	152	159	908	50	32	3710	148	83
<i>S. pistillata</i>	499	31	8.09	551	38	66	5272	171	216	402	43	71	3814	254	367	428	43	38	4071	269	119
<i>S. pistillata</i>	499	31	8.09	716	22	43	3852	99	131	515	27	51	2765	127	167	545	27	28	2925	136	75
<i>S. pistillata</i>	499	31	8.09	934	29	49	3967	109	129	763	39	59	3252	146	165	782	39	30	3322	137	76
<i>S. pistillata</i>	499	31	8.09	982	31	48	4177	120	135	830	43	63	3533	157	174	846	41	33	3598	149	78
<i>S. pistillata</i>	499	31	8.09	853	42	57	5042	161	170	714	55	76	4188	225	239	735	52	37	4328	218	101
<i>S. pistillata</i>	499	31	8.09	616	22	51	4449	127	162	433	25	59	3127	164	241	461	27	31	3316	169	93
<i>S. pistillata</i>	499	31	8.09	728	22	45	3696	91	119	524	27	51	2660	123	155	551	27	27	2798	125	71
<i>S. pistillata</i>	499	31	8.09	859	29	50	4359	125	152	689	38	62	3510	176	190	712	34	33	3623	164	85
<i>S. pistillata</i>	925	28	7.90	976	50	56	5092	143	172	841	64	76	4387	212	221	856	59	40	4448	202	102
<i>S. pistillata</i>	925	28	7.90	871	37	56	4875	126	156	704	47	69	3944	190	215	725	44	37	4067	173	89
<i>S. pistillata</i>	925	28	7.90	798	36	53	4778	126	168	624	42	66	3704	173	232	644	41	32	3855	165	93
<i>S. pistillata</i>	925	28	7.90	957	39	53	4749	126	155	806	51	69	3978	175	195	819	47	36	4062	174	94
<i>S. pistillata</i>	925	28	7.90	854	35	48	4401	104	138	670	41	61	3463	149	199	693	41	31	3572	144	84
<i>S. pistillata</i>	885	31	7.97	918	54	60	5023	151	167	777	66	76	4290	225	234	801	66	38	4383	203	100
<i>S. pistillata</i>	885	31	7.97	350	23	42	3406	79	145	172	17	33	1667	96	168	nd	nd	nd	nd	nd	
<i>S. pistillata</i>	885	31	7.97	250	32	60	4365	216	419	134	23	46	2358	209	390	nd	nd	nd	nd	nd	
<i>S. pistillata</i>	885	31	7.97	926	56	50	5041	141	168	792	68	79	4315	223	237	809	63	38	4396	202	102
<i>S. pistillata</i>	2807	28	7.49	980	63	61	5616	172	185	863	72	85	4932	263	267	874	71	43	5004	236	115
<i>S. pistillata</i>	2807	28	7.49	967	60	64	5727														

Table S2

<i>Species</i>	pCO₂ (ppm)	T (°C)	pH_seawater (tot scale)	pH_{cf_light} (total scale)	pH_{cf_dark} (total scale)
<i>Pocillipora damicornis</i>	462	28	8.08	8.31	7.90
	467	28	8.07	9.34	8.58
	467	28	8.07	8.95	7.40
		average	8.08	8.87	7.96
<i>Pocillipora damicornis</i>	923	28	7.83	8.41	8.06
	919	28	7.81	7.97	8.08
	946	28	7.83	8.71	7.41
		average	7.83	8.36	7.85
<i>Pocillipora damicornis</i>	2857	28	7.37	8.23	7.27
	2807	28	7.37	8.51	7.04
	2824	28	7.37	7.77	7.64
		average	7.37	8.17	7.32
<i>Stylophora pistillata</i>	467	28	8.07	8.58	7.54
	467	28	8.07	8.87	7.03
	462	28	8.08	8.78	7.89
	470	28	8.07	8.91	8.44
		average	8.08	8.79	7.73
<i>Stylophora pistillata</i>	923	28	7.83	8.72	8.01
	919	28	7.81	8.69	8.48
	946	28	7.83	8.16	7.26
	946	28	7.83	8.25	7.41
		average	7.83	8.46	7.79
<i>Stylophora pistillata</i>	2857	28	7.37	7.98	7.58
	2807	28	7.37	7.54	7.19
	2807	28	7.37	8.44	7.76
	2824	28	7.37	8.55	7.79
		average	7.37	8.13	7.58
<i>Stylophora pistillata</i>	497	31	7.99	8.88	8.47
	490	31	7.97	8.44	7.33
	515	31	7.97	8.45	7.79
	467	31	8.06	8.80	7.96
		average	8.00	8.64	7.89
<i>Stylophora pistillata</i>	886	31	7.85	8.16	6.68
	886	31	7.85	7.55	6.54
	889	31	7.85	8.06	6.76
	889	31	7.84	8.05	7.55
		average	7.85	7.96	6.88
<i>Stylophora pistillata</i>	3221	31	7.37	8.04	6.97
	2997	31	7.37	7.68	7.16
	3346	31	7.37	7.97	7.03
	3346	31	7.37	8.08	6.79
		average	7.37	7.94	6.99

Table S3

Standard	$\delta^{11}\text{B}_1$ (‰)	$2\text{SD}_{\text{AE121}}$	n_{AE121}	$\delta^{11}\text{B}_2$ (‰)	$2\text{SD}_{\text{AE121}}$	n_{AE121}
NEP1	26.08	0.10	11	26.45	0.10	11
NEP2	26.53	0.11	14	26.39	0.11	14
NEP3	24.96	0.39	9			
NEP4	25.61	0.39	9			
NEP5	25.36	0.36	11	25.32	0.36	11
NEP6	25.59	0.30	5			
NEP7	25.48	0.09	5			
NEP8	25.47	0.09	5	25.51	0.09	5
NEP9	25.80	0.09	5	25.49	0.09	5
NEP10	25.42	0.15	3	25.32	0.15	3
NEP11	25.28	0.29	8	25.34	0.29	8
NEP12	25.27	0.29	8	25.47	0.29	8
NEP13	25.54	0.22	6			
NEP14	26.16	0.22	6	26.42	0.22	6
NEP15	25.86	0.22	4	25.95	0.22	4
NEP16	25.37	0.22	4	25.46	0.22	4
NEP17	26.41	0.22	4	26.21	0.22	4
NEP18	25.88	0.25	9	25.93	0.25	9
NEP19	25.83	0.19	3	25.72	0.19	3
NEP20	25.49	0.33	8	26.03	0.33	8
NEP21	26.48	0.33	8	26.06	0.33	8
NEP22	25.82	0.27	5	25.50	0.27	5
JCP-1-1	24.07	0.10				
JCP-1-2	24.17	0.11		24.17	0.10	
JCP-1-3	24.01	0.11				
JCP-1-4	23.92	0.26				
JCP-1-5	24.03	0.26		24.05	0.39	
JCP-1-6	24.18	0.36		24.16	0.36	
Standard	Average $\delta^{11}\text{B}$	2SD	n	Reference		
NEP	25.71	0.79	22	<i>this study</i>		
NEP	26.20	0.88	27	(80)		
NEP	25.80	0.89	6	(35)		
JCP-1	24.06	0.19	6	<i>this study</i>		
JCP-1	24.37	0.32	57	(80)		
JCP-1	24.42	0.28	7	(35)		

Table S4

This study

Table S5

pCO_{2sw}	T	Tank Date of sampling	δ¹¹B_{sw1}*	δ¹¹B_{sw2}*	δ¹¹B_{sw3}**	δ¹¹B_{sw4}***	δ¹¹B_{sw average}
(ppm)	(°C)		(‰)	(‰)	(‰)	(‰)	(‰)
400	28	1	14.4	41.26 ± 0.21 (2SD, nAE121 = 7)	41.29 ± 0.21 (2SD, nAE121 = 7)	41.02 ± 0.28 (2SD, nAE121=4)	41.19 ± 0.25
400	28	1	9.5	41.22 ± 0.21 (2SD, nAE121 = 7)	41.24 ± 0.21 (2SD, nAE121 = 7)	41.23 ± 0.15	41.23 ± 0.15
400	28	1	9.6	41.14 ± 0.21 (2SD, nAE121 = 7)	41.23 ± 0.21 (2SD, nAE121 = 7)	41.19 ± 0.15	41.19 ± 0.15
400	28	3	14.4	41.25 ± 0.21 (2SD, nAE121 = 7)	40.17 ± 0.21 (2SD, nAE121 = 7)	40.71 ± 0.15	40.71 ± 0.15
400	28	3	9.5	41.10 ± 0.21 (2SD, nAE121 = 7)	40.45 ± 0.21 (2SD, nAE121 = 7)	40.78 ± 0.15	40.78 ± 0.15
400	28	3	9.6	41.34 ± 0.21 (2SD, nAE121 = 7)	40.56 ± 0.21 (2SD, nAE121 = 7)	40.95 ± 0.15	40.95 ± 0.15
400	31	1	14.4	40.73 ± 0.21 (2SD, nAE121 = 7)	39.97 ± 0.21 (2SD, nAE121 = 7)	41.21 ± 0.27 (2SD, nAE121=5)	40.64 ± 1.25
400	31	1	9.5	40.47 ± 0.21 (2SD, nAE121 = 7)	39.71 ± 0.21 (2SD, nAE121 = 7)	40.09 ± 0.15	40.09 ± 0.15
400	31	1	9.6	40.32 ± 0.21 (2SD, nAE121 = 7)	39.78 ± 0.21 (2SD, nAE121 = 7)	40.05 ± 0.15	40.05 ± 0.15
1000	28	1	14.4	41.56 ± 0.21 (2SD, nAE121 = 7)	41.04 ± 0.21 (2SD, nAE121 = 7)	41.30 ± 0.15	41.30 ± 0.15
1000	28	1	9.5	41.57 ± 0.21 (2SD, nAE121 = 7)	41.12 ± 0.21 (2SD, nAE121 = 7)	41.34 ± 0.15	41.34 ± 0.15
1000	28	1	9.6	41.79 ± 0.21 (2SD, nAE121 = 7)	41.06 ± 0.21 (2SD, nAE121 = 7)	41.92 ± 0.27 (2SD, nAE121=5)	41.59 ± 0.92
1000	31	1	14.4	42.30 ± 0.21 (2SD, nAE121 = 7)	41.78 ± 0.21 (2SD, nAE121 = 7)	42.04 ± 0.15	42.04 ± 0.15
1000	31	1	9.5	42.27 ± 0.21 (2SD, nAE121 = 7)	41.55 ± 0.21 (2SD, nAE121 = 7)	41.91 ± 0.15	41.91 ± 0.15
1000	31	1	9.6	42.14 ± 0.21 (2SD, nAE121 = 7)	41.54 ± 0.21 (2SD, nAE121 = 7)	41.84 ± 0.15	41.84 ± 0.15
3000	28	1	14.4	41.11 ± 0.21 (2SD, nAE121 = 7)	40.70 ± 0.21 (2SD, nAE121 = 7)	40.91 ± 0.15	40.91 ± 0.15
3000	28	1	9.5	41.45 ± 0.21 (2SD, nAE121 = 7)	40.66 ± 0.21 (2SD, nAE121 = 7)	41.06 ± 0.15	41.06 ± 0.15
3000	28	1	9.6	41.24 ± 0.21 (2SD, nAE121 = 7)	40.66 ± 0.21 (2SD, nAE121 = 7)	40.95 ± 0.15	40.95 ± 0.15
3000	31	1	14.4	41.67 ± 0.21 (2SD, nAE121 = 7)	41.04 ± 0.21 (2SD, nAE121 = 7)	41.35 ± 0.15	41.35 ± 0.15
3000	31	1	9.5	41.60 ± 0.21 (2SD, nAE121 = 7)	40.98 ± 0.21 (2SD, nAE121 = 7)	41.49 ± 0.92	41.49 ± 0.92
3000	31	1	9.6	41.46 ± 0.21 (2SD, nAE121 = 7)	41.36 ± 0.21 (2SD, nAE121 = 7)	41.41 ± 0.15	41.41 ± 0.15

* Purification using columns chemistry (see text), δ¹¹B measured at the university of Brest.

** Purification using microsublimation (see text), δ¹¹B measured at the university of Cambridge.

Table S6**Temperature 28°C vs 31°C experiments**

<i>P. damicornis</i>				<i>S. pistillata</i>			
	400	1000	2800		400	1000	2800
δ¹¹B	p>0.05	p>0.05	p<0.05	δ¹¹B	p<0.05	p>0.05	p>0.05
pHcf	p>0.05	p>0.05	p<0.05	pHcf	p>0.05	p<0.05	p>0.05
DICcf	p<0.05	p>0.05	p<0.05	DICcf	p>0.05	p>0.05	p<0.05
Ωcf	p>0.05	p>0.05	p<0.05	Ωcf	p<0.05	p<0.05	p<0.05

pCO₂ 400 vs 2800 ppm experiments

<i>P. damicornis</i>			<i>S. pistillata</i>		
	28°C	31°C		28°C	31°C
δ¹¹B	p>0.05	p>0.05	δ¹¹B	p>0.05	p>0.05
pHcf	p>0.05	p>0.05	pHcf	p>0.05	p>0.05
DICcf	p>0.05	p>0.05	DICcf	p>0.05	p>0.05
Ωcf	p>0.05	p>0.05	Ωcf	p>0.05	p>0.05

pCO₂ 400 vs 1000 ppm experiments

<i>P. damicornis</i>			<i>S. pistillata</i>		
	28°C	31°C		28°C	31°C
δ¹¹B	p>0.05	p>0.05	δ¹¹B	p>0.05	p>0.05
pHcf	p>0.05	p>0.05	pHcf	p>0.05	p>0.05
DICcf	p>0.05	p>0.05	DICcf	p>0.05	p>0.05
Ωcf	p>0.05	p>0.05	Ωcf	p>0.05	p>0.05

Comparaison δ¹¹B at university of Cambridge and AIW

	<i>S. pistillata</i>	
	28°C	31°C
400 ppm	p>0.05	p>0.05
1000 ppm	p>0.05	p>0.05
2800 ppm	p>0.05	p>0.05

Comparison pH_{cf} from microprobe and δ¹¹B

<i>P. damicornis</i>			<i>S. pistillata</i>		
	28°C			28°C	31°C
400 ppm	p>0.05		400 ppm	p<0.05	p>0.05
1000 ppm	p>0.05		1000 ppm	p>0.05	p>0.05
2800 ppm	p>0.05		2800 ppm	p>0.05	p>0.05

Table S7**CULTURE CONDITIONS**

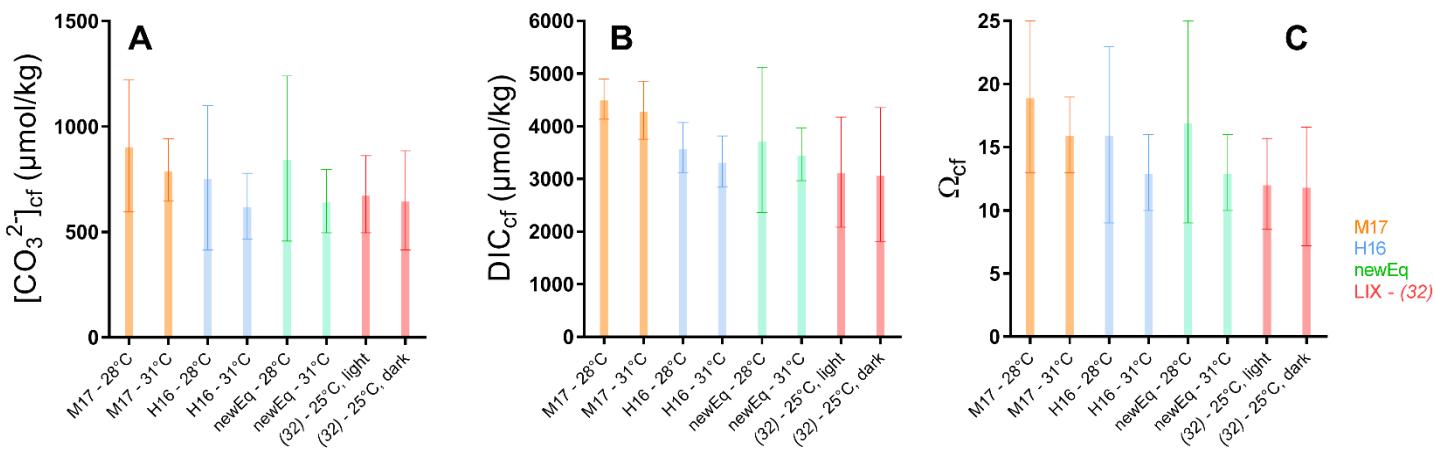
pCO_{2sw}	T	pH_{sw}	Tank	Li/Ca*	B/Ca*	Sr/Ca*
(ppm)	(°C)	total scale)		(μmol/mol)	(μmol/mol)	(mmol/mol)
<i>Pocillopora damicornis</i>						
462	28	8.14	1	6.5 ± 0.6	472 ± 11	8.43 ± 0.01
462	28	8.14	2	6.9 ± 0.6	545 ± 11	8.59 ± 0.01
462	28	8.14	3	7.1 ± 0.6	449 ± 11	8.85 ± 0.01
462	28	8.14	4	6.4 ± 0.6	492 ± 11	8.89 ± 0.01
462	28	8.14	1	7.5 ± 0.6	489 ± 11	9.51 ± 0.01
462	28	8.14	2	6.7 ± 0.6	460 ± 11	9.16 ± 0.01
483	31	8.09	4	5.8 ± 0.6	537 ± 11	9.42 ± 0.01
483	31	8.09	4	5.8 ± 0.6	537 ± 11	9.42 ± 0.01
483	31	8.09	1	7.3 ± 0.6	501 ± 11	7.63 ± 0.01
483	31	8.09		7.1 ± 0.6	500 ± 11	9.49 ± 0.01
483	31	8.09	3	6.4 ± 0.6	504 ± 11	8.25 ± 0.01
483	31	8.09	4	5.7 ± 0.6	470 ± 11	8.87 ± 0.01
931	28	7.90	2	5.9 ± 0.6	435 ± 11	8.92 ± 0.01
931	28	7.90	1	6.1 ± 0.6	558 ± 11	9.24 ± 0.01
931	28	7.90	3	6.7 ± 0.6	492 ± 11	9.30 ± 0.01
931	28	7.90	2	6.9 ± 0.6	491 ± 11	9.10 ± 0.01
931	28	7.90	4	6.8 ± 0.6	503 ± 11	9.04 ± 0.01
931	28	7.90	1	6.2 ± 0.6	619 ± 11	8.92 ± 0.01
908	31	7.97	4	7.5 ± 0.6	743 ± 11	9.14 ± 0.01
908	31	7.97	3	6.4 ± 0.6	474 ± 11	9.13 ± 0.01
908	31	7.97	1			
908	31	7.97	3	5.8 ± 0.6	592 ± 11	9.37 ± 0.01
908	31	7.97	3	6.5 ± 0.6	524 ± 11	8.23 ± 0.01
908	31	7.97	1	7.6 ± 0.6	441 ± 11	8.73 ± 0.01
2884	28	7.49	1	6.5 ± 0.6	460 ± 11	8.92 ± 0.01
2884	28	7.49	4	7.1 ± 0.6	466 ± 11	8.76 ± 0.01
2884	28	7.49	3	7.5 ± 0.6	422 ± 11	9.26 ± 0.01
2884	28	7.49	2	9.8 ± 0.6	496 ± 11	9.30 ± 0.01
2884	28	7.49	2			
3303	31	7.55	4	9.2 ± 0.6	485 ± 11	9.29 ± 0.01
3303	31	7.55	2	7.5 ± 0.6	486 ± 11	9.21 ± 0.01
3303	31	7.55	3	6.2 ± 0.6	538 ± 11	7.21 ± 0.01
3303	31	7.55	4	6.7 ± 0.6	518 ± 11	7.16 ± 0.01
3303	31	7.55	1	6.5 ± 0.6	449 ± 11	8.19 ± 0.01
3303	31	7.55	4	6.8 ± 0.6	509 ± 11	8.46 ± 0.01
3303	31	7.55	2		523 ± 11	

Stylophora pistillata

462	28	8.14	2	7.7 ± 0.6	4.67 ± 0.09	7.62 ± 0.01
462	28	8.14	2	8.0 ± 0.6	4.68 ± 0.09	9.06 ± 0.01
462	28	8.14	2	8.1 ± 0.6	4.68 ± 0.09	9.11 ± 0.01
462	28	8.14	4	8.6 ± 0.6	5.04 ± 0.09	7.73 ± 0.01
462	28	8.14	1	7.7 ± 0.6	5.08 ± 0.09	8.65 ± 0.01
462	28	8.14	2	8.0 ± 0.6	4.62 ± 0.09	8.62 ± 0.01
483	31	8.09	2	8.1 ± 0.6	5.81 ± 0.09	9.40 ± 0.01
483	31	8.09	4	7.3 ± 0.6	4.36 ± 0.09	9.16 ± 0.01
483	31	8.09	1	7.2 ± 0.6	4.12 ± 0.09	7.75 ± 0.01
483	31	8.09	1	7.2 ± 0.6	4.13 ± 0.09	7.83 ± 0.01
483	31	8.09	4	8.3 ± 0.6	4.78 ± 0.09	8.91 ± 0.01
483	31	8.09	3	7.9 ± 0.6	4.87 ± 0.09	9.31 ± 0.01
483	31	8.09	1	7.7 ± 0.6	4.07 ± 0.09	7.55 ± 0.01
483	31	8.09	1	6.9 ± 0.6	4.08 ± 0.09	9.13 ± 0.01
931	28	7.90	2	8.2 ± 0.6	5.06 ± 0.09	9.20 ± 0.01
931	28	7.90	4	7.6 ± 0.6	4.71 ± 0.09	8.75 ± 0.01
931	28	7.90	1	9.3 ± 0.6	7.75 ± 0.09	8.81 ± 0.01
931	28	7.90	3	7.5 ± 0.6	5.01 ± 0.09	9.24 ± 0.01
931	28	7.90	2	7.4 ± 0.6	5.86 ± 0.09	9.37 ± 0.01
908	31	7.97	3			
908	31	7.97	1	7.0 ± 0.6	4.77 ± 0.09	9.01 ± 0.01
908	31	7.97	3	7.7 ± 0.6	4.82 ± 0.09	8.63 ± 0.01
908	31	7.97	4	7.8 ± 0.6	4.57 ± 0.09	8.79 ± 0.01
908	31	7.97	1	7.7 ± 0.6	5.96 ± 0.09	9.52 ± 0.01
908	31	7.97	2	7.3 ± 0.6	5.05 ± 0.09	8.95 ± 0.01
2884	28	7.49	3	8.4 ± 0.6	5.10 ± 0.09	9.05 ± 0.01
2884	28	7.49	3	8.7 ± 0.6	5.67 ± 0.09	9.43 ± 0.01
2884	28	7.49	4	8.0 ± 0.6	4.98 ± 0.09	9.07 ± 0.01
2884	28	7.49	4	8.2 ± 0.6	5.14 ± 0.09	9.18 ± 0.01
3303	31	7.55	4	6.9 ± 0.6	4.54 ± 0.09	9.25 ± 0.01
3303	31	7.55	2	6.7 ± 0.6	4.47 ± 0.09	9.10 ± 0.01
3303	31	7.55	3	7.0 ± 0.6	4.59 ± 0.09	9.17 ± 0.01
3303	31	7.55	3	7.1 ± 0.6	4.66 ± 0.09	8.97 ± 0.01
3303	31	7.55	1	7.7 ± 0.6	5.21 ± 0.09	9.39 ± 0.01
3303	31	7.55	2	6.8 ± 0.6	4.64 ± 0.09	7.51 ± 0.01

* "Uncertainty is calculated as 2 SD of repeated measurements of the CamWuellestorf standard.

S. pistillata



P. damicornis

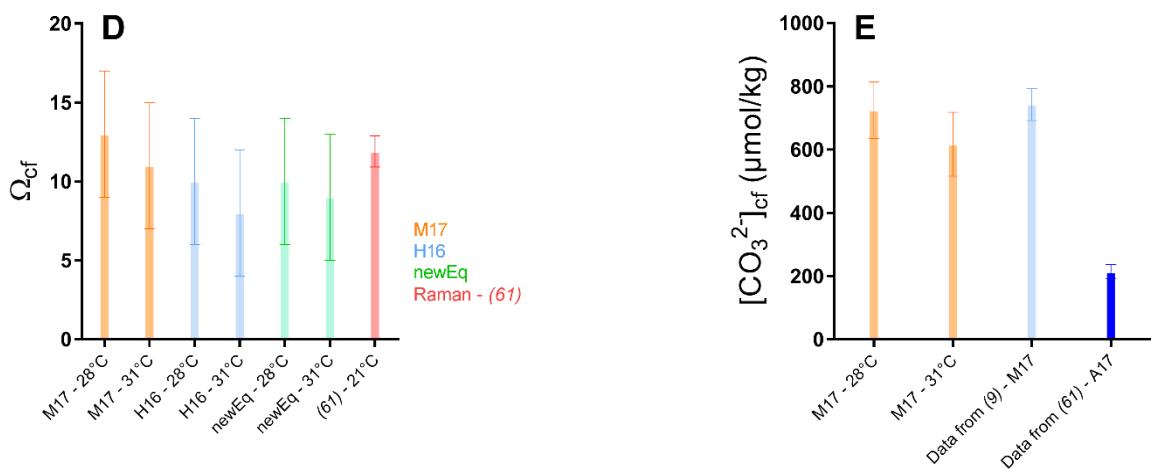


Figure S1: Comparison between boron derived carbonate parameters of the calcifying fluid based different K_D formulations and independent measurements. Comparison of carbonate parameters calculated from boron proxies with different K_D ((10) ‘M17’, (33) ‘H16’, (8) ‘new eq’) and independent measurements for *S. pistillata* (**A**, **B**, **C**) and *P. damicornis* (**D**, **E**). Carbonate ion concentration of the calcifying fluid ([CO₃²⁻]_{cf}), dissolved inorganic carbon of the calcifying fluid (DIC_{cf}), saturation state of aragonite of the calcifying fluid (Ω_{cf}). **A** and **E**: [CO₃²⁻]_{cf}; **B**: DIC_{cf}; **C** and **D**: Ω_{cf}. For *S. pistillata* (**A**, **B**, **C**). The data reported here are from the control treatment (pCO₂ ~400 ppm). The carbonate parameters are in the range of independent LIX microelectrode measurements from (32). For *P. damicornis*, independent measurements based on Raman spectroscopy (61) are consistent with data from ‘M17’ using [Ca]_{cf}= [Ca]_{sw}. Recalculating [CO₃²⁻]_{cf} with the K_D definition from (34) (‘A17’, **E**) and data from (61) yields values that are greater than in ‘A17’, but similar to estimates of [CO₃²⁻]_{cf} from (9). Independent measurements of [CO₃²⁻]_{cf} (e.g., via LIX microelectrode) do not presently exist for *P. damicornis* but would help refine the B/Ca proxy of [CO₃²⁻]_{cf} and identify optimal K_D formulation. Error bars represent 1 standard deviation from the mean.

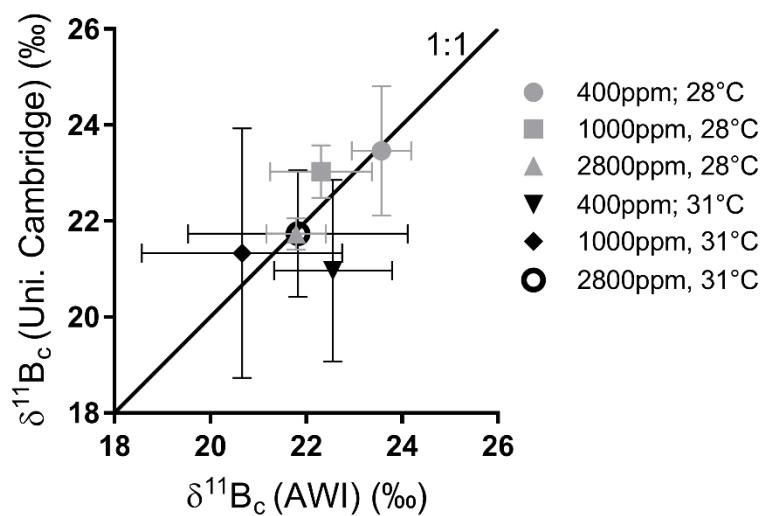


Figure S2: Analytical $\delta^{11}\text{B}$ comparison between the University of Cambridge and the Alfred Wagner Institute. Two-independent measurements of $\delta^{11}\text{B}$ for *S. pistillata* carried out at the University of Cambridge ('Uni. Cambridge') and at the Alfred Wagner Institute ('AWI'). Regression comparing results from the two labs are not significantly different from the 1:1 line ($p>0.05$; Welch-t test). These results cross-validate the $\delta^{11}\text{B}$ analytical procedures of both laboratories and show that the reported $\delta^{11}\text{B}$ values are reproducible by independent laboratories at the 95% confidence level. Error bars represent 2 standard deviation from the mean.

pistillata carried out at the University of Cambridge ('Uni. Cambridge') and at the Alfred Wagner Institute ('AWI'). Regression comparing results from the two labs are not significantly different from the 1:1 line ($p>0.05$; Welch-t test). These results cross-validate the $\delta^{11}\text{B}$ analytical procedures of both laboratories and show that the reported $\delta^{11}\text{B}$ values are reproducible by independent laboratories at the 95% confidence level. Error bars represent 2 standard deviation from the mean.

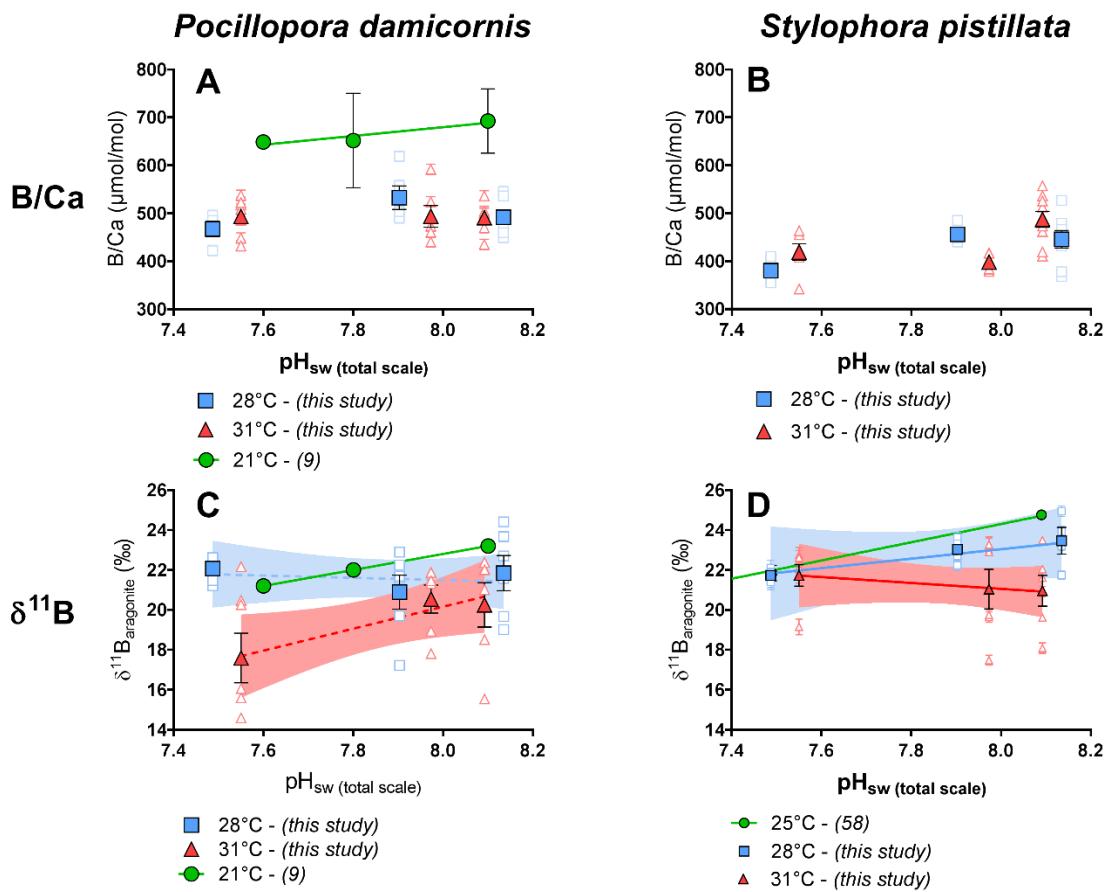


Figure S3: B/Ca and δ¹¹B measured in this study. Analytical results relative to treatment seawater pH (pH_{sw}) (blue squares: 28°C, red triangles: 31°C). A and B: show B/Ca for *P. damicornis* and *S. pistillata*, respectively. C and D show δ¹¹B for *P. damicornis* and *S. pistillata*, respectively. Error bars represent 1 standard error, envelopes represent 95% confidence interval of the linear regressions.

REFERENCES AND NOTES

1. T. P. Hughes, K. D. Anderson, S. R. Connolly, S. F. Heron, J. T. Kerry, J. M. Lough, A. H. Baird, J. K. Baum, M. L. Berumen, T. C. Bridge, D. C. Claar, C. M. Eakin, J. P. Gilmour, N. A. J. Graham, H. Harrison, J. P. A. Hobbs, A. S. Hoey, M. Hoogenboom, R. J. Lowe, M. T. McCulloch, J. M. Pandolfi, M. Pratchett, V. G. Schoepf, Torda, S. K Wilson, Spatial and temporal patterns of mass bleaching of corals in the Anthropocene. *Science* **359**, 80–83 (2018).
2. A. C. Baker, P. W. Glynn, B. Riegl, Climate change and coral reef bleaching: An ecological assessment of long-term impacts, recovery trends and future outlook. *Estuar. Coast. Shelf Sci.* **80**, 435–471 (2008).
3. S. Reynaud, N. Leclercq, S. Romaine-Lioud, C. Ferrier-Pagés, J. Jaubert, J. P. Gattuso, Interacting effects of CO₂ partial pressure and temperature on photosynthesis and calcification in a scleractinian coral. *Glob. Chang. Biol.* **9**, 1660–1668 (2003).
4. K. R. N. Anthony, D. I. Kline, G. Diaz-Pulido, S. Dove, O. Hoegh-Guldberg, Ocean acidification causes bleaching and productivity loss in coral reef builders. *Proc. Natl. Acad. Sci. U.S.A.* **105**, 17442–17446 (2008).
5. R. Rodolfo-Metalpa, F. Houlbrèque, É. Tambutté, F. Boisson, C. Baggini, F. P. Patti, R. Jeffree, M. Fine, A. Foggo, J.-P. Gattuso, J. M. Hall-Spencer, Coral and mollusc resistance to ocean acidification adversely affected by warming. *Nat. Clim. Change* **1**, 308–312 (2011).
6. A. L. Cohen, T. A. McConaughey, Geochemical perspectives on coral mineralization. *Rev. Mineral. Geochem.* **54**, 151–187 (2003).
7. L. P. Cameron, C. Reymond, J. Bijma, J. Büscher, D. De Beer, R. T. Eagle, Symbiont-assisted calcifying fluid pH elevation aids coral resilience to ocean acidification. *In review* (2020).
8. T. M. DeCarlo, M. Holcomb, M. T. McCulloch, Reviews and syntheses: Revisiting the boron systematics of aragonite and their application to coral calcification. *Biogeosciences* **15**, 2819–2834 (2018b).

9. S. Comeau, C. E. Cornwall, M. T. McCulloch, Decoupling between the response of coral calcifying fluid pH and calcification to ocean acidification. *Sci. Rep.* **7**, 7573 (2017a).
10. M. T. McCulloch, J. P. D’Olivo, J. Falter, M. Holcomb, J. A. Trotter, Coral calcification in a changing world and the interactive dynamics of pH and DIC upregulation. *Nat. Commun.* **8**, 15686 (2017).
11. *IPCC: Climate Change 2014—The Physical Science Basis*, Intergovernmental Panel on Climate Change, Ed., (Cambridge Univ. Press, 2014).
12. D. Allemand, C. Ferrier-Pagès, P. Furla, F. Houlbrèque, S. Puverel, S. Reynaud, É. Tambutté, S. Tambutté, D. Zoccola, Biomineralisation in reef-building corals: From molecular mechanisms to environmental control. *Comptes Rendus Palevol* **3**, 453–467 (2004).
13. J. Erez, The source of ions for biomineralization in foraminifera and their implications for paleoceanographic proxies. *Rev. Mineral. Geochemistry* **54**, 115–149 (2003).
14. J. B. Ries, A physicochemical framework for interpreting the biological calcification response to CO₂-induced ocean acidification. *Geochim. Cosmochim. Acta* **75**, 4053–4064 (2011).
15. T. A. McConaughey, R. H. Falk, Calcium-proton exchange during algal calcification. *Biol. Bull.* **180**, 185–195 (1991).
16. P. Furla, I. Galgani, I. Durand, D. Allemand, Sources and mechanisms of inorganic carbon transport for coral calcification and photosynthesis. *J. Exp. Biol.* **203**, 3445–3457 (2000).
17. D. Zoccola, P. Ganot, A. Bertucci, N. Caminiti-Segonds, N. Techer, C. R. Voolstra, M. Aranda, E. Tambutté, D. Allemand, J. R. Casey, S. Tambutté, Bicarbonate transporters in corals point towards a key step in the evolution of cnidarian calcification. *Sci. Rep.* **5**, 9983 (2015).

18. A. Moya, S. Tambutté, A. Bertucci, E. Tambutté, S. Lotto, D. Vullo, C. T. Supuran, D. Allemand, D. Zoccola, Carbonic anhydrase in the scleractinian coral *Stylophora pistillata*: Characterization, localization, and role in biomineralization. *J. Biol. Chem.* **283**, 25475–25484 (2008).
19. N. Allison, I. Cohen, A. A. Finch, J. Erez, A. W. Tudhope, Corals concentrate dissolved inorganic carbon to facilitate calcification. *Nat. Commun.* **5**, 5741 (2014).
20. S. Von Euw, Q. Zhang, V. Manichev, N. Murali, J. Gross, L. C. Feldman, T. Gustafsson, C. Flach, R. Mendelsohn, P. G. Falkowski, Biological control of aragonite formation in stony corals. *Science* **356**, 933–938 (2017).
21. J. L. Drake, M. F. Schaller, T. Mass, L. Godfrey, A. Fu, R. M. Sherrell, Y. Rosenthal, P. G. Falkowski, Molecular and geochemical perspectives on the influence of CO₂ on calcification in coral cell cultures. *Limnol. Oceanogr.* **63**, 107–121 (2018).
22. T. Mass, A. J. Giuffre, C.-Y. Sun, C. A. Stifler, M. J. Frazier, M. Neder, N. Tamura, C. V. Stad, M. A. Marcus, P. U. P. A. Gilbert, Amorphous calcium carbonate particles form coral skeletons. *Proc. Natl. Acad. Sci. U.S.A.* **114**, E7670–E7678 (2017b).
23. A. Akiva, M. Neder, K. Kahil, R. Gavriel, I. Pinkas, G. Goobes, T. Mass, Minerals in the pre-settled coral *Stylophora pistillata* crystallize via protein and ion changes. *Nat. Commun.* **9**, 1880 (2018).
24. A. Venn, E. Tambutté, M. Holcomb, D. Allemand, S. Tambutté, Live tissue imaging shows reef corals elevate pH under their calcifying tissue relative to seawater. *PLOS ONE* **6**, e20013 (2011).
25. A. J. Giuffre, A. C. Gagnon, J. J. De Yoreo, P. M. Dove, Isotopic tracer evidence for the amorphous calcium carbonate to calcite transformation by dissolution–reprecipitation. *Geochim. Cosmochim. Acta* **165**, 407–417 (2015).
26. T. M. DeCarlo, Characterizing coral skeleton mineralogy with Raman spectroscopy. *Nat. Commun.* **9**, 5325 (2018).

27. A. Akiva, M. Neder, K. Kahil, R. Gavriel, I. Pinkas, G. Goobes, T. Mass, Reply to: Characterizing coral skeleton mineralogy with Raman spectroscopy. *Nat. Commun.* **9**, 5324 (2018).
28. D. Evans, P. B. Webb, K. Penkman, R. Kröger, N. Allison, The characteristics and biological relevance of inorganic amorphous calcium carbonate (ACC) precipitated from seawater. *Cryst. Growth Des.* **19**, 4300–4313 (2019).
29. N. G. Hemming, G. N. Hanson, Boron isotopic composition and concentration in modern marine carbonates. *Geochim. Cosmochim. Acta* **56**, 537–543 (1992).
30. V. Mavromatis, V. Montouillout, J. Noireaux, J. Gaillardet, J. Schott, Characterization of boron incorporation and speciation in calcite and aragonite from co-precipitation experiments under controlled pH, temperature and precipitation rate. *Geochim. Cosmochim. Acta* **150**, 299–313 (2015).
31. J. Noireaux, V. Mavromatis, J. Gaillardet, J. Schott, V. Montouillout, P. Louvat, C. Rollion-Bard, D. R. Neuville, Crystallographic control on the boron isotope paleo-pH proxy. *Earth Planet. Sci. Lett.* **430**, 398–407 (2015).
32. D. S. Sevilgen, A. A. Venn, M. Y. Hu, E. Tambutté, D. de Beer, V. Planas-Bielsa, S. Tambutté, Full in vivo characterization of carbonate chemistry at the site of calcification in corals. *Sci. Adv.* **5**, eaau7447 (2019).
33. M. Holcomb, T. M. DeCarlo, G. A. Gaetani, M. McCulloch, Factors affecting B/Ca ratios in synthetic aragonite. *Chem. Geol.* **437**, 67–76 (2016).
34. N. Allison, Reconstructing coral calcification fluid dissolved inorganic carbon chemistry from skeletal boron: An exploration of potential controls on coral aragonite B/Ca. *Heliyon* **3**, e00387 (2017).
35. J. N. Sutton, Y.-W. Liu, J. B. Ries, M. Guillermic, E. Ponzevera, R. A. Eagle, $\delta^{11}\text{B}$ as monitor of calcification site pH in divergent marine calcifying organisms. *Biogeosciences* **15**, 1447–1467 (2018).

36. Y. W. Liu, J. N. Sutton, J. B. Ries, R. A. Eagle, Regulation of calcification site pH is a polyphylectic but not always governing response to ocean acidification. *Sci. Adv.* **6**, eaax1314 (2020).
37. A. A. Venn, E. Tambutté, N. Caminiti-Segonds, N. Techer, D. Allemand, S. Tambutté, Effects of light and darkness on pH regulation in three coral species exposed to seawater acidification. *Sci. Rep.*, **9**, 2201 (2019).
38. M. T. McCulloch, J. P. D'Olivo, J. Falter, L. Georgiou, M. Holcomb, P. Montagna, J. A. Trotter, Boron isotopic systematics in scleractinian corals and the role of pH up-regulation. *Boron Isotopes* 145–162 (2018).
39. A. A. Venn, E. Tambutte, M. Holcomb, J. Laurent, D. Allemand, S. Tambutte, Impact of seawater acidification on pH at the tissue–skeleton interface and calcification in reef corals. *Proc. Natl. Acad. Sci. U.S.A.* **110**, 1634–1639 (2013).
40. F. A. Al-Horani, S. M. Al-Moghrabi, D. de Beer, The mechanism of calcification and its relation to photosynthesis and respiration in the scleractinian coral *Galaxea fascicularis*. *Mar. Biol.* **142**, 419–426 (2003).
41. W.-J. Cai, Y. Ma, B. M. Hopkinson, A. G. Grottoli, M. E. Warner, Q. Ding, X. Hu, X. Yuan, V. Schoepf, H. Xu, C. Han, T. F. Melman, K. D. Hoadley, D. T. Pettay, Y. Matsui, J. H. Baumann, S. Levas, Y. Ying, Y. Wang, Microelectrode characterization of coral daytime interior pH and carbonate chemistry. *Nat. Commun.* **7**, 11144 (2016).
42. S. Comeau, E. Tambutté, R. C. Carpenter, P. J. Edmunds, N. R. Evensen, D. Allemand, C. Ferrier-Pagès, S. Tambutté, A. A. Venn, Coral calcifying fluid pH is modulated by seawater carbonate chemistry not solely seawater pH. *Proc. R. Soc. B* **284**, 20161669 (2017b).
43. C. L. Ross, J. L. Falter, M. T. McCulloch, Active modulation of the calcifying fluid carbonate chemistry ($\delta^{11}\text{B}$, B/Ca) and seasonally invariant coral calcification at sub-tropical limits. *Sci. Rep.* **7**, 13830 (2017).
44. P. W. Glynn, Coral reef bleaching: Ecological perspectives. *Coral Reefs* **12**, 1–17 (1993).

45. R. Berkelmans, J. K. Oliver, Large-scale bleaching of corals on the Great Barrier Reef. *Coral reefs* **18**, 55–60 (1999).
46. J. P. D’Olivo, M. T. McCulloch, Response of coral calcification and calcifying fluid composition to thermally induced bleaching stress. *Sci. Rep.* **7**, 2207 (2017).
47. J. P. D’Olivo, G. Ellwood, T. M. DeCarlo, M. T. McCulloch, Deconvolving the long-term impacts of ocean acidification and warming on coral biomineralisation. *Earth Planet. Sci. Lett.* **526**, 115785 (2019).
48. O. Hoegh-Guldberg, G. J. Smith, The effect of sudden changes in temperature, light and salinity on the population density and export of zooxanthellae from the reef corals *Stylophora pistillata* Esper and *Seriatopora hystrix* Dana. *J. Exp. Mar. Biol. Ecol.* **129**, 279–303 (1989).
49. C. B. Bove, J.B. Ries, S.W. Davies, I.T. Westfield, J. Umbanhowar, K.D. Castillo. Common Caribbean corals exhibit highly variable responses to future acidification and warming. *Proc. R. Soc. B.* **286**, 20182840 (2019).
50. Y. Loya, K. Sakai, K. Yamazato, Y. Nakano, H. Sambali, R. van Woesik, Coral bleaching: The winners and the losers. *Ecol. Lett.* **4**, 122–131 (2001).
51. J. P. Gattuso, D. Allemand, M. Frankignoulle, Photosynthesis and calcification at cellular, organismal and community levels in coral reefs: A review on interactions and control by carbonate chemistry. *Am. Zool.* **39**, 160–183 (1999).
52. N. J. Silbiger, G. Goodbody-Gringley, J. F. Bruno, H. M. Putnam, Comparative thermal performance of the reef-building coral *Orbicella franksi* at its latitudinal range limits. *Mar. Biol.* **166**, 126 (2019).
53. R. Rowan, Thermal adaptation in reef coral symbionts. *Nature* **430**, 742–742 (2004).
54. C. D. Clausen, A. A. Roth, Effect of temperature and temperature adaptation on calcification rate in the hermatypic coral *Pocillopora damicornis*. *Mar. Biol.* **33**, 93–100 (1975).

55. J. B. Ries, A. L. Cohen, D. C. McCorkle, Marine calcifiers exhibit mixed responses to CO₂-induced ocean acidification. *Geology* **37**, 1131–1134 (2009).
56. K. D. Castillo, J. B. Ries, J. F. Bruno, I.T. Westfield, The reef-building coral *Siderastrea siderea* exhibits parabolic responses to ocean acidification and warming. *Proc. R. Soc. B* **281**, 20141856 (2014).
57. S. Krief, E. J. Hendy, M. Fine, R. Yam, A. Meibom, G. L. Foster, A. Shemesh, Physiological and isotopic responses of scleractinian corals to ocean acidification. *Geochim. Cosmochim. Acta* **74**, 4988–5001 (2010).
58. R. H. McLachlan, J. T. Price, S. L. Solomon, A. G. Grottoli, Thirty years of coral heat-stress experiments: A review of methods. *Coral Reefs* **39**, 885–902 (2020).
59. S. Tambutté, E. Tambutté, D. Zoccola, D. Allemand, Organic matrix and biomineralization of scleractinian corals, in *Handbook of Biomineralization: Biological Aspects and Structure Formation* (Wiley, 2007), pp. 243–259.
60. T. M. DeCarlo, S. Comeau, C. E. Cornwall, M. T. McCulloch, Coral resistance to ocean acidification linked to increased calcium at the site of calcification. *Proc. R. Soc. B Biol. Sci.* **285**, 20180564 (2018a).
61. W. Sun, S. Jayaraman, W. Chen, K. A. Persson, G. Ceder, Nucleation of metastable aragonite CaCO₃ in seawater. *Proc. Natl. Acad. Sci. U.S.A.* **112**, 3199–3204 (2015).
62. M. Holcomb, A. A. Venn, E. Tambutté, S. Tambutté, D. Allemand, J. Trotter, M. McCulloch, Coral calcifying fluid pH dictates response to ocean acidification. *Sci. Rep.* **4**, 5207 (2014).
63. C. Langdon, M. J. Atkinson, Effect of elevated pCO₂ on photosynthesis and calcification of corals and interactions with seasonal change in temperature/ irradiance and nutrient enrichment. *J. Geophys. Res.* **110**, C09S07 (2005).

64. S. H. C. Noonan, K. E. Fabricius, Ocean acidification affects productivity but not the severity of thermal bleaching in some tropical corals. *ICES J. Mar. Sci.* **73**, 715–726 (2016).
65. C. B. Wall, T.-Y. Fan, P. J. Edmunds, Ocean acidification has no effect on thermal bleaching in the coral *Seriatopora caliendrum*. *Coral Reefs* **33**, 119–130 (2013).
66. A. A. Venn, C. Bernardet, A. Chabenat, E. Tambutté, S. Tambutté, Paracellular transport to the coral calcifying medium: Effects of environmental parameters. *J. Exp. Biol.* **223**, jeb227074 (2020).
67. S. Hohn, C. Reymond, Coral calcification, mucus, and the origin of skeletal organic molecules. *Coral Reefs* **38**, 973–984 (2019).
68. T. C. LaJeunesse, J. E. Parkinson, P. W. Gabrielson, H. J. Jeong, J. D. Reimer, C. R. Voolstra, S. R. Santos, Systematic revision of Symbiodiniaceae highlights the antiquity and diversity of coral endosymbionts. *Curr. Biol.* **28**, 2570–2580.e6 (2018).
69. R.M. Key, A. Kozyr, C. L. Sabine, K. Lee, R. Wanninkhof, J. L. Bullister, R. A. Feely, F. J. Millero, C. Mordy, T.-H. Peng, A global ocean carbon climatology: Results from Global Data Analysis Project (GLODAP). *Global Biogeochem. Cycles* **18**, GB4031, (2004).
70. R. N. Roy, L. N. Roy, K. M. Vogel, C. Porter-Moore, T. Pearson, C. E. Good, F. J. Millero, D. M. Campbell, The dissociation constants of carbonic acid in seawater at salinities 5 to 45 and temperatures 0 to 45°C. *Mar. Chem.* **44**, 249–267 (1993).
71. A. Mucci, The solubility of calcite and aragonite in seawater at various salinities, temperatures, and one atmosphere total pressure. *Am. J. Sci.* **283**, 780–799 (1983).
72. F. E. Grubbs, Procedures for detecting outlying observations in samples. *Dent. Tech.* **11**, 1–21 (1969).
73. D. de Beer, A. Glud, E. Epping, M. Kühl, A fast-responding CO₂ microelectrode for profiling sediments, microbial mats, and biofilms. *Limnol. Ocean.* **42**, 1590–1600 (1997).

74. P. S. Davies, Short-term growth measurements of corals using an accurate buoyant weighing technique. *Mar. Biol.* **101**, 389–395 (1989).
75. M. Guillermic, S. Misra, R. Eagle, A. Villa, F. Chang, A. Tripati, Seawater pH reconstruction using boron isotopes in multiple planktonic foraminifera species with different depth habitats and their potential to constrain pH and pCO₂ gradients. *Biogeosciences* **17**, 3487–3510 (2020).
76. M., Gutjahr, L., Bordier, E., Douville, J., Farmer, G. L., Foster, E., Hathorne, B. Hönisch, D. Lemarchand, P. Louvat, M. M. Culloch, J. Noireaux, N. Pallavicini, I. Rodushkin, P. Roux, J. Stewart, F. Thil, C.-F. You, Boron Isotope Intercomparison Project (BIIP): Development of a new carbonate standard for stable isotopic analyses, in *EGU General Assembly Conference Abstracts (Vol. 16)* (2014)
77. M. Holcomb, T. M. DeCarlo, V. Schoepf, D. Dissard, K. Tanaka, M. McCulloch, Cleaning and pre-treatment procedures for biogenic and synthetic calcium carbonate powders for determination of elemental and boron isotopic compositions. *Chem. Geol.* **398**, 11–21 (2015).
78. S. Misra, M. Greaves, R. Owen, J. Kerr, A. C. Elmore, H. Elderfield, Determination of B/Ca of natural carbonates by HR-ICP-MS, *Geochem. Geophys. Geosyst.* **15**, 1617–1628 (2014).
79. K. Klochko, A. J. Kaufman, W. Yao, R. H. Byrne, J. A. Tossell, Experimental measurement of boron isotope fractionation in seawater. *Earth Planet. Sci. Lett.* **248**, 261–270 (2006).
80. S. Barker, M. Greaves, H. Elderfield, A study of cleaning procedures used for foraminiferal Mg/Ca paleothermometry. *Geochem. Geophys. Geosyst.* **4**, 8407 (2003).
81. E. J. Catanzaro, C. E. Champion, A. L. Garner, G. Marinenko, K. M. Sappenfield, W. R. Shields, Boric Acid; Isotopic and Assay Standard Reference Materials (U.S. Natl. Bur. Stand. Spec., Publ., 1970), pp. 260–17, 70p.
82. O. Nir, A. Vengosh, J. S. Harkness, G. S. Dwyer, O. Lahav, Direct measurement of the boron isotope fractionation factor: Reducing the uncertainty in reconstructing ocean paleo-pH, *Earth Planet. Sci. Lett.* **414**, 1–5 (2015).

83. J. Gaillardet, D. Lemarchand, C. Göpel, G. Manhès, Evaporation and sublimation of boric acid: Application for boron purification from organic rich solutions. *Geostand. Newslet.* **25**, 67–75 (2001).
84. B.-S. Wang, C.-F. You, K.-F. Huang, S.-F. Wu, S. K. Aggarwal, C.-H. Chung, P.-Y. Lin, Direct separation of boron from Na- and Ca-rich matrices by sublimation for stable isotope measurement by MC-ICP-MS, *Talanta* **82**, 1378–1384 (2010).
85. S. Misra, R. Owen, J. Kerr, M. Greaves, H. Elderfield, Determination of $\delta^{11}\text{B}$ by HR-ICP-MS from mass limited samples: Application to natural carbonates and water samples. *Geochim. Cosmochim. Acta* **140**, 531–552 (2014b).
86. J. W. B. Rae, Boron isotopes in Foraminifera: Systematics, biomineralisation, and CO₂ reconstruction, in *Boron Isotopes. Advances in Isotope Geochemistry*, H. Marschall, G. Foster, Eds. (Springer, 2018).
87. M. Raitzsch, J. Bijma, A. Benthien, K.-U. Richter, G. Steinhoefel, M. Kučera, Boron isotope-based seasonal paleo-pH reconstruction for the Southeast Atlantic – A multispecies approach using habitat preference of planktonic foraminifera. *Earth Planet. Sci. Lett.* **487**, 138–150 (2018).
88. N. S. Lloyd, A. Y. Sadekov, S. Misra, Application of 10¹³ ohm Faraday cup current amplifiers for boron isotopic analyses by solution mode and laser ablation multicollector inductively coupled plasma mass spectrometry. *Rapid Commun. Mass Spectrom.* **32**, 9–18 (2018).