ELECTRONIC ANNEX

EA 1 Coral Culture

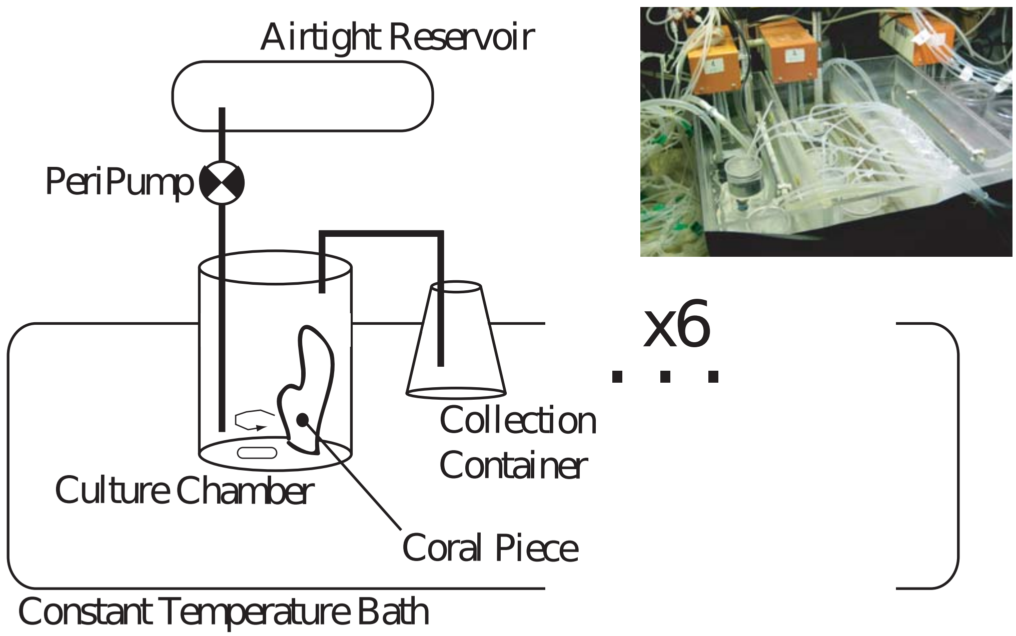

Figure 1: Flow through culture apparatus. Five coral were grown in separate airtight and headspace free culture chambers. Well mixed and isotopically enriched seawater was pumped through the culture chambers. A specific aragonite saturation was maintained in each chamber. One additional coral was grown without isotope enrichment under ambient carbonate ion conditions as a control.

EA 2 The Carbonate System of the Culture Solutions

Flow rates and the alkalinity of each chamber are summarized in Figures 1–2. Where there is missing flow or alkalinity data, values were interpolated from bracketing measurements. All the alkalinity, pH, DIC and flow measurements collected during this study as well as calculated carbonate chemistry are sumerized in the Table 1. Average aragonite saturation (Ω) of each culture chamber was calculated from these data, and this Ω is used to identify each culture condition throughout the text. Carbonate system measurements and calculations are described in the main text.

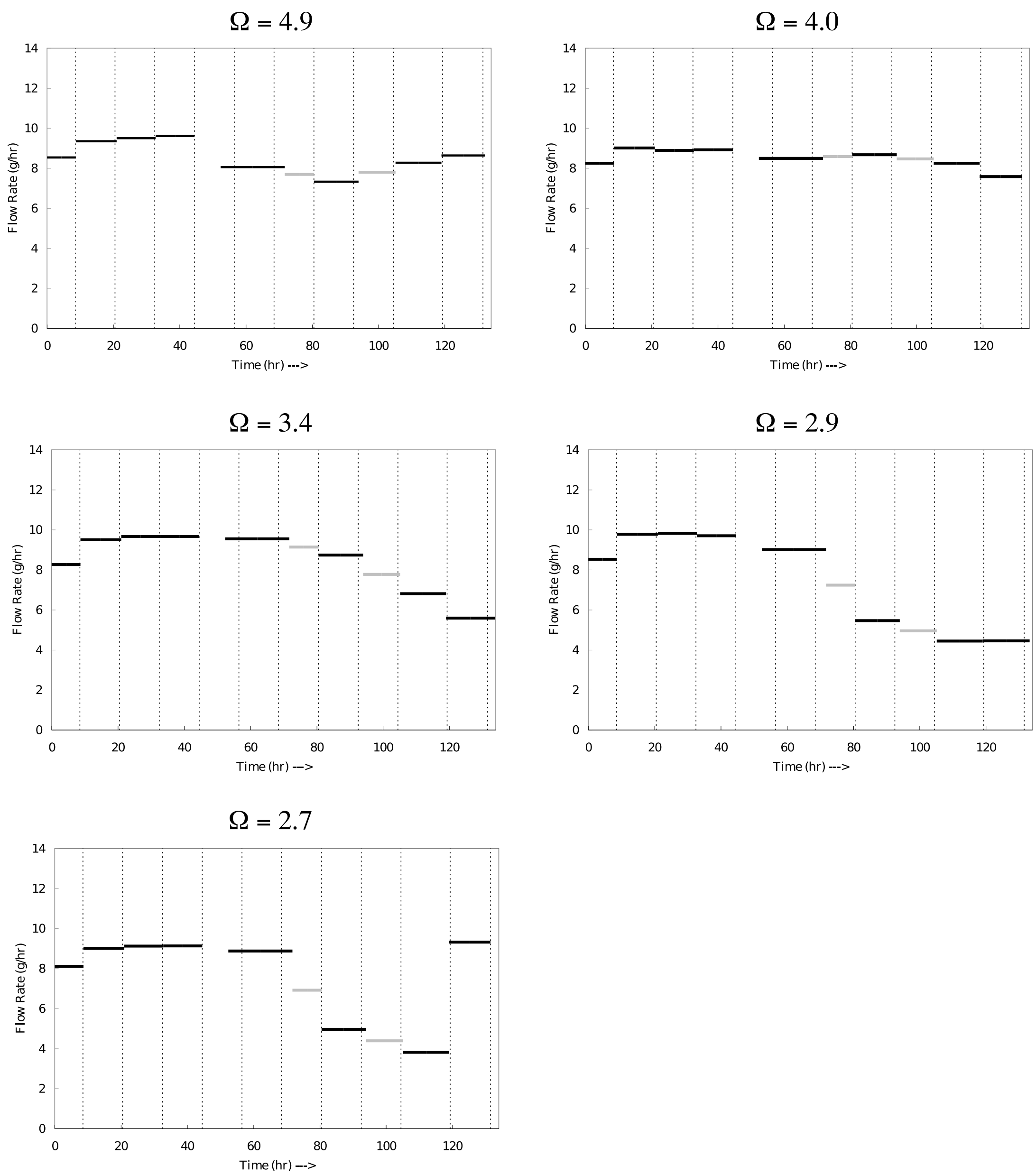

Figure 1: **Flow Rate Through Culture Chambers** in g/hr. Short jump in flow rate after the first interval resulted from an adjustment to peri-pump speed. Although measurements were taken during most of the experiment, flows do not exist for all time or alkalinity points, nor do alkalinities exist for all flow and time points, owing to sample size and time constraints. Grey bars represent interpolated flows to fill missing data.

Figure 2 Alkalinity of accumulated culture chamber outflow during growth experiment. Flat and bold horizontal lines mark the reservoir alkalinity: the alkalinity flowing into the culture chamber through the peri-pumps. A mid-experiment shift in reservoir alkalinity is a result of adding an REE time-mark dissolved in HCl to each bag with approximate re-titration of the alkalinity to the original condition. The alkalinity of each culture chamber output is plotted as horizontal bars, where the start and end of the bar signify the beginning and end of the collection period. Grey horizontal bars mark interpolated values as alkalinity was not measured for all time points due to sample size or time limitations. Vertical dashed lines mark the transition between subsequent light and dark photo-periods, starting with light at the far left.

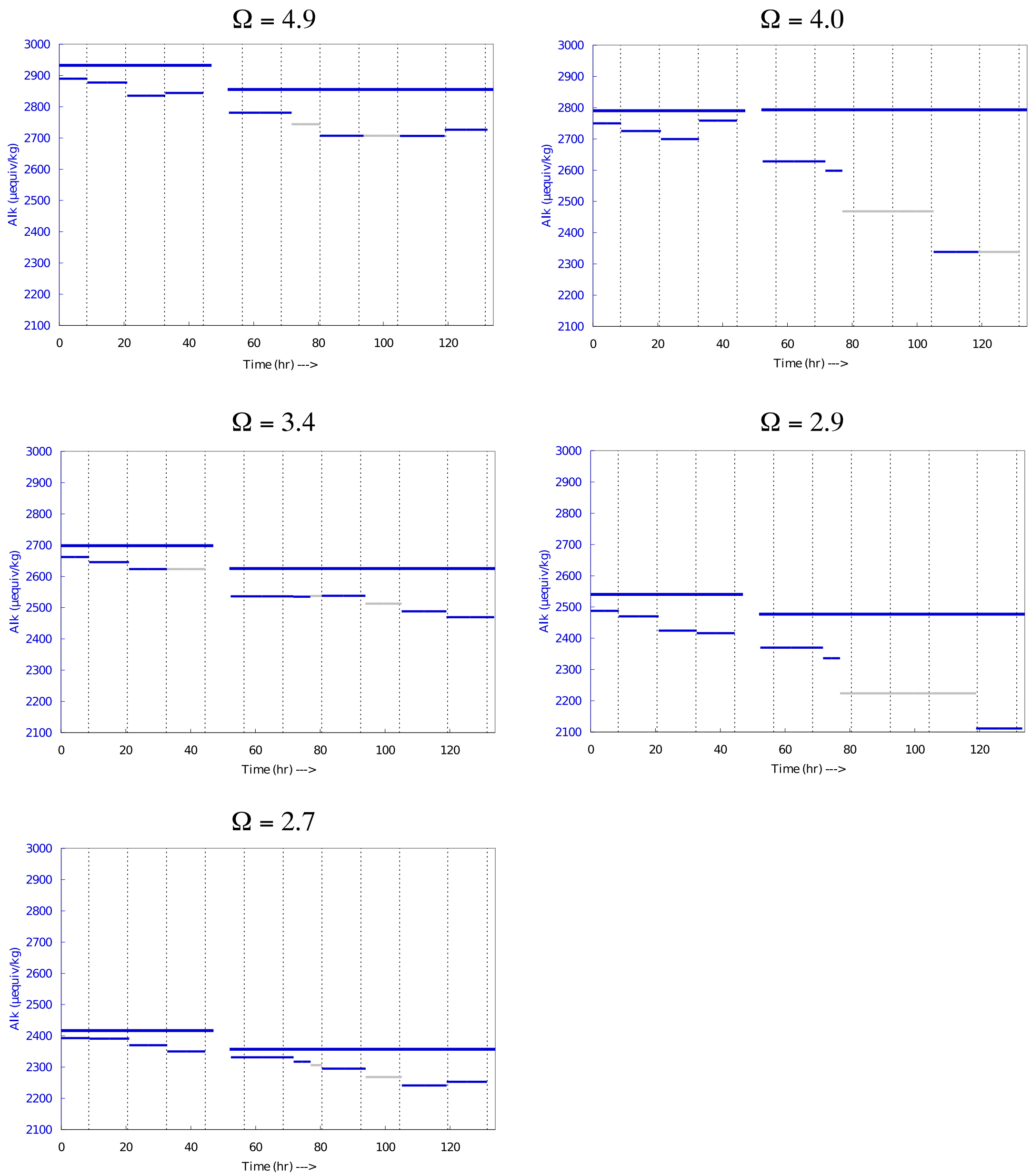

Figure 2:

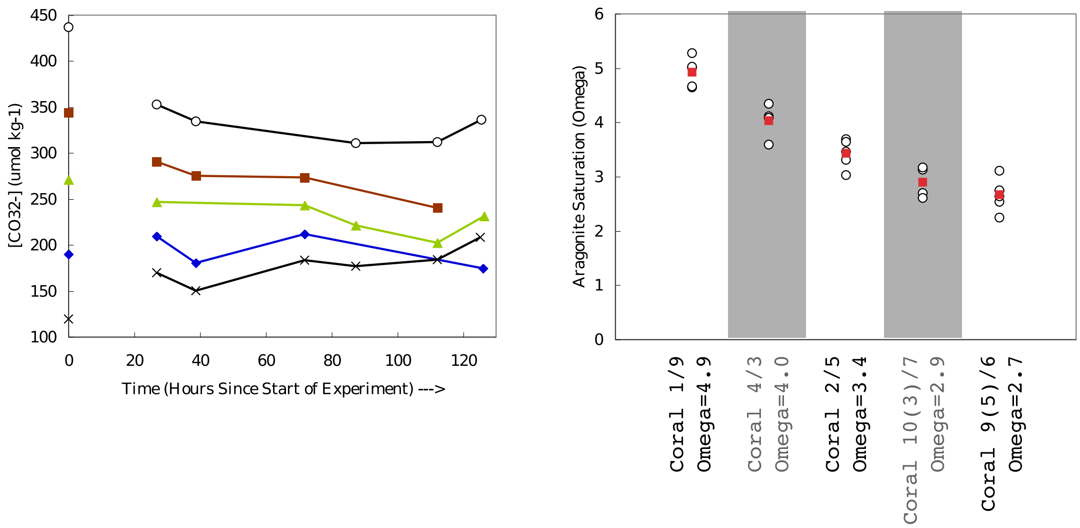

Figure 3: **LEFT:** $[CO_3^{2-}]$ in Culture Solutions During Culture Experiment. Time in hours from start of experiment. Value at time 0, on left axis corresponds to initial reservoir $[CO_3^{2-}]$. (◯) Ω=4.9; (■) Ω=4.0; (▲) Ω=3.4; (♦) Ω=2.9; (×) Ω=2.7. **RIGHT:** (◯) Calculated aragonite saturation in each chamber during coral culture where coral are labeled by an unique numbering system and the mean Omega for that coral. (■) Average aragonite saturation of chamber.

Table 1: Summary of carbonate system measurements during coral growth. Gray lines roughly distinguish the first half of the experiment from the second half of the experiment. Calculations and measurements explained in method section.

date	Container #	diurnal cycle	Start Time	Final Time	duration (hr)	intial mass (g)	final mass (g)	flow (g/hr)
Dec-10-2007	1	Resirviour - initial						
Dec-12-2007	1	Resirviour- post RRE						
Dec-15-2007	1	Resirviour-final						
Dec-10-2007	1	Day	10:00 AM	6:40 PM	8.67	46.6	120.6	8.54
Dec-10-2007	1	Night	6:40 PM	7:00 AM	12.33	46.9	162.2	9.35
Dec-11-2007	1	Day	7:00 AM	6:45 PM	11.75	46.6	158.3	9.51
Dec-11-2007	1	Night	6:45 PM	6:30 AM	11.75	46.9	159.8	9.61
Dec-12-2007	1	Day+Night	2:24 PM	9:45 AM	19.35	46.6	202.4	8.05
Dec-13-2007	1	Day (short)	9:45 AM					
Dec-13-2007	1	Night	6:30 PM	8:00 AM	13.50	46.9	145.8	7.33
Dec-14-2007	1	Night	7:10 PM	9:00 AM	13.83	46.9	161.4	8.28
Dec-15-2007	1	Day	9:00 AM	10:11 PM	13.18	**44.2**	158.1	8.64
Dec-10-2007	2	Resirviour - initial						
Dec-12-2007	2	Resirviour- post RRE						
Dec-15-2007	2	Resirviour-final						
Dec-10-2007	2	Day	10:00 AM	6:40 PM	8.67	46.7	118.3	8.26
Dec-10-2007	2	Night	6:40 PM	7:00 AM	12.33	46	163.2	9.50
Dec-11-2007	2	Day	7:00 AM	6:45 PM	11.75	46.7	160.3	9.67
Dec-11-2007	2	Night	6:45 PM	6:30 AM	11.75	46	159.6	9.67
Dec-12-2007	2	Day+Night	2:24 PM	9:45 AM	19.35	46.7	231.4	9.55
Dec-13-2007	2	Day (short)	9:45 AM					
Dec-13-2007	2	Night	6:30 PM	8:00 AM	13.50	46	164	8.74
Dec-14-2007	2	Night	7:10 PM	9:00 AM	13.83	46	140.2	6.81
Dec-15-2007	2	Day	9:00 AM	11:42 PM	14.70	**44.6**	126.8	5.59
Dec-10-2007	3	Resirviour - initial						
Dec-12-2007	3	Resirviour- post RRE						
Dec-15-2007	3	Resirviour-final						
Dec-10-2007	3	Day	10:00 AM	6:40 PM	8.67	47.1	121	8.53
Dec-10-2007	3	Night	6:40 PM	7:00 AM	12.33	46.2	166.8	9.78
Dec-11-2007	3	Day	7:00 AM	6:45 PM	11.75	47.1	162.5	9.82
Dec-11-2007	3	Night	6:45 PM	6:30 AM	11.75	46.2	160.2	9.70
Dec-12-2007	3	Day+Night	2:24 PM	9:45 AM	19.35	47.1	221.4	9.01
Dec-13-2007	3	Day (short)	9:45 AM					
Dec-13-2007	3	Night	6:30 PM	8:00 AM	13.50	46.2	119.9	5.46
Dec-14-2007	3	Night	7:10 PM	9:00 AM	13.83	46.2	107.6	4.44
Dec-15-2007	3	Day	9:00 AM	11:12 PM	14.20	**44.6**	107.8	4.45
Dec-10-2007	4	Resirviour - initial						
Dec-12-2007	4	Resirviour- post RRE						
Dec-15-2007	4	Resirviour-final						
Dec-10-2007	4	Day	10:00 AM	6:40 PM	8.67	46.5	118	8.25
Dec-10-2007	4	Night	6:40 PM	7:00 AM	12.33	47.1	158.2	9.01
Dec-11-2007	4	Day	7:00 AM	6:45 PM	11.75	46.5	151	8.89
Dec-11-2007	4	Night	6:45 PM	6:30 AM	11.75	47.1	151.9	8.92
Dec-12-2007	4	Day+Night	2:24 PM	9:45 AM	19.35	46.5	210.9	8.50
Dec-13-2007	4	Day (short)	9:45 AM					
Dec-13-2007	4	Night	6:30 PM	8:00 AM	13.50	47.1	164.2	8.67
Dec-14-2007	4	Night	7:10 PM	9:00 AM	13.83	47.1	161.2	8.25
Dec-15-2007	4	Day	9:00 AM	9:47 PM	12.78	**44.1**	141	7.58
Dec-10-2007	5	Resirviour - initial						
Dec-12-2007	5	Resirviour- post RRE						
Dec-15-2007	5	Resirviour-final						
Dec-10-2007	5	Day	10:00 AM	6:40 PM	8.67	46.8	117.1	8.11
Dec-10-2007	5	Night	6:40 PM	7:00 AM	12.33	46.8	158	9.02
Dec-11-2007	5	Day	7:00 AM	6:45 PM	11.75	46.8	154	9.12
Dec-11-2007	5	Night	6:45 PM	6:30 AM	11.75	46.8	154.1	9.13
Dec-12-2007	5	Day+Night	2:24 PM	9:45 AM	19.35	46.8	218.5	8.87
Dec-13-2007	5	Day (short)	9:45 AM					
Dec-13-2007	5	Night	6:30 PM	8:00 AM	13.50	46.8	113.8	4.96
Dec-14-2007	5	Night	7:10 PM	9:00 AM	13.83	46.8	99.5	3.81
Dec-15-2007	5	Day	9:00 AM	9:28 PM	12.47	**44.5**	160.7	9.32

Table 2: Continued summary of carbonate system measurements during coral growth.

date	Container #	diurnal cycle	pH	ALK (μmol eq / kg)	DIC (μmol/kg)	est DIC err	[CO3] (ALK,DIC)	[CO3] (pH,ALK)	Omega (pH,ALK)
Dec-10-2007	1	Resirviour - initial	8.519	2932				450	6.73
Dec-12-2007	1	Resirviour- post RRE	8.500	2844	2242	22	427	424	6.34
Dec-15-2007	1	Resirviour-final	8.516	2866				437	6.54
Dec-10-2007	1	Day		2890					
Dec-10-2007	1	Night		2877					
Dec-11-2007	1	Day	8.383	2835	2285	23	392	353	5.28
Dec-11-2007	1	Night	8.348	2844	2321	70	374	335	5.00
Dec-12-2007	1	Day+Night		2781					
Dec-13-2007	1	Day (short)	8.367						
Dec-13-2007	1	Night	8.335	2707	2261	23	317	311	4.65
Dec-14-2007	1	Night	8.337	2706	2258	23	318	312	4.66
Dec-15-2007	1	Day	8.379	2726	2256	23	333	337	5.03
Dec-10-2007	2	Resirviour - initial	8.289	2698				287	4.29
Dec-12-2007	2	Resirviour- post RRE	8.250	2626	2250	23	267	261	3.90
Dec-15-2007	2	Resirviour-final	8.260	2624	2258	23	261	265	3.96
Dec-10-2007	2	Day		2662					
Dec-10-2007	2	Night		2646					
Dec-11-2007	2	Day	8.220	2623	2318	23	222	247	3.69
Dec-11-2007	2	Night	8.176		2304	69			
Dec-12-2007	2	Day+Night		2536					
Dec-13-2007	2	Day (short)	8.232	2535				244	3.64
Dec-13-2007	2	Night	8.178	2538	2219	22	227	222	3.31
Dec-14-2007	2	Night	8.140	2488				203	3.03
Dec-15-2007	2	Day	8.219	2469				232	3.46
Dec-10-2007	3	Resirviour - initial	8.117	2540				198	2.96
Dec-12-2007	3	Resirviour- post RRE	8.088	2471	2211	22	188	183	2.73
Dec-15-2007	3	Resirviour-final	8.104	2483	2224	22	188	189	2.83
Dec-10-2007	3	Day		2488					
Dec-10-2007	3	Night		2470					
Dec-11-2007	3	Day	8.173	2424	2258	23	131	209	3.13
Dec-11-2007	3	Night	8.094	2416	2171	65	177	180	2.70
Dec-12-2007	3	Day+Night		2370					
Dec-13-2007	3	Day (short)	8.202	2336				212	3.17
Dec-13-2007	3	Night	8.172						
Dec-14-2007	3	Night	8.107						
Dec-15-2007	3	Day	8.152	2111				174	2.61
Dec-10-2007	4	Resirviour - initial	8.397	2790				355	5.31
Dec-12-2007	4	Resirviour- post RRE	8.395	2793	2232	22	397	354	5.30
Dec-15-2007	4	Resirviour-final	8.410	2498	2239	22	189	322	4.82
Dec-10-2007	4	Day		2750					
Dec-10-2007	4	Night		2725					
Dec-11-2007	4	Day	8.296	2699	2103	21	415	290	4.34
Dec-11-2007	4	Night	8.252	2758	2355	71	290	275	4.12
Dec-12-2007	4	Day+Night		2628					
Dec-13-2007	4	Day (short)	8.284	2598				273	4.09
Dec-13-2007	4	Night	8.268		2206	22			
Dec-14-2007	4	Night	8.273	2338	2208	22	109	240	3.59
Dec-15-2007	4	Day	8.353		2140	21			
Dec-10-2007	5	Resirviour - initial	7.915	2417				128	1.91
Dec-12-2007	5	Resirviour- post RRE	7.872	2355	2170	22	140	114	1.70
Dec-15-2007	5	Resirviour-final	7.887	2359	2224	22	112	118	1.76
Dec-10-2007	5	Day		2393					
Dec-10-2007	5	Night		2391					
Dec-11-2007	5	Day	8.073	2370	2278	23	91	170	2.54
Dec-11-2007	5	Night	8.014	2350	2165	65	140	151	2.25
Dec-12-2007	5	Day+Night		2331					
Dec-13-2007	5	Day (short)	8.126	2317				183	2.74
Dec-13-2007	5	Night	8.112	2295				177	2.64
Dec-14-2007	5	Night	8.147	2241				184	2.75
Dec-15-2007	5	Day	8.213	2253	1938	19	214	208	3.11
Dec-10-2007	6	Resirviour - initial	8.118	2616				205	3.06
Dec-12-2007	6	Resirviour- post RRE	8.080	2550	2274	23	201	186	2.78
Dec-15-2007	6	Resirviour-final	8.116	2555				199	2.98
Dec-10-2007	6	Day		2589					
Dec-10-2007	6	Night		2595					
Dec-11-2007	6	Day	8.107	2579	2117	21	321	198	2.96
Dec-11-2007	6	Night	8.092	2571	2306	69	195	192	2.87
Dec-12-2007	6	Day+Night		2551					
Dec-13-2007	6	Day (short)	8.173	2527				219	3.27
Dec-13-2007	6	Night			2199	22			
Dec-14-2007	6	Night	8.220	2481				233	3.49
Dec-15-2007	6	Day	8.250	2459				243	3.64

EA 3. Barium Isotope Results of Bulk Coral Surface Fractions

In addition to ^{43}Ca and ^{87}Sr, ^{136}Ba was also enriched by about 30-fold in the coral culture solution. This isotope was only used for supplemental growth rate data - as described in this section. Barium isotope data were collected from coral micro samples with barium isotope ratios measured on faraday cups using a dedicated method on the Neptune MC-ICP-MS. The isotope ^{136}Ba is enriched in the culture solution; however, xenon, a trace contaminant in the argon plasma, interferes with this and several other barium isotopes. To explicitly correct for the minor xenon interference, the isotopes ^{129}Xe and ^{131}Xe were monitored and used to calculate the xenon contribution at mass 136 assuming natural xenon abundances. Repeated measurements of several natural abundance geological materials, including a deep-sea coral, demonstrate that $^{136}Ba/^{138}Ba$ can be measured within 1%, an uncertainty much smaller than the several fold enrichment of the culture solution.

Culture solution barium isotope data was not measured, instead the end-member isotope ratio of the culture solution was estimated by fitting all measured pairs of 136/138 and 43/48 to the mixing equation with two tunable parameters: the culture solution isotope ratio, $(136/38)_x$, and the relative Ba/Ca of the newly grown to the initial skeleton, q (Albared, 1995, p. 19). The Matlab based fitting method minimizes the sum of the squares of the difference between model and data using the multi-dimensonal optimization function *fminsearch*. High 136/138 data points were weighted to be more significant in the fit to minimize the problems seen at low q in test cases using 87/88 vs. 43/48 . A few different q and $(136/38)_x$ are possible, depending upon the initial seed values for these parameters, but values that fit the data and where the mixing line appears to pass through most of the points are unique with q ~0.35, $(136/138)_x$ ~3.2. This approach assumes that the q of all corals are identical, which is an untested assumption. This assumption and spike modeling only affects the position of the top dashed line, not the individual measured coral data-points. The measured data, mixing model and estimated solution 136Ba/138Ba are shown in Figure 1. The barium isotope ratio 136/138 for each coral and by skeletal region is summarized in Figure 2, showing similar patterns as the 43/48 data: the maximum extent of enrichment increases with Ω and the immediate surface and spines are also most enriched in ^{136}Ba.

References:

Albared, F (1995) *Introduction to Geochemical Modeling.* Cambridge University Press, p. 19.

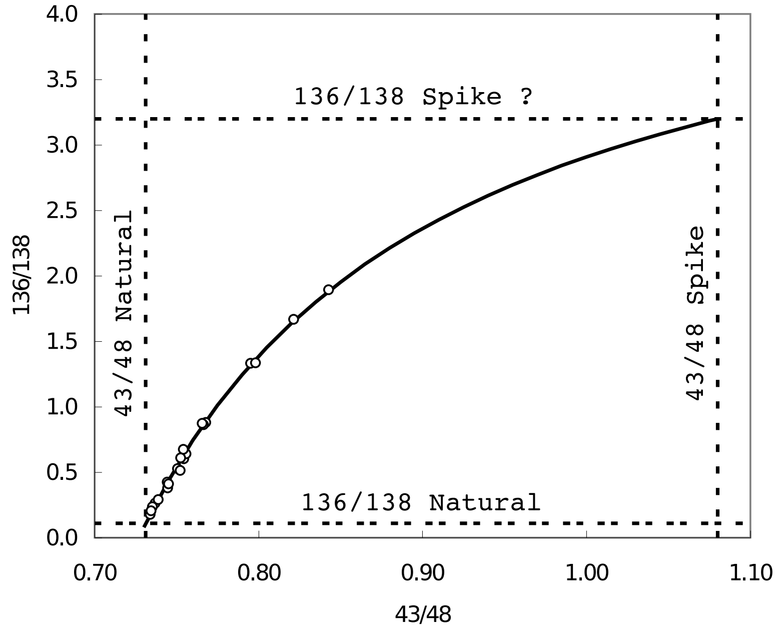

Figure 1: (◯) Barium isotope ratios of coral micro-samples shows incorporation of ^{136}Ba demonstrating skeletal growth during the experiment and co-precipitation of barium. (Solid line) Data were fit to a 2-end-memeber mixing line by adjusting the unknown parameters q and the 136/138 of the spike end-member as described above. The estimated values from the fit are q ∼0.35, $(136/138)_x$ ∼3.2. As with strontium and calcium isotopes, un-enriched isotopes of barium are not enriched in the coral skeleton.

Figure 2 LEFT: Barium isotope ratios of coral micro-samples plotted separately by growth condition show the extent of isotope incorporation increases from bottom to top, following aragonite saturation (Ω) like 43/48 and 87/88. **RIGHT:** The 136/138 ratio is still plotted on the y-axis, but the data are separated depending upon the skeletal region. New growth is regionally distributed following a similar pattern as 43/48, but with a larger relative signal reflecting the higher culture solution enrichment in ^{136}Ba. All plots have identical y-axes.

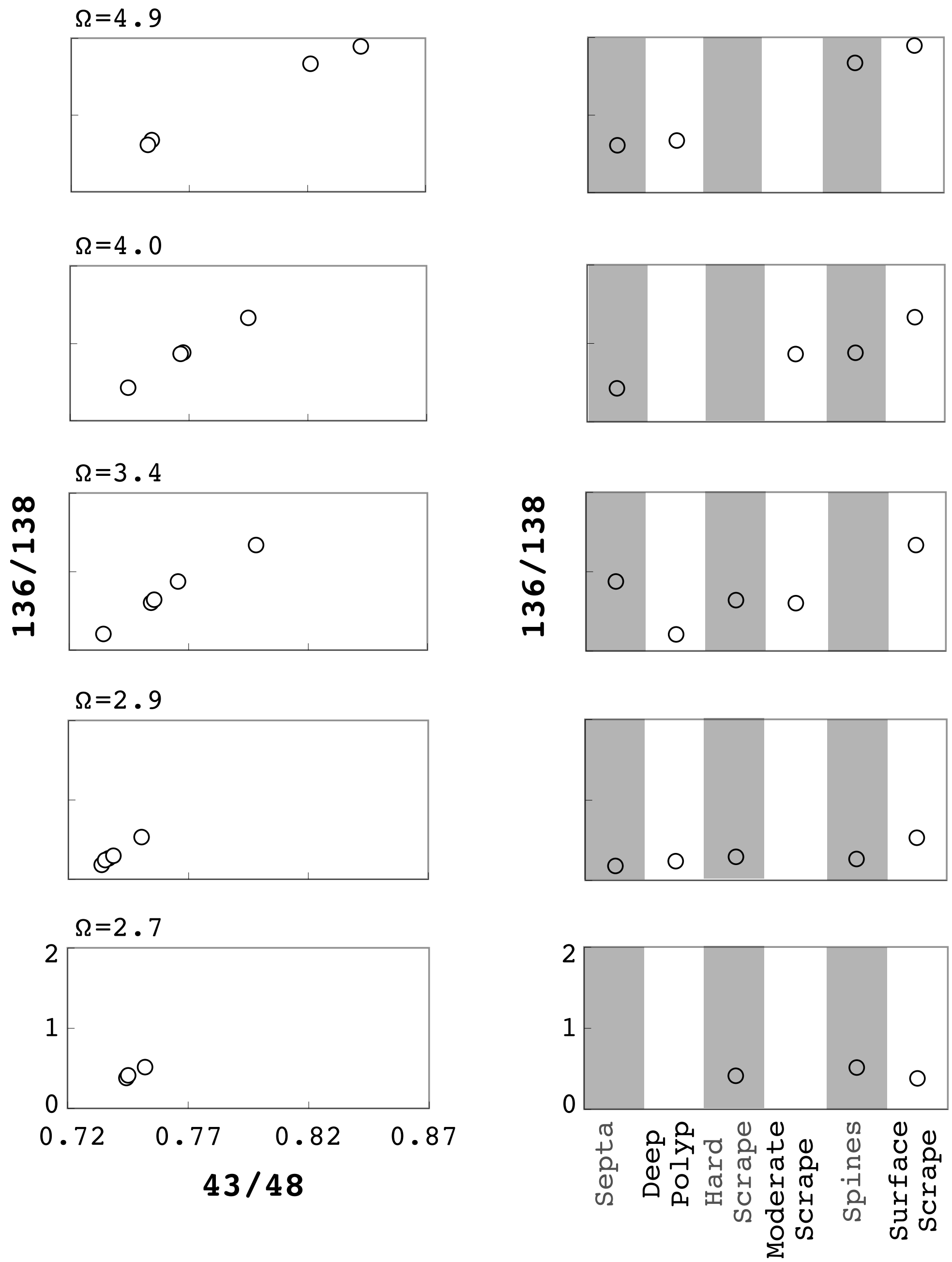
Ω=4.9
Ω=4.0
Ω=3.4
Ω=2.9
Ω=2.7
136/138
136/138
2
1
0
2
1
0
0.72
0.77
0.82
0.87
43/48
Septa
Deep Polyp
Hard Scrape
Moderate Scrape
Spines
Surface Scrape

Figure 2:

EA 4. Skeletal Me/Ca Ratios for Each Culture Condition

Table 1. Mean skeletal Me/Ca ratios for each culture as measured by NanoSIMS analysis.

Omega	Mean Sr/Ca	Mean Mg/Ca	n
2.7	9.29	13.4	1
2.9	9.32	6.9	7
3.4	9.23	5.1	3
4.0	9.19	6.4	7
4.9	9.21	6.6	1

Table 1:

Table 2. Skeletal Me/Ca ratios of each NanoSIMS measurement by culture condition, analytical session, and spine ID. Three spines were measured in each of the two coral cultured at Ω equal to 4.0 and 2.9; two spines were measured for the coral at Ω equal to 3.4; and one spine was sampled from each of the coral cultured at Ω equal to 4.9 and 2.7

Aragonite Saturation	Sr/Ca (mmol/mol)	D_SrCa	Mg/Ca (mmol/mol)	D_MgCa	Spine ID	Analytical Session
2.7	9.29	1.06	13.4	2.61	956_AB_0A	N4
2.9	9.55	1.09	8.26	1.61	1037_AA_A1	N3
2.9	9.57	1.10	7.87	1.53	1037_AA_A1	N3
2.9	8.88	1.02	7.61	1.48	1037_AB_0B	N4
2.9	9.49	1.09	6.82	1.33	1037_AB_0C	N4
2.9	9.76	1.12	7.23	1.41	1037_AB_0C	N4
2.9	9.17	1.05	5.55	1.08	1037_AB_0C	N4
2.9	8.80	1.01	5.10	0.99	1037_AB_0C	N4
3.4	8.93	1.02	5.14	1.00	25_AA_02	N3
3.4	9.23	1.06	5.81	1.13	25_AA_02	N3
3.4	9.54	1.09	4.41	0.86	25_AB_0B	N4
4.0	9.18	1.05	7.37	1.43	43_AA_A2	N3
4.0	9.23	1.06	6.03	1.17	43_AA_A2	N3
4.0	9.42	1.08	6.06	1.18	43_AA_A2	N3
4.0	9.39	1.07	3.63	0.71	43_AA_A4	N3
4.0	8.77	1.00	7.34	1.43	43_AB_0C	N4
4.0	9.31	1.07	6.35	1.23	43_AB_0C	N4
4.0	9.04	1.03	8.17	1.59	43_AB_0C	N4
4.9	9.21	1.05	6.65	1.29	19_AB_a	N4

Table 2:

EA 5. Time resolved calcification rate of coral in each culture chamber by alkalinity flux balance method.

Figure 1. Time resolved calcification rate of coral in each culture chamber by alkalinity flux balance method. For the early part of the experiment, when separate day and night samples were collected regularly, many of the chambers appear to exhibit a diurnal cycle with light enhanced calcification during the day. For the three coral with a clear diurnal cycle, those with with Ω values of 4.9, 3.4 and 2.9, dark calcication is 45–65% less than light calcication. The lowest aragonite saturation coral calcifies at a slower rate than the other chambers by a factor of two. Culture chamber Ω=4.0 exhibits anomalously high calcification rates, largely due to a late experiment increase in calcification. (**Note:** the data for culture chamber Ω=4.0 is plotted on an expanded scale.) Flat and bold horizontal lines mark the calcification rate, where the start and end of the line signify the beginning and end of the chamber outflow collection period. Gray horizontal bars mark interpolated values as either alkalinity or flow was not measured for all time points. Vertical dashed lines mark the transition between subsequent light and dark photo-periods, starting with light at the far left. All flow and carbonate system data used to calculate calcification rate are plotted and tabulated in the supplemental information above.

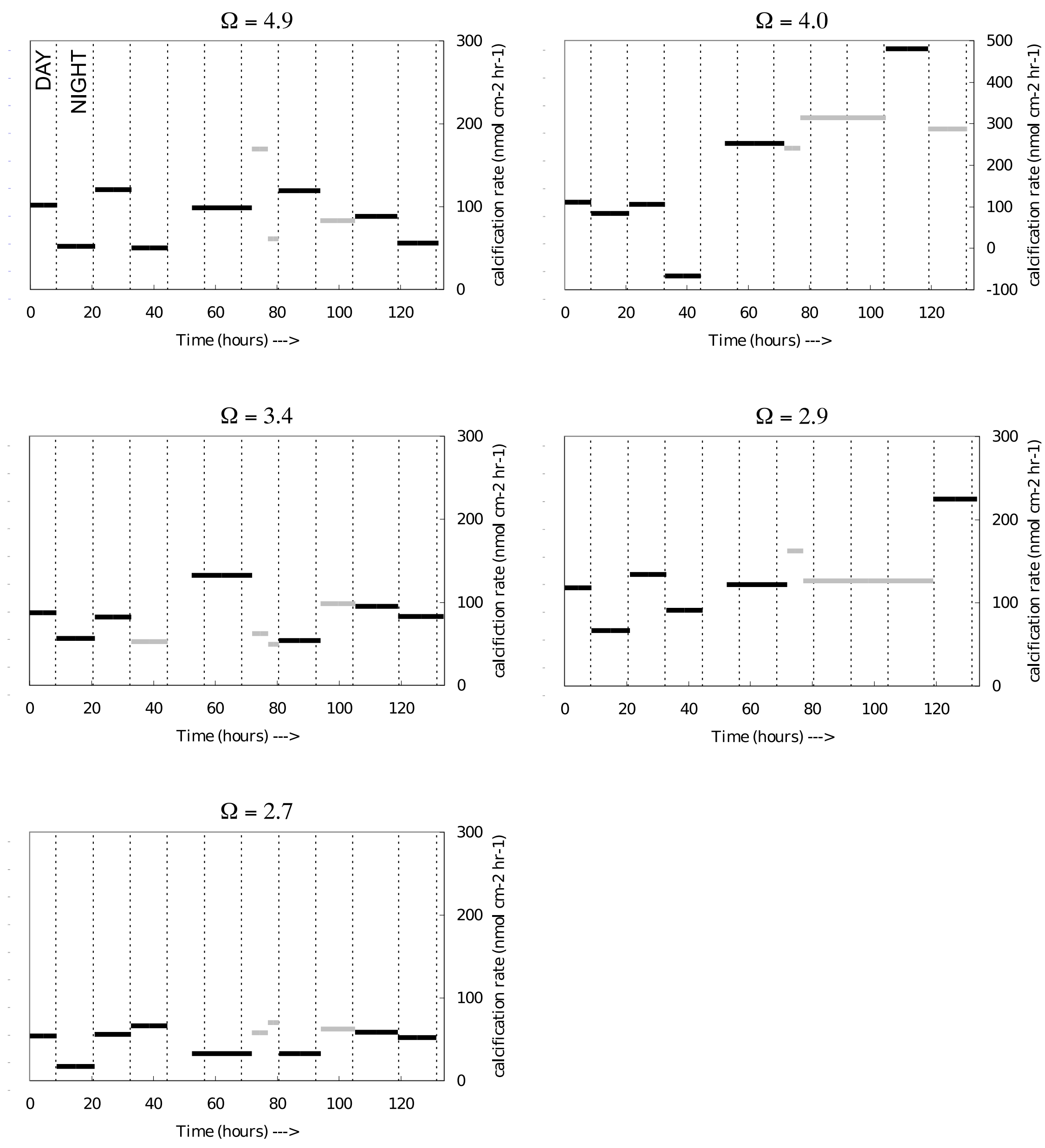
Ω = 4.9
DAY
NIGHT
0
20
40
60
80
100
120
Time (hours) --->
0
100
200
300
calcifiction rate (nmol cm-2 hr-1)
Ω = 4.0
Time (hours) --->
-100
0
100
200
300
400
500
calcifiction rate (nmol cm-2 hr-1)
Ω = 3.4
Time (hours) --->
calcifiction rate (nmol cm-2 hr-1)
Ω = 2.9
Time (hours) --->
calcifiction rate (nmol cm-2 hr-1)
Ω = 2.7
Time (hours) --->
calcifiction rate (nmol cm-2 hr-1)

Figure 1: