Dolomite-rich coralline algae in reefs resist dissolution in acidified conditions

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Coral reef ecosystems develop best in high-flow environments but their fragile frameworks are also vulnerable to high wave energy. Wave-resistant algal rims, predominantly made up of the crustose coralline algae (CCA) *Porolithon onkodes* and *P. pachydermum*^{1,2}, are therefore critical structural elements for the survival of many shallow coral reefs. Concerns are growing about the susceptibility of CCA to ocean acidification because CCA Mg-calcite skeletons are more susceptible to dissolution under low pH conditions than coral aragonite skeletons³. However, the recent discovery⁴ of dolomite ($\text{Mg}_{0.5}\text{Ca}_{0.5}(\text{CO}_3)_2$), a stable carbonate⁵, in *P. onkodes* cells necessitates a reappraisal of the impacts of ocean acidification on these CCA. Here we show, using a dissolution experiment, that dried dolomite-rich CCA have 6–10 times lower rates of dissolution than predominantly Mg-calcite CCA in both high- CO_2 (~700 ppm) and control (~380 ppm) environments, respectively. We reveal this stabilizing mechanism to be a combination of reduced porosity due to dolomite infilling and selective dissolution of other carbonate minerals. Physical break-up proceeds by dissolution of Mg-calcite walls until the dolomitized cell eventually drops out intact. Dolomite-rich CCA frameworks are common in shallow coral reefs globally and our results suggest that it is likely that they will continue to provide protection and stability for coral reef frameworks as CO_2 rises.

Coralline algae form extensive carbonate structures on the high-energy windward side of many tropical coral reefs. For example, the algal rim on the fringing reef of Rodrigues Island (Indian Ocean) is ~11 km long, 4 m thick and in parts protrudes ~1 m above the reef flat⁶, providing substantial protection for island communities from high-energy waves. Only the surface veneer (the top few millimetres) of CCA is living⁷ and the dense carbonate underneath the algal rim is predominantly *in situ* CCA skeleton and overlapping layers of coral branches cemented together by CCA crusts⁶. Development of these reef structures is dependent on preservation of the dead CCA skeleton post-mortem. Thus, understanding how declining seawater pH will affect this skeletal preservation is of paramount importance if we are to understand the changes to coral reef structural stability in a high- CO_2 world.

In the 1950s–1970s the mineral composition of coralline algae skeletons was determined to be ~12–18 mol% Mg-calcite^{8–10}. However, many bulk chemical analyses of tropical coralline algae showed a surplus of magnesium compared with those determined

by X-ray diffraction (XRD) using Mg-calcite peak position^{8,9}. Recently, we discovered this discrepancy was due to the presence of previously undetected dolomite and magnesite (MgCO_3) forming within the cell spaces⁴. Past determinations of thermodynamic solubility for coralline algae were based on the assumption that they were composed of Mg-calcite^{10–12}. As dolomite was not believed to form in the modern marine environment, determining dolomite solubility under these conditions was considered of limited importance¹². Dolomite stability has been inferred from the geologic record with a noted correlation between dolomite abundance and periods of higher CO_2 (lower CO_3 saturation state) in the Phanerozoic eon⁵ indicating dolomite stability under lower pH conditions.

We carried out dissolution experiments on fragments (~1 cm³) of CCA (*P. onkodes*) collected fresh, then dried, from the Heron Island reef front (Great Barrier Reef, Australia) and exposed to ambient sea water as a control and an enriched CO_2 treatment (Methods). pH (National Bureau of Standards scale) ranged from 7.85 to 8.55 (control) and 7.69–8.44 (treatment) tracking natural diurnal changes measured in the lagoon water¹³ (Supplementary Tables S1–S3 and Figs S1 and S2). Weight changes from experiments using living CCA are a combination of growth processes and skeletal dissolution¹⁴. Previous dissolution experiments have used dried, powdered CCA (refs 10,11), in beakers, with pH conditions not representative of the coral reef environment. The aim of this experiment was to determine the relationship between the mol% MgCO_3 of the CCA skeleton and dissolution without the influence of living processes. Although it was necessary to dry the CCA until dead, the crusts were kept intact so as to obtain results most closely replicating dissolution of exposed skeleton in the natural environment. Understanding this non-biotic dissolution process is important because when the CCA skeleton is exposed in the reef, for example by bio-erosion or breakages, then, without the protection of organic membranes, dissolution will be constrained by the skeletal composition (mineral and structural)¹².

Considering the prevailing theories that Mg-calcites with higher Mg content will undergo greatest dissolution, we were surprised to find a trend in the opposite direction (Fig. 1a). After ten days in the control and CO_2 treatments, coralline algae from the higher mol% group (17.27–18 mol% MgCO_3 ; by XRD, Methods) had significantly less ($p < 0.001$) weight loss than the lower mol% group (16.3–17.45 mol% MgCO_3). The higher mol% group had

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Figure 1 | Dependence of weight loss of coralline algae on composition (mol% MgCO_3). **a**, Weight loss versus Mg-calcite composition, showing a trend for higher weight loss with lower Mg content in both control ($R = -0.74$) and high ($R = -0.69$) CO_2 treatment samples. The slopes are significantly different (Supplementary Table S3b). The more Mg-rich CCA have the most asymmetrical Mg-calcite XRD peaks. Mg contents determined using the Mg-calcite peak position. **b**, Typical XRD scans for D^f (dotted line) and D^p CCA (solid line). Mg-C, Mg-calcite; D, dolomite range (M.C.N. *et al.*, manuscript in preparation); M, magnesite. **c**, Weight loss versus Mg-calcite composition as determined using the asymmetrical peak position (M.C.N. *et al.*, manuscript in preparation; asymm mol%; Supplementary Fig. S3). Compared with **a**, which shows the same samples, the regression has improved, with control ($R = -0.87$) and high CO_2 ($R = -0.77$). The slopes are significantly different (Supplementary Table S3b).

an average weight loss of 0.17% (s.d. 0.13) and 0.51% (s.d. 0.19), respectively, which was $\sim 91\%$ and 83% less than the lower mol% group (Supplementary Table S3a). This trend was also observed in a five-day *in situ* ocean acidification experiment¹⁵. The Mg-calcite XRD peaks for the more Mg-rich CCA demonstrated extreme asymmetry (Fig. 1b), which we discovered indicated the presence of dolomite and magnesite⁴. The less Mg-rich CCA showed only slight asymmetry and this was confirmed to represent a lesser amount of dolomite. We developed a simple technique to numerically describe this asymmetry (M.C.N. *et al.*, manuscript in preparation; Supplementary Fig. S3) and found a negative correlation between this dolomite and magnesite asymmetry and weight loss (Fig. 1c); control: $R = -0.87$ ($p = 0.01$), and high CO_2 : $R = -0.77$ ($p = 0.01$; statistics summary Supplementary Table S3b). We classify the CCA with asymmetry >24 mol% MgCO_3 as dolomite rich (D^f) and those <24 mol% MgCO_3 as dolomite poor (D^p) (Methods).

Next, to understand the differences between the D^f and D^p CCA that could be constraining the dissolution, we compared the physical distribution of dolomite within the D^f and D^p CCA (scanning electron microscopy (SEM), Methods). The key difference was that only the D^f CCA had dolomite lining the regular cell spaces (Fig. 2a), whereas D^p had Mg-calcite (Fig. 2b). Both D^f and D^p CCA had cell infill commencing $\sim 50\text{--}100\text{ }\mu\text{m}$ below the surface. In D^f CCA this cell infill could be magnesite (Fig. 2c) or dolomite, whereas in D^p CCA, cells were either left void or infilled with Mg-calcite (Fig. 2d) and infrequently, magnesite (Supplementary Fig. S4). Dolomite lining in the D^f CCA formed as rhombs and submicrometre-sized mounds (Fig. 2e–g). In both the D^p and D^f CCA the reproductive conceptacles contained dolomite (Fig. 3a,b, enlargements Supplementary Figs S5 and S6). A particularly intriguing difference in their natural dissolution process is revealed in the bottom $100\text{ }\mu\text{m}$; the D^f CCA was visibly dense whereas that of the D^p CCA was mostly porous owing to limited cell infill (Fig. 3c,d). We used a gridded point count (Supplementary Information) to estimate the porosity for D^f CCA at 6% and D^p CCA at 65% , a figure that closely matched the tenfold difference in dissolution between the D^f and D^p CCA. We estimate that the stable dolomite reduces the reactive surface area in D^f CCA by $\sim 45\%$ (estimated from the point count). The net dissolution process seems to be one of selective mineral

dissolution and precipitation. In the base of the D^f CCA, Mg-calcite fills cells, magnesite was absent and the dolomite rims remained intact, thus retaining density. In contrast, in the D^p CCA the cell infill and interfilament Mg-calcite had dissolved, and only the cell-lining Mg-calcite remained. It seems that the process of physical break-up in the D^f CCA occurs through the dissolution of the interfilament and cell-wall Mg-calcite until sufficient wall material has been removed for the dissolution-resistant dolomite cell cast to drop out intact (Fig. 4a,b). These dolomite cell casts are not only thermodynamically stable but also physically harder than the surrounding Mg-calcite (Fig. 4c). In the D^f CCA, alteration to mineralogy seems to commence about $500\text{--}600\text{ }\mu\text{m}$ up from the base (Supplementary Fig. S7) and similarly in the D^p CCA. Aragonite also infilled discrete cells (Supplementary Fig. S8) and replaced parts of the CCA skeleton. The common Mg-calcite cell infill in the D^p and absence from the D^f (excluding the exposed base) implies that it is unlikely that the D^p is a mid-stage in the formation of D^f CCA. Some CCA had XRD asymmetry that was between D^f and D^p ; SEM revealed banding of layers with and without dolomite rims and little cell infill (Supplementary Fig. S9).

To confirm the sequence of mineral dissolution and removal we performed an etching experiment on the D^f and D^p CCA (Methods). We found no evidence of cell rim dolomite dissolution; however, dolomite seems to be removed from conceptacles (Supplementary Fig. S10). In both samples the interfilament Mg-calcite is preferentially removed followed by the cell wall Mg-calcite (Supplementary Fig. S11a–f). Freshwater experiments on dolomite limestone have demonstrated that dissolution rates of dolomite are independent of pH between 6 and 8 (ref. 16) and that water flow velocity is the strongest control on dissolution rates of calcite¹⁷. Indeed, pore space and permeability are the key parameters influencing skeletal breakdown in temperate coralline algae in undersaturated conditions¹⁸. We propose that stability of the D^f CCA is conferred by their low porosity reducing water flow velocity throughout the lower crust, thereby reducing all dissolution reaction rates^{17,19} and allowing re-precipitation of Mg-calcite within cell spaces. These processes combined result in a net physical break-up to an order of magnitude less than that for D^p CCA without dolomite cell lining. The degree of this stability will be influenced by the quantity of dolomite and cell infill.

Figure 2 | Comparison of intracellular mineralization in the D^f and D^p coralline algae. **a**, D^f CCA (H305) has cells lined with dolomite (DL), whereas cell walls and interfilament calcified areas are composed of Mg-calcite (Mg-C). **b**, D^p CCA (H311) shows cells with an Mg-calcite lining (Mg-CL). **c**, D^f CCA (H305) has magnesite (Mag) cell infill. Dolomite lining (white arrows) forms a narrow rim between the Mg-calcite cell wall and the cell infill. **d**, D^p CCA (H56) has cell infill by concentric rings of Mg-calcite. **e**, D^f CCA (H305); close up of dolomite rhombs forming cell lining. **f**, (H305) dolomite cell infill with organic coating. **g**, CCA (H320) shows dolomite rims with dolomite submicrometre-sized mounds on the surface. Scale bars, 5 µm (**a–d**) and 2 µm (**e–g**).

The next question is how prevalent is this dolomite phenomenon? To answer this we determined the mineralogy of samples collected from multiple coral reefs from the Pacific and Caribbean. We found D^f CCA in our samples from shallow reef locations at Heron Island (southern Great Barrier Reef), Lizard Island (northern Great Barrier Reef), Okinawa (northern Pacific) and the Caribbean (Supplementary Table S5 and Figs S12 and S13). Dolomite was most commonly found in dense crusts (>3 mm) from high-energy, light environments and was absent from thin crusts growing in shaded locations. CCA skeleton in a reef front algal rim core⁶ from Rodrigues (Indian Ocean) demonstrated asymmetry comparable to D^f of fresh CCA (Supplementary Table S5 and Figs S14–S16). These samples were from 35 to 80 cm and 3.2 m down core, an estimated age of 290–670 yr and 2,670 yr, respectively, indicating that this biomineralized dolomite is stable long after the organism has died. We reviewed previous studies that recorded bulk magnesium measurements higher than ~18 mol% MgCO₃ or XRD asymmetry (for example, refs 8,9,20) to determine whether these CCA may have had the type of dolomite mineralization we have detailed here. Every one of the six coral reefs in those studies had algal-ridge-building CCA with bulk magnesium amounts or XRD profiles that matched our assessment for D^f, five of these with magnesite, (Supplementary Tables S6a–d and Fig. S17) and included multiple species. By combining these published reports with our results we demonstrate that D^f CCA are

present in the tropical Indian, Atlantic, North and South Pacific oceans (Supplementary Map S1). Dolomite was not detected in temperate samples in our study (three locations) or in the reviewed studies, suggesting that its formation may be primarily constrained by temperature. These results are in accord with evidence from the geological record for a correlation with higher temperatures and dolomite formation⁵.

The final question of importance is whether these D^f CCA will continue to survive and produce dolomite under predicted future CO₂ levels. Previous studies have suggested that CCA may be susceptible to ocean acidification^{14,21,22}; however, not all have found negative outcomes²³. Crucially, none of these studies replicated the high-energy environments in which the D^f crusts form. The low dissolution rates for the D^f CCA in our experimental high-CO₂ treatment demonstrate that these CCA skeletons are unlikely to suffer annual net dissolution in this scenario. The reef front does not experience the extreme diel pH fluctuations as used in our experiment; this will probably further reduce dissolution rates and the net impact will be also be governed by biological tissue coverings, reef attachment, growth and bio-erosion¹⁴. The high dissolution rate for the D^p CCA is concerning as this indicates that there may be no contribution to the reef lagoon sediment from their skeletons as p_{CO_2} approaches the experimental levels of ~500–700 ppm.

Although the exact process driving dolomite formation in the CCA has yet to be determined, considering the abundance of

Figure 3 | Overview of D' and D^P coralline algae with evidence of natural dissolution processes at the base exposed to sea water and corresponding XRD patterns. Both samples were living at the time of collection and were kept out of the experimental tanks as dry controls. **a**, D' CCA—dolomite and magnesite fill the conceptacles (thick black arrows). Banding of dolomite cell infill (white arrow) and magnesite infill (thin black arrow) suggests a seasonal influence on mineralization; scale bar, 1 mm (enlargements Supplementary Figs S6 and S7). **b**, D^P CCA—dolomite (dark grey) is detected only in reproductive conceptacle spaces (black arrows), whereby some conceptacles have normal cell regrowth (narrow white arrow). Small patches of aragonite (white) infill (thick white arrows) are common; scale bar, 1 mm. **c**, D' CCA—rims remain dolomite (white arrows) as in layers above; cell infill is now only Mg-calcite with no magnesite remaining; scale bar, 50 μ m. XRD (inset) of this bottom layer (black) shows the Mg-calcite (Mg-C) peak and the separate peak for dolomite (D), and the magnesite peak (M) is absent compared to the total sample (red). **d**, D^P CCA—cell rims are Mg-calcite (light grey). Cells are empty (black) or infilled with Mg-calcite. Fluffy black material over cells is resin; scale bar, 100 μ m. Mg-calcite XRD (inset) peak shows minimal dolomite asymmetry in the base layer (black), which is marginally less than for the total sample (red).

sedimentary dolomite in greenhouse epochs⁵ and the evidence for an organic driver^{4,24,25}, it is reasonable to suggest that dolomite biomineralization is not inhibited by low saturation state. Support for this notion comes from a recent study demonstrating that dolomite can form abiotically in red algae polysaccharide solutions at starting pH of 7.7–7.9 (ref. 24). Interestingly, magnesium uptake was positively correlated with polysaccharide concentration. CCA are rich in polysaccharides²⁶ and light can concentrate polysaccharides at the cell perimeter of red algae²⁷. In addition, dolomite formation seems to occur as a process of cell infilling in cells not in direct contact with external water conditions. Considering these studies together with our observations, it seems probable that dolomite mineralization in the CCA is not driven primarily by seawater saturation state. Rather, mineralization is probably reliant on, first, the provision of sufficiently concentrated nucleating sites (organic templates with the CCA), perhaps driven by light and temperature; the subsequent dolomite mineralization may then depend on a further set of suitable environmental conditions, possibly the key being temperature.

Although our data show D' CCA with cell infill are not impervious to increasing dissolution under both present and higher CO₂, this distinctive dolomite intracellular calcification clearly provides substantial resistance to dissolution in comparison with predominantly Mg-calcite CCA. Laboratory experiments used to determine Mg-calcite dissolution rate data resulted in diagenetic outcomes, that is, the formation of substantial amounts of calcite (for example, ref. 10), that were not observed in our samples (Supplementary Fig. S17). This suggests that the dissolution data derived

from these experiments and subsequent comparisons to aragonite may not be applicable to CCA in their natural environment. We do not ignore that reef stability may be reduced under projected future conditions; however, the stability of dolomite-enriched algal ridge coralline algae offers a positive light in a potentially gloomy future for coral reefs. Until the process and drivers of dolomite formation are understood, the biological response of CCA to higher CO₂ (and probably temperature), and therefore its ultimate contribution to reef stability, will remain uncertain.

Methods

CCA *P. onkodes* were collected for the dissolution experiment from the reef front of Heron Island in 2009 (details in ref. 4). Crusts collected had pink living surfaces and exposed bases and were broken off the reef, not dug out. Four crusts of fresh CCA were cleaned by hand of any epiphytes and loose material using a small wooden pick and brush; no chemical cleaning was applied. These crusts were broken into 25 pieces of approximately 1 cm³. They were sun dried for two days including cleaning time, in the oven at 40 °C for 9 h and confirmed as no longer photosynthetically active, using a pulse-amplitude-modulated fluorometer. All samples were subject to an equal amount of drying time before the experiment. CCA were dry weighed to the nearest milligram, sensitivity ± 0.001 g. The CCA pieces were randomly distributed between the control ($n = 3$) and treatment ($n = 3$) flow-through tanks (tank set-up, flow-through system and CO₂ control are as described in refs 15,28). Dry controls were kept and not used in the experiment to identify any changes in mineralogy due to treatment effect; the XRD results were comparable to samples from both control and treatment tanks (Supplementary Table S3a). After ten days in treatment tanks, samples were sun dried for seven days and re-weighed. All samples were subject to an equal amount of drying time after the experiment. There was no correlation between starting weight and weight lost. Dissolved inorganic carbon and alkalinity in tanks were determined as in ref. 15. A Mettler Toledo

Figure 4 | D' CCA crust on coral branch. Example of the natural break-up of the CCA crust (the surface of this 1-cm-thick crust was living at the time of collection, collected from Heron reef front 0–2 m depth). **a**, SEM of dolomite cells at the base of a D' CCA (H601). The Mg-calcite cell wall is disintegrating, leaving the dolomite casts of the cells (DL) protruding until sufficient framework has been removed so that the cell casts drop out. p, Mg-calcite pit connector; c, cell wall interior; scale bar, 20 µm. **b**, Living coralline (H601) overgrowing coral. There is a visible gap between the CCA and the coral where the base of the CCA was exposed to sea water; wide arrow—location of SEM image in **a**; pink surface is the living coralline layer and dolomite infill starts 100–200 µm down into the crust. It is not known whether the dolomite fills in living or dead cells; scale bar, 1 cm. **c**, Lowest layer subsample (H305) after grinding in a mortar and pestle for XRD, demonstrating that dolomite casts are resistant to grinding whereas the surrounding Mg-calcite has been reduced to a submicron size.

pH meter was used for discrete pH measurements. XRD was undertaken after the completion of the experiment. XRD and SEM with energy-dispersive spectroscopy followed⁴ and the dolomite range was determined as in M.C.N. *et al.* (manuscript in preparation). For classification of D' versus D^p CCA we classify those above 24 asym. mol% as D'; however, we also compare XRD peak asymmetry shape to check that the dolomite asymmetry matches samples with D' mineralogy as confirmed by SEM (as detailed in Fig. 2). Visual inspection of the XRD for the two samples just less than 24 mol% showed that the curve in the dolomite slope was less than that for samples with D' mineralogy (see legend to Supplementary Table S5 for further discussion).

For etching, polished samples in resin were placed in a 200 ml beaker of deionized water with the pH adjusted by the addition of HNO₃ or HCl. In the first etching for 1 h, the pH ranged from 7.98–8.01; in the second etching for 6 h, the pH ranged from 7.7–7.82. The water was stirred continuously and the temperature ranged from 25 to 28 °C. To assess the mineralogy of previous studies, information on XRD and bulk magnesium was compared with that from our studies where mineralogy had also been confirmed by SEM with energy-dispersive spectroscopy.

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Author contributions

M.C.N. and B.N.O. designed initial project; M.C.N., B.D.R. and D.I.K. carried out Heron Island experimental work and water chemistry measurements; U.T. assisted with subsequent analyses and project design. G.D.-P., sample identification and design of experimental tank facilities; A.K. and W.H.A., sample collection and identification. M.C.N., U.T. and W.H.A., SEM. M.C.N. and U.T., XRD analysis. C.B., M.G. and J.P., sample collection, survey, XRD and data analyses. M.C.N. and U.T. wrote and edited the manuscript and all authors contributed.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to M.C.N.

Competing financial interests

The authors declare no competing financial interests.

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Carbonate chemistry data for dissolution experiments

	Control pH			High CO ₂ pH			av. Temp. °C
	Tank 1	Tank 2	Tank 3	Tank 4	Tank 5	Tank 6	
avg	8.17	8.15	8.15	7.88	7.90	7.84	26.90
st. dev	0.17	0.18	0.15	0.17	0.17	0.16	1.77
lowest	7.87	7.85	7.87	7.68	7.69	7.64	25
highest	8.55	8.52	8.43	8.16	8.3	8.14	30.5
range	0.68	0.67	0.56	0.48	0.61	0.5	5.5

Table 1: Summary of measured pH and temperature in tanks.

Figure 1: Comparison of control and treatment measured pH. Treatment pH tracks control by ~ -0.2 pH from midnight to noon, larger offset of ~ -0.3 – 0.4 during later afternoon / early evening.

	averages control					averages high CO ₂				
CO ₂ -sys constants	11/12 5.30am	12/12 12.00	13/12 6pm	14/12 4.30am	15/12 11pm	11/12 5.30am	12/12 12.00	13/12 6pm	14/12 4.30am	15/12 11pm
Salinity	34.70	34.70	34.77	34.80	34.83	34.70	34.70	34.77	34.80	34.70
Temp	25.70	29.97	28.13	25.37	25.97	25.70	29.57	27.57	25.50	26.33
Total carbon	1972.37	1779.24	1742.32	2132.37	1874.75	2034.24	1938.95	2086.47	2170.58	2055.03
Total Alkalinity	2284.07	2258.77	2237.80	2287.83	2221.33	2302.30	2271.97	2222.93	2295.50	2208.83
pH total	8.06	8.25	8.30	7.76	8.12	7.98	8.04	7.69	7.68	7.75
HCO ₃	1740.65	1444.81	1399.64	1984.20	1625.32	1827.21	1693.68	1947.54	2034.08	1910.59
CO ₃	221.06	329.15	337.95	123.83	240.81	193.74	235.24	111.93	106.74	120.95
pCO ₂	382.64	209.83	180.18	866.90	311.98	477.35	395.03	1015.22	1063.63	856.70
Omega-C	5.34	8.02	8.20	2.99	5.81	4.68	5.73	2.71	2.58	2.93
Omega-A	3.53	5.37	5.46	1.97	3.84	3.09	3.83	1.80	1.70	1.94

Table 2: Calculated carbonate parameters using CO₂-sys (following ref. 30), High CO₂ tracks control by ~+200 ppm in the morning and +500-800 ppm in the evening.

Comparison of pH data to lagoon measurements

Figure 2: Comparison of pH data this study to hourly measurements taken from the lagoon for the 5th-12th of December 2009³¹. Santos *et al.*³¹ measured pH in the lagoon adjacent to the intake pipes sourcing seawater for this study. The control pH in our study is comparable to the Santos data excepting the extra high pH recorded on the 8th and 11th of Dec. The CO₂ treatment pH is comparable to the Santos environment for several of the dawn measurements however is well below the environment during the later afternoon.

Table of results for dissolution

Control tanks	Mol% MgCO ₃	Asymm Mol% MgCO ₃	Wt % Arag	weight loss	tank	start weight (gms)	final weight (gms)	Difference (gms)	Sub- sample
Dolomite rich group									
h301	17.96%	27.25%	0.00%	0.11%	1	2.3405	2.3379	0.0026	q
h303	17.96%	27.25%	0.00%	0.01%	2	1.5404	1.5402	0.0002	q
h307	18.00%	27.18%	0.00%	0.29%	1	0.518	0.5165	0.0015	q
h305	*			0.27%	3	1.6032	1.5989	0.0043	q
Control	17.88%	27.40%	0.00%						q
Average weight loss 0.17%, St.dev 0.13 %, n = 4									
Dolomite poor group									
h309	16.51%	17.95%	55.63%	1.65%	1	1.1459	1.127	0.0189	r
h311**	16.65%	18.96%	39.64%	1.65%	2	1.9657	1.9332	0.0325	r
h313	16.99%	18.24%	56.85%	1.68%	3	1.3551	1.3324	0.0227	r
Control	16.41%	17.71%	32.96%						r
h327	17.02%	19.25%	7.62%	1.68%	3	1.4404	1.4162	0.0242	t
h321	17.00%	23.97%	0.00%	1.70%	2	1.4753	1.4502	0.0251	s
h317	16.31%	18.09%	31.93%	1.77%	2	2.361	2.3191	0.0419	s
h315	17.53%	19.53%	0.00%	2.15%	1	1.444	1.413	0.031	s
Control	17.50%	18.87%	0.00%						s
h325	16.95%	19.13%	3.80%	2.24%	2	4.2547	4.1594	0.0953	t
h323	16.99%	19.90%	6.18%	2.26%	1	5.3147	5.1944	0.1203	t
Control	17.08%	18.47%	15.25%						t
Average weight loss 1.89 %, St. dev 0.28 %, n = 9									
High CO₂ tanks									
Dolomite rich group									
h302	17.77%	26.40%	0.00%	0.30%	4	2.0281	2.022	0.0061	q
h304	17.90%	26.28%	0.00%	0.39%	5	1.3195	1.3144	0.0051	q
h308	17.25%	26.74%	0.00%	0.64%	4	1.225	1.2171	0.0079	q
h306	17.67%	28.24%	0.00%	0.69%	6	1.3505	1.3412	0.0093	q
Average weight loss 0.51 %, St. dev 0.19 %, n = 4									
Dolomite poor group									
h324	16.46%	18.20%	8.85%	2.01%	4	2.8279	2.7711	0.0568	t
h314	17.08%	20.17%	5.51%	2.46%	6	1.2627	1.2316	0.0311	r
h318	17.43%	21.09%	0.00%	2.47%	5	2.0603	2.0094	0.0509	s
h310	17.23%	19.91%	4.92%	2.59%	4	1.0945	1.0662	0.0283	r
h316	17.25%	19.24%	4.74%	2.75%	4	1.6714	1.6254	0.046	s
h320***	16.79%	23.22%	0.00%	3.42%	6	1.0202	0.9853	0.0349	s
h312	17.01%	19.02%	53.77%	4.25%	5	1.2554	1.2021	0.0533	r
h326	16.59%	19.12%	13.39%	4.54%	5	1.0304	0.9836	0.0468	t
Average weight loss 3.06 %, St. dev 0.92 %, n = 8									

Table 3a: Dissolution experiment results and mineralogy. Mol% MgCO₃ determined according to ³². Asymm. Mol% MgCO₃ determined according to M.C.N. *et al.* (manuscript in preparation). Aragonite % determined using area under the curve method ³³. Samples with the least weight loss typically had no aragonite, but there is no clear trend with aragonite and weight loss in the remainder of the group. *subsample kept intact for SEM, mineralogy matched other q subsamples. **Assessed as D^p by XRD, confirmed in SEM, magnesite also detected in one cell layer however not detectable in XRD (Fig. 5 SI). *** The XRD line lay between the dolomite rich and dolomite poor lines in the dolomite range however crossed into the magnesite shoulder. SEM showed this sample had bands of dolomite rich and dolomite poor layers and was without substantial cell in-fill (Fig. 10 SI). Sample letter refers to the piece of crust which they were broken from. Control is the dry subsample kept from each crust and did not go into tanks. Quantification of dolomite has not been determined as typical methods using curve fitting programs rely on single peaks and the dolomite in the CCA ranges from 38 - 62 mol% MgCO₃ resulting in a continuum on the XRD trace making quantification by determining the area under the curve problematic.

Table 3b statistics

	Line	R	R ²	P value 2 tailed test	df	error
Control mol%	$y = -1.0483x + 0.1941$	-0.74	0.55	0.01	9	0.00257
Control Asymm. mol%	$y = -0.1871x + 0.0545$	-0.87	0.76	0.01	9	0.00257
High CO ₂ mol%	$y = -2.2382x + 0.4076$	-0.69	0.48	0.02	9	0.004357
High CO ₂ Asymm. mol%	$y = -0.3384x + 0.0971$	-0.77	0.60	0.01	9	0.004357

Statistics summary for Figure 1a and 1c main text. Between control and high CO₂, the gradients for the mol% and Asymm. mol% are significantly different, $p = 0.03$ (mol%) $p = 0.0038$ (Asymm), $df = 21$. The differences in mass loss for the dolomite rich and dolomite poor samples are significant for both control and high CO₂, $p < 0.001$ for both.

Methods for calculating Mol% MgCO_3 for asymmetrical XRD Mg-Calcite peaks

Figure 3: Xray diffraction peak selection for asymmetry mol% MgCO_3 . Red curve CCA H311 (D^p), aqua curve CCA H308 (D^f). Mg-C Mg-calcite peak, D dolomite range (M.C.N. *et al.*, manuscript in preparation), M magnesite. The usual method for selecting the peak position d -value to use in a mol% calibration equation is to select the highest point of the curve and use the d -value at this position. For these two curves the highest points are nearly aligned and the mol% for the d -values are $D^p = 16.65$ and $D^f = 17.25$ mol% MgCO_3 . If this was the only information used to compare samples then the conclusion may be erroneously drawn that the mineralogy is similar, however the asymmetry of the curves is clearly substantially different. The XRD scan processing program we used, EVA Diffrac

Plus, has a function to calculate the centre of gravity of a curve (done by using the area function to take a line across the base of the curve – the arrows in this figure- this returns both the area under the curve and the gravity centre). The gravity centre peak position is calculated by the program using the mean of each measurement interval weighted by the net intensity. The result is a gravity centre peak position skewed by the asymmetry, and simply, the more asymmetry then the further right (higher 2θ , lower d -value) of the highest point the gravity centre is located. Thus in this example the D^f sample, visibly strongly asymmetrical, has a gravity centre peak further right (towards lower d - value which results in a higher calculated mol% $MgCO_3$) than the D_p CCA. The asymmetry mol% (calculated from the d -value at the gravity centre) is 26.74 mol% $MgCO_3$, whereas the asymmetry mol% for the D_p CCA is only 18.96 mol% $MgCO_3$. Note the asymmetry mol% is not an average mol% $MgCO_3$ for the magnesium in all the minerals (when there is dolomite and /or magnesite present). The asymmetry mol% is a quick, reproducible, numerical representation of the curve asymmetry resulting from the presence of higher magnesium carbonates, dolomite and magnesite. The mineralogy of these two samples was confirmed by SEM-EDS.

Gridded point count of base 100 microns in Fig. 3

Type	Dolomite rich (H302)	Dolomite poor (H56)
Dolomite	14.8 %	Not detected
Mg-calcite cell wall	Not detected	31.2 %
Inter-cell Mg-calcite	58.0 %	1.6 %
Intra-cell Mg-calcite	20.6 %	2.6 %
Inter-cell space	3.0 %	9.0 %
Intra-cell space	3.7 %	55.6 %
Aragonite	Not detected	Not detected
Total	100 %	100 %

Table 4: Mapping- H302 4 lines down and 4 across, H56 4 lines down, 3 across, approximately 30 microns apart. Percentage is linear distance for each category above.

Additional SEM images

Figure 4: Magnesite (M) in cell spaces of D^p CCA H311. **a** Back-scatter electron image, **b** secondary electron image. This magnesite was not detected in the XRD analysis and only one patch was found in the sample. There are no dolomite rims, however the perimeter where the dolomite rims are usually found is void (black in BSE). This suggests that the mineralization processes forming dolomite and magnesite are independent. Mg-calcite (Mg-C).

Figure 5: Differing conceptacle mineral in-fill in D^p H56. **a** cell re-growth in conceptacle, partially dolomite (D), cell spaces filled by aragonite (A), scale 50 μ m. **b** Conceptacle 1 (Ct-1) near surface with partial cell re-growth, Mg-calcite, Conceptacle 2 (Ct-2) has dolomite pillar in the conceptacle centre and Mg-calcite (C) cells, scale 200 μ m. **c** conceptacle rimmed by dolomite and dolomite in the centre, scale 50 μ m. **d** partial Mg-calcite cell re-growth visible in centre, dolomite appears to have nucleated on organic fabric, scale 100 μ m.

Figure 6: conceptacle mineral in-fill in D^r. **a** CCA H302 Conceptacle 1 (Ct-1) in-filled by magnesite, Conceptacle 2 partial cell re-growth, conceptacle 3 dolomite in-fill (after 2nd etching). **b** Cell re-growth in conceptacle 1 and 2 (before etching). Cells are dolomite (grey), scale 200 μ m. **c** CCA H47 Magnesite and aragonite in-filling conceptacle, scale 100 μ m. **d** secondary electron image of **c**, aragonite is a smooth cement whereas magnesite is coarse. White is charging indicating empty space. scale 100 μ m.

Figure 7: Transition from main crust to exposed base layers in dolomite rich coralline (H302). The main crust (c) has magnesite, dolomite and Mg-calcite, the base layers (b) have only dolomite rims and Mg-calcite. There are also small patches of aragonite (A – white). The base ~400-600 microns in both types of coralline algae show alteration indicating that this is the typical penetration of seawater into the lower crust. The transition in this sample takes place over ~50-60 microns (t) suggesting the process is relatively rapid.

Figure 8: Aragonite cell in-fill and crust replacement in base layers of dolomite rich coralline (Sample *P. onkodes* H47). Cell in-fill by aragonite (arrows), fabric destructive replacement by aragonite (A). Dolomite rims remain in the lower layers as does Mg-calcite cell wall however there is no magnesite. Typically in the dolomite rich samples aragonite was detected in the base layers and proximal to holes in the main crust, presenting as both discrete cell replacement, usually with the dolomite rims preserved and fabric destructive patches. This suggests a diagenetic process that transforms unstable mineralogy, i.e. Mg-calcite, and magnesite to aragonite or in-fills non-mineralised spaces.

Figure 9: Bands of dolomite rich and dolomite poor layers in H320. The XRD scan line lay between that for D^p and D^r in the dolomite range however formed a low shoulder towards magnesite. **a**

conceptacles filled with magnesite and rimmed by Mg-calcite. Banding of dolomite rims suggests a seasonal influence on formation, scale 500 μm . **b** enlargement showing D^p with thicker inter-filament areas and thin or no dolomite rims and D^f less inter-filament Mg-calcite and thicker dolomite rims, scale 100 μm .

Figure 10: Dissolution of dolomite in conceptacles after etching. **a** after 1 hour etching, sub-micron grains of dolomite (composition confirmed by SEM-EDS) on organic framework in conceptacle. **b** after 6 hours etching dolomite grains removed (arrows) and conceptacle interior framework is more translucent. Contrast settings are not the same for both pictures as contrast is adjusted throughout the SEM session depending on distance and focus settings.

Figure 11: Progressive etching experiment of dolomite rich coralline algae (H302). **a** and **d**, Back scattered electron image of polished D^fCCA section prior to etching, light grey to white – Mg-calcite, grey - dolomite, dark grey to black – void. **b** is **a** etched 1 hr, pH 8. Mg-calcite removed to expose dolomite cell fusion between 2-3 and 2-4. **c** Secondary electron image of **b**, cell wall Mg-calcite is prominent around the edges of dolomite rims and inter-filament Mg-calcite is depleted. Crack in dolomite at 2 caused by multiple EDS measurements. **e** Is **d** etched 6 hrs, pH 7.7-7.8. Mg-calcite has been preferentially removed, leaving dolomite cell shapes in relief. **f** Secondary electron image enlargement of **e**, showing that inter-filament Mg-calcite (Mg-C_{IF}) was removed. Cell wall Mg-calcite (Mg-C_{CW}) crystals appear to be attached perpendicular to the dolomite lining underneath. Dolomite crystals on the exterior of the cell lining are nano-scale. scale bars 10 μm.

Summary table of mineralogy (present study)

Location	Location	Environment	Species	D ⁺ , Mag	D ⁺ , Mag?	D ⁺	<D ^p <D ⁺	D ^p	<Mg-C<D ^p	Mg-Calcite
Caribbean (collected 1972)	St. Croix	Algal Ridge, intertidal	<i>Porolithon</i> <i>Pachydermum</i>					X		
	Virgin Gorda	Reef flat, 1m	<i>P.</i> <i>Pachydermum</i>							X
	St. Croix	Acropora reef, 3-10m	<i>P.</i> <i>Pachydermum</i>	X						
	St. Thomas	Rocky ground, CCA covered, 0-3m	<i>P.</i> <i>Pachydermum</i>		X *					
Papua New Guinea	Ily Ily	~0-5m,	<i>P. onkodes</i>			X *		X		
Japan, Ryukyu Islands	Okinawaji ma Island	<5m	<i>P. onkodes</i>	X	X			X		X
	Ishigaki Island	<5m	<i>Pneophyllum</i> <i>conicum</i>					X		
	Ishigaki Island	<5m	<i>Mesophyllum</i> <i>erubescens</i>					X		
	Okinoerabu Island	<5m	<i>P. onkodes</i>			X		X		
	Okinawaji ma Island	<5m	<i>Neogoniolithon</i> <i>megalocystum</i>				X			
	Okinawaji ma Island	<5m	<i>Lithophyllum</i> <i>kotschyanum</i>			X * *	X			
	Okinoerabu Island	<5m	<i>L. insipidum</i>				X			
	Okinawaji ma Island	<5m	<i>P. conicum</i>			?	X	?		
	Okinawaji ma Island	micro-atoll at moat	<i>Hydrolithon</i> <i>reinboldii</i>							X
	Okinoerabu Island	<5m	<i>N. brassica-</i> <i>florida</i>							X
	Okinawaji ma Island	<5m	<i>Mastophora</i> <i>rosea</i>							X
	Okinoerabu Island	<5m	<i>P. conicum</i>						X	
Great Barrier Reef	Lizard Island		<i>P. onkodes</i>			X *				
	Heron Island	<5m to reef crest	<i>P. onkodes</i>	X *	X	X	X **	X *		X
	Heron Island	Reef crest	<i>L. mustard</i>					X *		
	Heron Island Core	Windward reef front core – 20cm, 5.6m down core	~1cm thick crust (not dated)					X		

Rodrigues, Indian Ocean	Rodrigues Core	Windward algal ridge core -35cm, 3.2m down core	~1cm thick crust (290, 2666 yrs)			X				
	Rodrigues core	Windward algal ridge core – 50cm, 80cm, down core	~1cm thick crust (~417, 667yrs)				?	X		
Bermuda		cup reefs	<i>Neogoniolithon</i> sp.							X
New South Wales	Merimbula	tidal pool	?articulated							X
South Australia	Adelaide, Encounter Bay	0.5 m	?							X
Victoria	Point Westall	2-3m, on rocks, rhodoliths	<i>Neogoniolithon</i> <i>brassica -</i> <i>florida.</i>							X
	“	“	<i>Lithothamnion</i>							X
	“	“	?							X

Table 5: Summary of mineralogy for samples analysed by XRD. This table is a summary of 147 samples analysed by us (includes samples referred to in refs. 30, 34). Classification was made by comparing the XRD scan to a scan of a CCA with mineralogy confirmed by SEM for each of the; Dolomite rims plus magnesite (D^f , Mag), Dolomite rims (D^f), Mg-calcite and dolomite conceptacles (D^p), Mg-calcite only (Mg-C). Where identification was between D^f and D^p but closest to D^p it was classified as D^p . $<D^f < D^p$ is for scans that were between D^p and D^f but closest to D^f , likewise for $<Mg-C < D^p$. Samples of *P.onkodes* that were visibly porous and bio-eroded tended toward D^p and Mg-calcite and could be broken by hand, whereas the D^f and magnesite crusts were dense and mostly clean of bio-erosion and required a hammer or considerable force to break. * mineralogy confirmed by SEM, **confirmed by SEM, however not all layers had dolomite rims.

A note on classifying dolomite rich versus dolomite poor. For the experimental data set we identify the asymmetry mol% of 24 as the figure for delineating between dolomite rich and dolomite poor, however this should not be used as an absolute figure for future studies without first confirming by SEM how the dolomite is present. CCA without magnesite can have dolomite cell lining, dolomite cell in-fill and an XRD curve shape in the dolomite range that matches or is greater than the dolomite rich (asymm. >27 mol%) samples, yet have an asymmetry mol% that is only 23-24 mol% because of the absence of magnesite (for example, this was the case for *P. onkodes* from Lizard Is. and PNG). The two samples (H320 and H321) with asymm. mol% of ~23 mol% (Fig. 1 in the main text) had by XRD a dolomite curve shape that was less than that for the dolomite rich samples with asymm ~27 mol%, however the lower part of the curve extended toward the magnesite position thus giving the reasonably high numerical value. SEM of H320 showed that the dolomite lining though present, was not consistently throughout the sample (Fig. 10 SI) which may explain both the higher asymmetry measurement and the higher amount of dissolution compared to the dolomite rich samples with consistent dolomite cell lining. The asymmetry mol% method is a tool that allows rapid classification of the mineralogy types present so that those most representative of the groupings can be selected for SEM, this is useful when hundreds of samples are being analysed by XRD.

Core samples. Rodrigues: The base of this 3.7 m long core was dated as 3052 yrs old, $\pm$ 258 yrs with an average accretion rate (AAR) of 1.2 m/ky³⁵. The ages provided in this table are estimates using the published AAR. Heron: this core has not been dated, core drilled 1998 using core equipment in Rees *et al.*³⁵ The mol% MgCO₃ for the Mg-calcite was 15-16 mol% MgCO₃ ~1-2 mol% lower than the fresh samples and this resulted in the asymmetry mol % for the dolomite rich samples being lower (21-22 mol% MgCO₃) than for the fresh samples, however the scan shape in the dolomite range clearly matches fresh samples with confirmed dolomite cell lining.

Spatial variability of mineralogy. Our reef survey included CCA growing on top of dead coral branches and underneath, a maximum distance apart of 2cm. The CCA on top had dolomite and magnesite, the CCA underneath had a symmetrical XRD scan indicating no dolomite. It seems that mineral variability occurs on a centimetre scale and considering these CCA were both exposed to the same water temperature, chemistry and probably comparable water energy, this suggests that light is the final control on dolomite formation. Mineral variability on a reef scale has not been comprehensively determined however the dolomite rich samples found to date have been from high energy and shallow (less than 5m) environments.

Figure 12: XRD scans from lowest layers of CCA crust for dolomite rich CCA. *P. onkodes* H305 Heron Island, (Black line), *P. onkodes*, 07-844, Bise, Okinawajima Island (green). *P. pachydermum* St. Croix, Caribbean (Pink), *P. onkodes*, reef front, Heron Is. GBR (Blue). A separate dolomite peak is visible in all but the reef front (blue) sample. Subsamples were taken by very gently scraping the underneath of the CCA crust as this often, but not always, displays a separated peak or increased dolomite asymmetry and thus is easier to confirm the presence of dolomite than using only the bulk sample scan, (following methods in M.C.N. *et al.*, manuscript in preparation) D- dolomite range, Mg-C- Mg-calcite, F- Fluorite, A- aragonite.

Figure 13: full XRD scan for Caribbean *P. pachydermum* base subsample. No indication of ordering at ordering reflections (101) or (015). Mg-Calcite peak overlies ordering reflection (021).

Figure 14: XRD scans for core CCA. **a** Heron core, red 20cm, black and blue 5.6 metres, aqua line-disordered dolomite ~50 mol% MgCO_3 . D- dolomite range, Mg-C- Mg-calcite, F- Fluorite, A- aragonite, H- halite. **b** Rodrigues core, red 320cm, orange 35cm, pink 50cm, green 80cm. There is no trend with depth down core and dolomite asymmetry. The dolomite peaks of 320 cm and 35 cm are comparable to those from the lowest layer of fresh CCA that had a separate dolomite peak in SI figures 12 and 13.

Figure 15: full XRD scan for Rodrigues core CCA at 35cm. No indication of ordering at ordering reflections (101) or (015). Mg-Calcite peak overlies ordering reflection (021) .

Figure 16: full XRD scan for Rodrigues core CCA at 3.2m. No indication of ordering at ordering reflections (101) or (015). Mg-Calcite peak overlies ordering reflection (021) .

Re-assessment of mineralogy in published studies for temperate and tropical coralline algae

Milliman *et al.* 1971³⁶

Specimen	Mol% MgCO ₃ (XRD) *	Total Mg by wet chemistry **	Curve assessment by Milliman ***	Our assessment			
				Dr, Mag	Dr	Dp	Mg-C
Milliman table 1, re-assessment							
<i>Jania</i> sp	14.3	18.6	Symmetrical				X
<i>Jania</i> sp	10.9	14.4	“				X
<i>Lithothamnium</i> sp	6.2 ¹	11	Asymmetrical				X
<i>L. australe</i>	11.8	18 ²	“			X	?
<i>L. indicum</i>	10.8	16.5	“				X
<i>L. glaciale</i> ³	9.6	13	“				X
“	8.8	18.1	“		X	? ⁴	
<i>Lithophyllum incrustans</i>	11.3	15.1	Symmetrical				X
<i>L. solutum</i>	10.6	17.7	“				X
<i>Porolithon</i> sp.	16.1	28.8	Strongly asymm.	X			
“	14.4	24.2	“	? ⁵	X		
<i>Goniolithon frutescens</i>	13.6	19.2	Asymmetrical			X	
“	16	20.65	“		?	X	
“	15.1	20.7	“		?	X	
“	12.8	20.6	“		?	X	
<i>G. pallescens</i>	13.4	22.64	“		X		
<i>G.fosliei</i>	14.6	18.7	“			?	X
<i>G. strictum</i>	15.5	18.8	“			?	X
Milliman table 2, summary of results, average by genera							
<i>Jania</i> (n= 10)			symmetrical				X
<i>Corallina</i> (n=6)			Asymmetrical			X	
<i>Amphiroa</i> (n=3)			Strongly asymmetrical	?	X		
<i>Lithothamnium</i> (n=12)			Asymmetrical			X	
<i>Lithophyllum</i> (n=14)			Symmetrical				X
<i>Goniolithon</i> (n=7)			Asymmetrical			X	
<i>Porolithon</i> (n=3)			Strongly asymmetrical	X	X		

Table 6a

* The XRD correlation curve used by Milliman returns approximately 2 mol% MgCO₃ less than using the Goldsmith³² curve that we use. Further, the published fluorite peak position used as the standard to align the XRD curves has been refined since the 1970's from 3.15 to 3.15564 and this results in a difference of ~1.5 mol% in the determination, these two factors together would result in the mol% MgCO₃ being ~ 3-3.5 mol% higher if the scans were reprocessed using the modern fluorite position and the Goldsmith curve that we used for our analyses. Therefore when considering the difference

between the XRD mol% and the bulk (wet chem.) mol%, a difference of less than 3.5 mol% could be within measurement error.

** Milliman published this as a total weight %, here it is converted to estimated mol%.

*** See M.C.N. *et al.*, (manuscript in preparation) for comparison of these categories to known dolomite CCA XRD results.

¹ Although this has an asymmetrical curve and excess magnesium, the low XRD mol% indicates that the XRD curve would not have passed over the dolomite range and therefore the excess magnesium was likely present as higher phases of Mg- Calcite up to 25 mol% MgCO₃.

² To compare the total Mg to Mol% MgCO₃ by XRD we use an estimate of what the excess magnesium will be. D^p - presuming a maximum of 5% of the sample is dolomite (i.e. conceptacle spaces) and Mg-calcite Mol% MgCO₃ is 16.5 mol%, then bulk will be 17.9 %, an excess of 1.4 mol% MgCO₃. D^r -, estimating dolomite content to range from 18-25 % of the total, then bulk Mg = ~21.6 – 23.6 mol% MgCO₃, for bulk measurements significantly higher than these it is considered likely that magnesite is present. Note that aragonite is present in many CCA samples thus diluting the bulk Mg measurements and it is possible that samples classified as Mg-C based on this comparison may be D^p or D^r.

³ Milliman noted that the Mg-calcite peaks for the tropical *L. glaciale* were more asymmetrical than the temperate. The collection locations are not recorded in Milliman's table.

⁴ Where the assessment is uncertain, X marks the most likely and ? the other possible assessment.

⁵ This lower bulk Mg may be a result of aragonite in the skeleton diluting the final mol% MgCO₃ or it is possible that most cell in-fill is by dolomite rather than magnesite as seen in discrete bands in Fig. 3.

Chave 1954³⁷

Location	Temp.	Specimen	Mol% MgCO ₃ (XRD)	Total Mg by wet chemistry	Our assessment			
					Dr, Mag	Dr	Dp	Mg-C
Adak Is. Alaska	5.2	<i>Lithothamnion</i> sp.	9					X
“	“	“	7.7					X
Mount Desert, Maine	6	“	12					X
“	“	“	12					X
Honshu, Japan	15.5	“	15.2					X
La Jolla, Calif.	17	<i>Bossea</i> sp.	11.9					X
“	“	<i>Lithothamnium</i> sp.	14.1					X
Okinoshima, Japan	18	“	15.5					X
Bermuda	23	<i>Amphiroa</i> sp.		22.36		X		
“	“	<i>Lithothamnium</i> sp.	16.4					X
“	“	“		14.85				X
Florida keys	26	<i>Goniolithon</i> sp.		25.95	X			
“	“	“		28.75	X			
Palau	28	<i>Lithophyllum</i> sp.		20.93		X	?	
Guam	“	“		21.07		X	?	

Table 6b

Other studies

Location	Temp.	Specimen	Mol%	Total Mg by	Our assessment
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			MgCO ₃ (XRD)	wet chemistry				
					Dr,Mag	Dr	Dp	Mg-C
		<i>Goniolithon</i> ³⁸	18.1	22.3		X		
		<i>Neogoniolithon</i> ³⁸	18	23		X		
		<i>Amphiroa rigida</i> ³⁹		See Fig. 12 SI		X	?	
Corsica		<i>Lithothamnium</i> sp ⁴⁰		15.5 ⁴			X	?
Bermuda		<i>Amphiroa</i> ⁴¹		19.5 ⁴		X		
Bermuda		<i>Amphiroa fragilissima</i> ⁴²	17.5					X
Rodriguez		<i>Goniolithon</i> ⁴³	21	24-29 ⁵	X	X		
Marshall Is, Likiep atoll	27.4 – 29.3	<i>Goniolithon</i> ^{44, 45}		Author description ⁶		X		
“	“	<i>P. gardineri</i> “		Noted Mg- rich rims dolomite composition	X			
Tuamotu Is, Raroia atoll	26.1- 27.5	<i>P. aequinoctiale</i> FOSLIE “		(48-49) microprobe		X	?	
Marshall Is, Ujae Atoll	27.5 – 29.9	<i>P. onkodes</i> “		53 Microprobe		X	?	

Table 6c

⁴ Bischoff noted that both samples had broadened XRD curves however the Lithothamnium was strongly asymmetric and electron microprobe of both samples detected domains with up to 10 mol% MgCO₃ higher than the average.

⁵ Schmalz detected brucite in one and only one sample of many analysed that had 24-29 mol% MgCO₃. The published XRD pattern shows asymmetry with a visible hump on the dolomite side of the Mg-calcite peak and possible magnesite shoulder.

⁶ Spot measurements by electron microprobe. Results of Moberly⁴⁴ discussed in Nash *et al.*³⁴. Moberly discussed at length the presence of magnesium rich conceptacles, magnesium enriched linings in cells (approaching dolomite) in *Goniolithon* and *Porolithon* from the tropical pacific and measured magnesite in a conceptacle of *P. Gardineri*

Clarke and Wheeler 1922⁴⁶

Location	Temp	Specimen **all collected from reefs, rocks or near low tide level**	No XRD	Total Mg by wet chemistry	Our assessment			
					Dr, Mag	Dr	Dp	Mg- C
Newfoundland, Conception bay		<i>Lithothamnium glacial</i>		10.93				X
Timor, Haingsisi		<i>L. erubescens</i>		16.96				X
Panama, Point		<i>Archaeolithotham</i>		13.09				X

Toro		<i>nium episporum</i>						
Nr Hawaii, Palmyra Is.		<i>Lithophyllum craespedium</i>		19.6		?	X	
Gulf of Calif. Bay of La Paz		<i>Lithophyllum pallens</i>		15.46				X
Porto Rico, Salinas Bay		<i>Lithophyllum daedaleum</i>		19.03			X	
Porto Rico, Culebra Is.		<i>Lithophyllum antillarum</i>		16.35				X
Madagascar N, Coetivy Is.		<i>Lithophyllum oncodes</i>		18.17			?	x
Jamaica, Fort Clarence		<i>Lithophyllum intermedium</i>		16.59				X
Bahamas, dollar harbor		<i>Lithophyllum pachydermum</i>		15.08				X
New Guinea		<i>Lithophyllum tamiense</i>		20.02		?	X	
Porto Rico, Lemon Bay		<i>Amphiroa fragilissima</i>		18.41			X	?
Newfoundland, Torbay		<i>Phymatolithon compactum</i>		10.93				X
Porto Rico, Culebra Island		<i>Goniolithon acropetum</i>		19.24		?	X	
Bahamas, Bemini Harbor		<i>Goniolithon strictum</i>		24	X			
Florida, Soldiers Key		“		25.17	X			
Samples collected by Dr Howe								
Cocos-Keeling Is		<i>Goniolithon frutescens</i>		13.8			?	
Torres St, Murray Is		<i>Goniolithon orthoblastum</i>		13.66			?	
Cocos-Keeling Is		<i>Lithophyllum kaiseri</i>		15.33			?	
Clarke and Wheeler considered the samples collected by Dr Howe suspiciously low results for tropical species and had further samples collected that were possibly younger. Based on our work it is probable that these samples had amounts of aragonite which diluted the magnesium %, ICP-AES of our samples with dolomite asymmetry reached as low as 13.54% (reported in ref. 34), aragonite ranged from zero to 55 % of the samples we analysed (table 1 this document).								
Bahamas, Dollar Harbor		<i>Lithophyllum pachydermum</i> – upper layer, solid		24.95	X			
		“ lower layer, porous, discoloured		15.43				X Arag?
Bahamas, Bemini Harbor		<i>Goniolithon strictum</i> – upper branches		22.98		X		
		“ lower branches		23.74		X		
For comparison to <i>L. pachydermum</i> we include results of ICP-AES mol% MgCO ₃ for layers of <i>P. oncodes</i> (H47 total 32.08 mol% MgCO ₃ reported in ref. 34):								
Top 1mm		31.58						
2 nd layer		35.58						
3 rd layer with		17.72						

arag.								
Base 2mm		46.5						
Average		32.845						
Results from Prof. Cary								
Samoa		Calcareous algae		36.36	X			
Sth Florida, Tortugas		“		25.32	X			
Results from A. Damour								
Mediterranean Sea		<i>Lithophyllum</i>		12.76				X? arag
Coast of Algeria		<i>Melobesia</i> sp		14.44				X? arag
Antilles		<i>Amphiroa tribulus</i>		19.29		?	X	
Other tables included in Clarke and Wheeler are excluded as Mg contents recognized by authors as being significantly lower than theirs and perhaps not reliable or representative.								

Table 6d

Mineralogy summary for main algal ridge coralline algae

Location	CCA	D ^R , Mag	D ^r
Florida keys ^a	<i>Goniolithon</i> sp.	X	
“	<i>G. strictum</i>	X	
Rodriguez ^{a,b}	<i>Goniolithon</i> sp.	X	
Marshall Is. ^a	“		X
“	<i>Porolithon gardineri</i>	X	
“	<i>P.onkodes</i>		X
Tuamatu ^a	<i>P. aequinoctiale</i>		X
Bahamas ^a	<i>G. strictum</i>	X	
Samoa ^a	Unidentified CCA	X	
GBR- Heron Is. ^b	<i>P.onkodes</i>	X	
GBR-Lizard Is. ^b	<i>P.onkodes</i>		X
Ryukyu islands ^b	<i>P.onkodes</i>	X	
Caribbean ^b	<i>P.pachydermum</i>	X	
PNG ^b	<i>P.onkodes</i>		X

Table 6e: Highest magnesium mineral composition assessed / measured for algal ridge coralline algae.

^a summary of previous studies tables 6a-d.

^b this study

Figure 17: Comparison of XRD analysis for samples with mineralogy confirmed by SEM to XRD results for coralline alga *Amphiroa rigida* used in Plummer *et al.*⁴⁰. The top panel is XRD before the Plummer dissolution experiment and the bottom XRD is their sample after their 70 day experiment. In the top figure our D^p (red) sample demonstrates less asymmetry than the *A. rigida* indicating the *A. rigida* must have had at least conceptacle dolomite. Our D^f with magnesite (blue) line traces the *A. rigida* line down to half way through the dolomite range and then levels out to extend to the magnesite position (M), this suggests that the *A. rigida* may have also had dolomite rims but not magnesite. The green line is an XRD for another *P. onkodes* (not in this study) examined in our lab that had dolomite rims and conceptacles and no magnesite (all confirmed by SEM-EDS). The close fit of this line to the *A. rigida* strongly suggests that *A. rigida* may have had dolomite rims and conceptacle dolomite. After dissolution the *A. rigida* now demonstrates slightly less asymmetry than our D^p sample suggesting that most the dolomite has been dissolved. This is in contrast to the lower layers of our samples exposed to seawater and undergoing natural dissolution processes where in-situ dolomite remains and there is often aragonite but no measurable calcite indicating that diagenetic alteration progresses differently in laboratory conditions.

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