

Decreased abundance of crustose coralline algae due to ocean acidification

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Owing to anthropogenic emissions, atmospheric concentrations of carbon dioxide could almost double between 2006 and 2100 according to business-as-usual carbon dioxide emission scenarios¹. Because the ocean absorbs carbon dioxide from the atmosphere^{2–4}, increasing atmospheric carbon dioxide concentrations will lead to increasing dissolved inorganic carbon and carbon dioxide in surface ocean waters, and hence acidification and lower carbonate saturation states^{2,5}. As a consequence, it has been suggested that marine calcifying organisms, for example corals, coralline algae, molluscs and foraminifera, will have difficulties producing their skeletons and shells at current rates^{6,7}, with potentially severe implications for marine ecosystems, including coral reefs^{6,8–11}. Here we report a seven-week experiment exploring the effects of ocean acidification on crustose coralline algae, a cosmopolitan group of calcifying algae that is ecologically important in most shallow-water habitats^{12–14}. Six outdoor mesocosms were continuously supplied with seawater from the adjacent reef and manipulated to simulate conditions of either ambient or elevated atmospheric carbon dioxide concentrations. The recruitment rate and growth of crustose coralline algae were severely inhibited in the elevated carbon dioxide mesocosms. Our findings suggest that ocean acidification due to human activities could cause significant change to benthic community structure in shallow-warm-water carbonate ecosystems.

Crustose coralline algae (CCAs) are a major calcifying component of the marine benthos from tropical to polar oceans at all depths within the photic zone in almost every habitat type^{13–15}. CCAs carry out key ecological roles on coral reefs, such as acting as framework organisms by cementing carbonate fragments into massive reef structures¹⁶, providing chemical settlement cues for reef-building coral larvae^{17,18} and as major producers of carbonate sediments¹². So far, the main focus of global climate change research on coral reefs has been the impact of rising temperatures on coral 'bleaching' and mortality, but lately the effects of ocean acidification have received increased attention^{7,8}. Experimental work has demonstrated that corals calcify more slowly under conditions of elevated pCO₂ and lower calcium carbonate saturation state^{6,19}, and studies have shown similar results for select species of calcifying macroalgae cultured in small incubation vessels^{20,21}. The purpose of our flow-through outdoor

mesocosm experiment was to provide empirical quantification of changes to benthic communities that may result from the decrease in calcium carbonate saturation state predicted for tropical and subtropical oceans over the next centuries. Our approach was novel in that the experiment was conducted in an outdoor flow-through system, enabling organisms with pelagic larvae to settle in the mesocosms and develop communities as natural recruitment occurred over several months. The mesocosms were designed to experience natural diurnal cycles in solar radiation, temperature and seawater chemistry typically occurring on tropical reef flats. Although previous work examined the effects of calcium carbonate saturation state on calcification rates of corals and coral communities in realistic mesocosm studies^{9,10,19,22}, none has examined how community structure may change under increasing degree of ocean acidification.

Our mesocosms showed marked diurnal cycles in seawater chemistry (Fig. 1) similar to those observed on other tropical reef flats (for example Δ 0.6 pH units²³). The encrusting algal community that recruited to acrylic cylinders placed in the treatment mesocosms was quite different from that found on cylinders from control mesocosms (Fig. 2). The recruitment rate and the percentage cover of CCAs on cylinders in treatment mesocosms at the end of the 51 d period were significantly lower than those in controls (Fig. 2a–c, Table 1). Mean percentage cover by non-calcifying algae (a mixed assemblage of macroalgal germlings, diatoms and small filamentous algae) was statistically higher on cylinders from treatment compared with control mesocosms (Fig. 2d, Table 1). Under high pCO₂ conditions, CCA recruitment rate and percentage cover decreased by 78 and 92%, respectively, whereas non-calcifying algae increased by 52% (Fig. 2) relative to controls. Decreased rates of space occupation by CCAs imply inhibition of growth and/or calcification, indicating that at least one step in the calcification process is being directly affected; however, the cellular and molecular mechanisms of calcification in these organisms remain elusive^{6,24}.

At tropical and subtropical seawater conditions, CCAs and many important reef calcifiers such as echinoderms, other calcifying algae and benthic foraminifera deposit Mg calcite minerals that contain significant mol% MgCO₃. CCAs in the present study contained 13.6 ± 0.4 mol% as determined from X-ray diffraction (XRD) analysis (see the Supplementary Information),

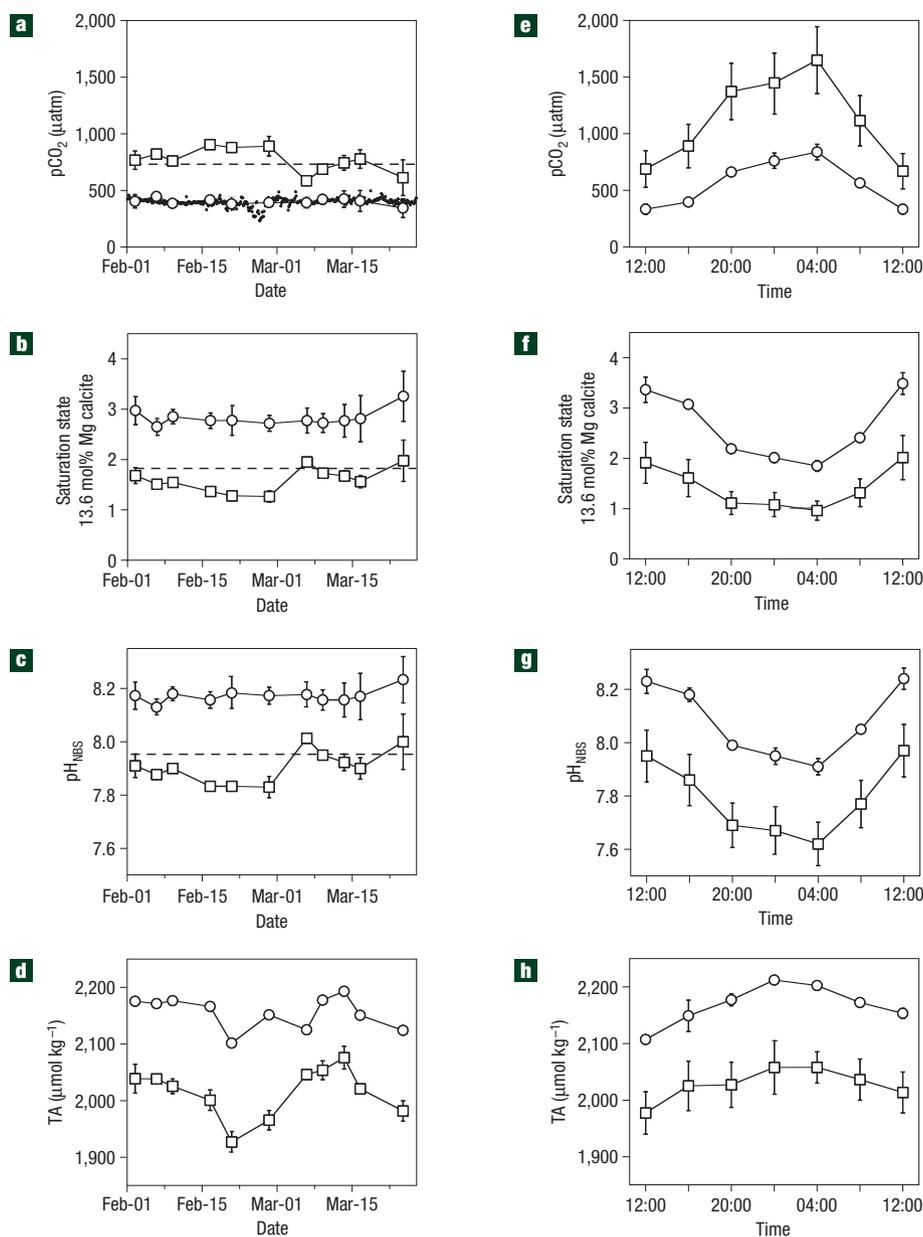


Figure 1 Seawater carbonate chemistry. **a–h**, Data observed at midday (**a–d**) and during a diurnal cycle (**e–h**) in control (circles) and treatment (squares) mesocosms. **a,e**, Partial pressure of CO₂ (pCO₂); black dots are surface seawater values reported by the CRIMP/CO₂ - NOAA PMEL buoy. **b,f**, Saturation state (Ω) with respect to 13.6 mol% Mg calcite. **c,g**, pH_{NBS}. **d,h**, Total alkalinity (TA). Data are means \pm 1 s.d. ($n = 3$ mesocosms). Dashed lines are values projected for the year 2100 (IPCC, IS92a). See Supplementary Information for tabulated data.

1 and there was no significant difference between treatment and
 2 control samples. Our results contrast with those of refs 20
 3 and 25, which reported that the Mg content of the calcifying
 4 alga *Porolithon gardineri* varied positively with seawater calcite
 5 saturation state, temperature and growth rate. The mechanisms
 6 controlling the concentration of Mg ions in the mineral structure
 7 of biogenic calcites are not well understood and probably exert
 8 different influences on different organisms²⁶. Large variability
 9 in the magnesium content among different taxa living in the
 10 same environment suggests that there is strong taxonomic
 11 control¹². Geographically, there is a convincing correlation between
 12 magnesium content within taxonomic groups and environmental
 13 parameters such as temperature and seawater carbonate saturation

state. This correlation has been attributed to growth rate, which is
 14 a function of temperature and carbonate saturation state²⁶. Control
 15 of Mg content in marine calcifiers warrants further investigation,
 16 as the amount of Mg incorporated in the mineral matrix directly
 17 affects its solubility. Biogenic Mg calcite phases containing a
 18 significant mol% MgCO₃ (>8–12 mol%) are more soluble than
 19 aragonite, the carbonate phase deposited by corals, and could
 20 initially be more susceptible to rising pCO₂ and decreasing seawater
 21 calcium carbonate saturation state^{27,28}. Nevertheless, the changes in
 22 seawater chemistry anticipated during the 21st century under the
 23 business-as-usual CO₂ emission scenario are sufficiently large to
 24 affect significantly both aragonite and Mg calcite precipitation rates
 25 and the organisms depositing these minerals.
 26

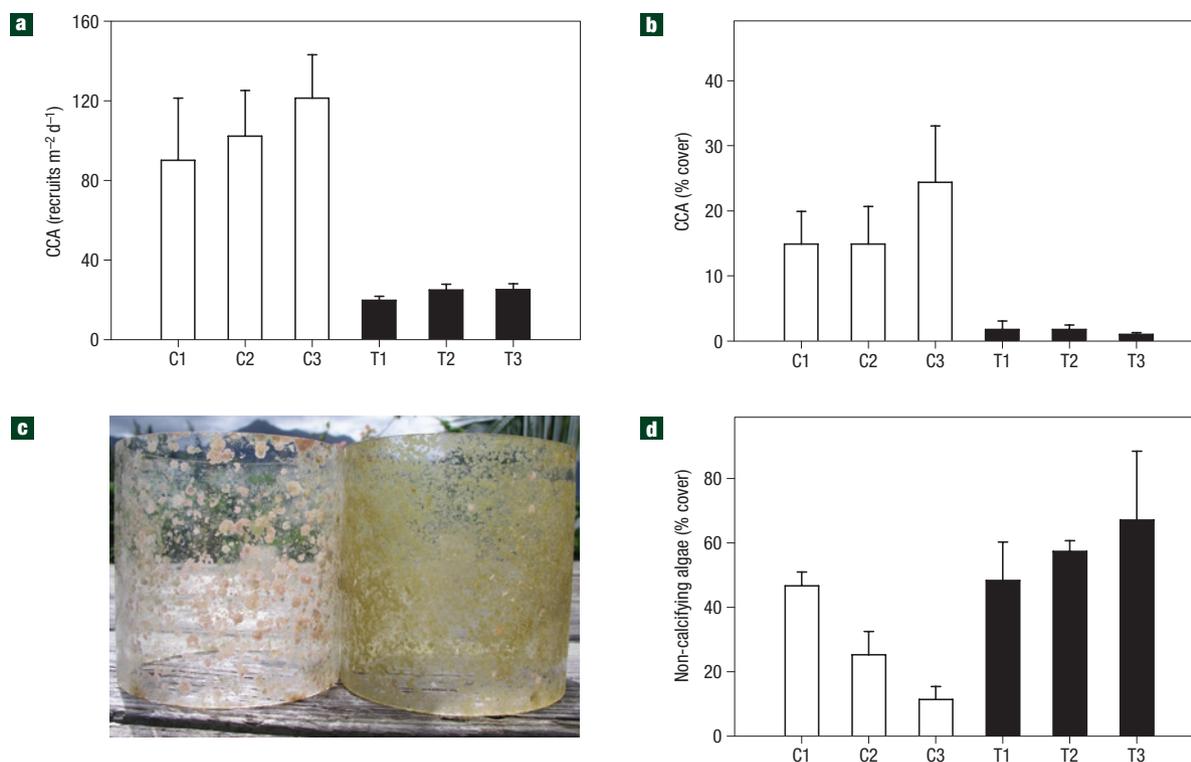


Figure 2 Encrusting algal communities on experimental cylinders. **a,b**, Recruitment rate (**a**) and percentage cover (**b**) of CCAs on cylinder surfaces from control (white bars) and treatment (black bars) mesocosms. **c**, Photograph of example cylinders from a control (left) and a treatment (right) mesocosm. **d**, Percentage cover of non-calcifying algae on cylinder surfaces from control (white bars) and treatment (black bars) mesocosms. Data are means \pm 1 s.d. ($n = 3$ cylinders). C = control and T = treatment, and the number refers to the replicate mesocosm. See Supplementary Information for tabulated data.

Table 1 Mean seawater carbonate chemistry near midday ($n = 11$ sample days), rate of CCA recruitment and percentage cover by CCAs and non-calcifying algae found on experimental cylinders in control and treatment mesocosms.

	Control $n = 3$	Treatment $n = 3$	One-way ANOVA by mesocosm		<i>A priori</i> contrast between treatment and control mesocosms	
	Mean (\pm 1 s.d.)		F	p	T	p
pCO ₂ (μ atm)*	400 (47)	765 (39)	49.2	<0.0001	8.35	<0.0001
Saturation state	2.74 (0.21)	1.55 (0.06)	53.8	<0.0001	8.10	<0.0001
13.6 mol% Mg calcite*						
pH _{NBS} *	8.17 (0.04)	7.91 (0.02)	53.7	<0.0001	8.52	<0.0001
Total alkalinity (μ mol kg ⁻¹)	2,156 (2.1)	2,016 (9.2)	45.7	<0.0001	4.29	= 0.0001
CCA (recruits m ⁻² d ⁻¹) [†]	104 (26.1)	23.3 (3.5)	28.2	<0.0001	11.7	<0.0001
CCA (% cover) [†]	18.1 (7.5)	1.51 (0.8)	21.4	<0.0001	10.1	<0.0001
Non-calcifying algae (% cover)	27.7 (16.0)	57.5 (14.8)	10.9	= 0.0004	5.84	<0.0001

*Rank transformation applied to data to meet assumptions of ANOVA.

[†] Square-root transformation applied to data to meet assumptions of ANOVA.

1 The lower percentage cover by CCA and higher mean
2 percentage cover by non-calcifying algae in the treatment
3 mesocosms compared with controls indicate that CCA may be less
4 competitive for space in a high-pCO₂ world, possibly accelerating
5 the shift from dominance by calcifying organisms to fleshy
6 algae observed on many reefs today²⁹. However, the effects of
7 ocean acidification on coverage by fleshy algae will depend on
8 complexities that we did not address in our experiment. Although
9 our study did show an increase in coverage by non-calcifying algae

10 on cylinders in the treatment mesocosms, we did not attempt to
11 replicate the natural compliment of herbivores found on Hawaiian
12 reef flats, and thus only microherbivores (for example sea hares
13 and amphipods) were in abundance. The variance in percentage
14 cover by non-calcifying algae found on our cylinders was high
15 within treatment (Fig. 2d), indicating that there were undoubtedly
16 factors other than carbonate saturation state and competition
17 with calcifying algae controlling this variable. Further, at the end
18 of our nine-month study, we did not see any patterns in total

(entire mesocosm) fleshy algal abundance or biomass related to treatment, whereas we did see the same inhibition of CCAs as on the cylinders (P.L.J. *et al.*, manuscript in preparation). It will be necessary to investigate the effects of ocean acidification on the ecological process of herbivory and nutrient availability, two factors important in controlling abundance of fleshy algae²⁹, to understand fully the consequences of decreased coverage by CCAs for benthic community structure. However, the projected decreased ability of CCAs to recruit and claim space in an ecosystem where competition for hard substratum is keen implies that more substrata will be available for colonization by other benthic organisms.

Under all proposed scenarios¹, continuous anthropogenic emissions of CO₂ to the atmosphere will result in a continuous decline in the pH and calcium carbonate saturation state of ocean waters, with all the ecological implications of such a change in a major Earth-surface-system carbon reservoir. The only way to slow or prevent the continuing acidification of surface ocean waters is to reduce the emissions of CO₂ from human activities to the atmosphere; however, because of the slow mixing rate of the oceans, they will continue to be a major sink of anthropogenic CO₂ emissions well into the future, and ocean acidification will continue to intensify. Our study demonstrates that changes in benthic community structure on coral reefs may occur owing to the impact of ocean acidification on ecological processes such as recruitment and competition for space. Extrapolation of experiments measuring decreases in calcification rates by various organisms to predict future reef accretion rates may underestimate the impacts of ocean acidification by failing to account for the replacement of calcifying organisms by those that do not produce calcium carbonate. Predicting changes in community structure resulting from ocean acidification and other stressors (for example high-temperature anomalies) will be important in modelling future rates of carbonate production by coral reefs and associated ecosystems.

METHODS

Six 1 × 1 × 0.5-m fibreglass mesocosm tanks were continuously supplied with flowing seawater pumped from 2 m depth at the edge of the coral reef at Moku O Loe (Coconut Island), Kaneohe Bay, Hawaii (21.4° N, 157.8° W), at a rate of eight litres min⁻¹ per mesocosm (complete turnover rate ≈ 1 h). Three mesocosms were randomly chosen by role of dice to be maintained at an ambient (control, mean midday ± s.d. = 401 ± 55 µatm pCO₂) chemical state, and the remaining three were maintained at a daytime pCO₂ level exceeding control conditions by 365 ± 130 µatm. The latter level at midday is near that expected by the end of the 21st century following the business-as-usual IS92a CO₂ emission scenario assuming equilibrium between the atmosphere and surface seawater (766 ± 118 µatm, Fig. 1a). Note that the pCO₂ of Kaneohe Bay and many other coral reef environments, on average, is greater than the overlying atmosphere³⁰. Furthermore, on diel timescales, the surface seawater pCO₂ may fluctuate significantly owing to changes in reef metabolism between day and night²³. Carbonate chemistry was altered with hydrochloric acid (HCl) diluted with tap water to a 10% solution added at 1.3 ml min⁻¹ via peristaltic pump to the inflow pipes of each treatment mesocosm (control mesocosms received tap water at the same rate). The amount of tap water added to the inflowing water represents a 0.016% addition and was not enough to affect salinity in the mesocosms. Treatments were initiated in the mesocosms on 31 October 2005. Temperature, salinity, dissolved oxygen and pH were measured and water samples were taken in all six mesocosms at least once per week around midday (10 a.m.–2 p.m. HST). Water samples were analysed for dissolved inorganic carbon and total alkalinity following standard procedures (see the Supplementary Information). Diurnal sampling (every 3 h for 24 h) was conducted on several occasions in order to quantify the daily natural variability in the mesocosms (for example Fig. 1e–h). Between 2 February and 24 March 2006, clear acrylic cylinders were added to the mesocosms (three replicates per mesocosm) in order to provide symmetrical substrata that could be removed and examined for encrusting community recruitment and development.

The resulting communities were quantified by taking six non-overlapping still photographs of cylinder surfaces and tabulating the presence/absence of crustose coralline and non-calcifying algae under randomly distributed points on the image using PhotoGrid (C. Bird, University of Hawaii) software ($n = 50$ points per image).

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Correspondence and requests for materials should be addressed to I.B.K. or A.J.A. Supplementary Information accompanies this paper on www.nature.com/naturegeoscience.

Author contributions

I.B.K., A.J.A., P.L.J. and F.T.M. contributed equally to the design and I.B.K., A.J.A. and K.S.R. contributed equally to carrying out the experiments. All authors contributed to data synthesis and writing of the manuscript.

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