

Ocean acidification accelerates net calcium carbonate loss in a coral rubble community

Amber D. Stubler¹ · Bradley J. Peterson²

Received: 12 October 2015 / Accepted: 10 March 2016
© Springer-Verlag Berlin Heidelberg 2016

Abstract Coral rubble communities are an important yet often overlooked component of a healthy reef ecosystem. The organisms inhabiting reef rubble are primarily bioeroders that contribute to the breakdown and dissolution of carbonate material. While the effects of ocean acidification on calcifying communities have been well studied, there are few studies investigating the response of bioeroding communities to future changes in pH and calcium carbonate saturation state. Using a flow-through pH-stat system, coral rubble pieces with a naturally occurring suite of organisms, along with bleached control rubble pieces, were subjected to three different levels of acidification over an 8-week period. Rates of net carbonate loss in bleached control rubble doubled in the acidification treatments (0.02 vs. 0.04% $\text{CaCO}_3 \text{ d}^{-1}$ in ambient vs. moderate and high acidification), and living rubble communities experienced significantly increased rates of net carbonate loss from ambient to high acidification conditions (0.06 vs. 0.10% $\text{CaCO}_3 \text{ d}^{-1}$, respectively). Although more experimentation is necessary to understand the long-term response and succession of coral rubble communities under projected conditions, these results suggest that rates of carbonate loss will increase in coral rubble as pH and calcium carbonate saturation states are reduced. This study demonstrates a need to thoroughly investigate the contribution of coral

rubble to the overall carbonate budget, reef resilience, recovery, and function under future conditions.

Keywords Bioerosion · *Cliona* · Rubble community · Coral reef · *Porites*

Introduction

Coral reefs are one of the most complex habitats in the marine environment and support an impressive array of biodiversity (Moberg and Folke 1999). Geologically, the health and persistence of coral reefs is dictated by the calcification, upward growth, and areal expansion of hermatypic corals, which must occur at a rate that exceeds calcium carbonate (CaCO_3) removal processes (Andersson and Gledhill 2013). When the balance between processes of carbonate accretion and erosion favors the precipitation of CaCO_3 , reef formation and growth will occur, sustaining the coral reef system. However, if CaCO_3 removal/dissolution is favored, further expansion of carbonate structures will be inhibited, and reefs will enter a state of net erosion, ultimately resulting in species loss, degradation, and reduced functionality of the coral reef ecosystem (Hutchings 1986; Glynn 1997; Andersson and Gledhill 2013; Kennedy et al. 2013; Silbiger et al. 2014).

Ocean acidification directly threatens this dynamic balance by simultaneously affecting the accretion and erosion processes on coral reefs. By definition, ocean acidification is an increase in dissolved CO_2 that results in reduced seawater pH (Doney et al. 2009). The subsequent reduction in the calcium carbonate saturation state (Ω) limits the ability of hermatypic organisms to precipitate CaCO_3 and results in an overall decrease in CaCO_3 production (Orr et al. 2005). Concurrently, acidification hastens the abiotic

Communicated by Geology Editor Prof. Chris Perry

✉ Amber D. Stubler
stublera@uncw.edu

¹ Department of Biology and Marine Biology, University of North Carolina Wilmington, Wilmington, NC, USA

² School of Marine and Atmospheric Sciences, Stony Brook University, Stony Brook, NY, USA

dissolution and physical breakdown of CaCO_3 while enhancing biologically mediated removal (hereafter referred to as bioerosion) (Wisshak et al. 2012; Andersson and Gledhill 2013). Experimental studies assessing acidification impacts on reef organisms have disproportionately evaluated accretion processes, focusing primarily on the calcification and growth of corals and other calcifying taxa. These studies have shown that many calcifying taxa display a negative response to acidification (e.g., Hoegh-Guldberg et al. 2007; Anthony et al. 2008; Kroeker et al. 2010, 2013), although the severity varies widely, even between closely related taxa (Ries et al. 2009; McCulloch et al. 2012; Chan and Connolly 2013). Comparatively few experimental assessments of eroding processes under acidified conditions have been conducted (Andersson and Gledhill 2013).

To date, only a few studies have evaluated the impacts of acidification on bioeroding organisms. Tropical boring sponges have received the majority of attention (Wisshak et al. 2012; Fang et al. 2013; Stubler et al. 2014, 2015), although the importance of endolithic microbioeroders (i.e., algae, fungi, cyanobacteria) has recently been demonstrated (Tribollet et al. 2009; Reyes-Nivia et al. 2013). Extrapolating from these studies, it is expected that bioerosion of carbonate material will increase as pH and Ω decline, altering net carbonate balance. Concurrent stressors, such as rising global temperatures, will undoubtedly influence reef bioerosion, with most studies indicating enhanced carbonate removal rates (Fang et al. 2013; Wisshak et al. 2013). Unfortunately, forecasting the effects of multiple environmental stressors on carbonate budgets remains a difficult prospect at most spatiotemporal scales (Kennedy et al. 2013), but it is believed that any increase in bioerosion rates could have serious implications for reef resilience (Perry et al. 2008).

Research on individual bioeroding taxa under acidification scenarios has allowed us to infer a broad picture of reef-level bioerosion expected in the future, yet it is likely that the effects of acidification on abiotic dissolution and bioerosion processes may be synergistic (Andersson and Gledhill 2013). Consequently, reductions in the growth of calcifying organisms, increases in bioerosion rates, and passive dissolution of carbonate material may result in net carbonate removal rates that differ from those yet predicted by single-taxon studies (Perry et al. 2008; Andersson and Gledhill 2013). Rubble communities may be an important indicator of these widespread changes to carbonate balance, because this is where many natural breakdown and dissolution processes are concentrated. In a short-term (24-h) study of a Hawaiian rubble community response to acidification and warming, Silbiger and Donahue (2015) found that the carbonate budget switched from net calcification to net dissolution as temperature and $p\text{CO}_2$

increased. The present study aimed to explore the impact of acidification on the rates of rubble community bioerosion over an 8-week period. We evaluated the effects of three levels of acidification (present day, year 2100, and year 2300) on the rate of net carbonate loss of bleached coral rubble and rubble harboring an established rubble community in the Caribbean, hypothesizing that community-level bioerosion will increase with acidification level.

Materials and methods

Rubble collection

Fragments of *Porites* sp. rubble (likely *P. furcata*) harboring a natural bioeroding community were collected at 1–2 m depth from a *P. furcata* reef tract surrounding a mangrove island in Bocas del Toro, Panama (9.349186°N, 82.258673°W) in late September 2013. Care was taken to ensure that each rubble piece was visually infested with the boring sponge *Cliona aprica*; other organisms, such as sipunculans, polychaetes, zoanthids, euendolithic algae, and crustose coralline algae (CCA), were also present on many of the fragments. Coral rubble pieces were all similar in size (3–5 cm length), and all had a similar degree of external bioerosion. A subset of the rubble fragments collected ($n = 45$) were bleached for 48 h in a 10% solution of sodium hypochlorite (replaced every 12 h) to remove all living organisms. After bleaching, the density of the rubble fragments was determined following the methods of Davies (1989); mean density (\pm SD) of rubble was $1.83 \pm 0.41 \text{ g cm}^{-3}$. The bleached rubble fragments were then soaked in deionized water (DIW) for 24 h and dried at 60 °C for 48 h. Dried bleached rubble fragments were uniquely identified with labels affixed with cyanoacrylate (CorAffix coral adhesive), and dry weights were obtained using an analytical balance (accuracy: $\pm 0.003 \text{ g}$). The remaining living rubble fragments were allowed to acclimate for 5 d in the flow-through system before being similarly tagged. Buoyant weights were obtained for the living coral rubble in a climate-controlled laboratory following the methods of Jokiel et al. (1978) and Davies (1989). Living and bleached rubble fragments were then randomly assigned and placed into experimental tanks.

Experimental design and set-up

The study ran from October to December 2013 and used a modified version of the flow-through pH-stat design described by Stubler et al. (2015). For the experimental system, 15 large reservoirs (200 L) were connected to the unfiltered, flow-through seawater system at the Smithsonian Tropical Research Station (STRI) Bocas del Toro wet

laboratory facility. In each reservoir, pH (NBS scale) was monitored continuously using a pH controller (Reef Fanatic) connected to a CO₂ regulator (Milwaukee MA957); whenever pH levels exceeded target values, the controller opened a valve that delivered CO₂ gas to the reservoir until target values were achieved (Anthony et al. 2008; Duckworth et al. 2012; Stubler et al. 2014, 2015). Target pH levels (NBS scale) were 8.1, 7.8, and 7.6 (hereafter: ambient, moderate, and high acidification treatments, respectively). These values were chosen to correspond to the ambient and projected levels of *p*CO₂ for the end of century (1200 μ atm) and year 2300 (2000 μ atm) based on the representative concentration pathway (RCP) 8.5 and extensions scenario (Meinshausen et al. 2011). Five replicate reservoirs were assigned to each level of acidification. The pH controllers were calibrated every 2–3 d using NBS/NIST traceable standards to prevent drift.

Each 200-L reservoir ($n = 15$) gravity-fed treated seawater to a small aquarium (1.8 L) at a rate of roughly 0.2 L min⁻¹ (aquarium residence time: ~ 10 min); the reservoirs also concurrently fed 11 other aquariums that were not involved in this study, resulting in a reservoir residence time of between 60 and 90 min. Within each small aquarium ($n = 15$), living rubble pieces ($n = 5$) and bleached rubble pieces ($n = 3$) were placed on plastic egg crate material. A greater number of living rubble pieces (which were planned pseudoreplicates within tanks; Hurlbert 1984) were placed within each aquarium to better capture the variability of living rubble community bioerosion rates. Once within the treatment aquaria, rubble pieces were left undisturbed except for regular cleaning and siphoning of tanks (every 3 d) until the experiment ended after 53 d in December 2013.

Seawater chemistry and monitoring

Daily measurements of pH (NBS scale), temperature, and salinity were recorded for each aquarium throughout the duration of the experiment. Carbonate chemistry parameters (e.g., dissolved inorganic carbon [DIC]) were characterized by collecting water samples (300 mL) directly from each reservoir at the beginning and end of the experiment. Water samples were preserved by adding 200 μ L of a saturated mercuric chloride (HgCl₂) solution and stored at 4 °C following NOAA's DIC sampling protocols (<http://www.pmel.noaa.gov>). DIC measurements were made using an EGM-4 environmental gas analyzer (PP Systems) after acidification and separation of the gas phase from seawater using a LiquiCel membrane (Membrana). The instrument was calibrated using standards made from sodium bicarbonate and provided a full recovery of Dr. Andrew Dickson's (UCSD, Scripps Institute of Oceanography) certified reference material for total inorganic carbon (Batch 135:

2036 μ mol DIC kg⁻¹ seawater). Using the program CO2SYS (Pierrot et al. 2006), levels of *p*CO₂, total alkalinity, and aragonite saturation state (Ω_a) were calculated from measurements of DIC, pH (NBS scale), temperature, and salinity using the GEOSECS constants (appropriate for pH measured on the NBS scale).

Response variables

For the living rubble fragments, the difference between initial and final buoyant weights was used to determine the net CaCO₃ loss for each fragment. The bleached coral fragments were soaked in DIW for 24 h to remove any salts and then dried at 60 °C for 48 h before final dry weights were obtained; the difference between initial and final dry weights were used to calculate the net carbonate loss. Due to the fine-scale complexity of the rubble pieces, we opted not to standardize the change in CaCO₃ mass to the surface area of the rubble because the wax-dip method for surface area estimation (Stimson and Kinzie 1991) was not able to accurately quantify the exposed area of interior channels and cavities found to be common within the rubble fragments (see discussion by Morse et al. 2007). Therefore, the change in CaCO₃ was standardized to the initial weight of the rubble fragment and 53-d experimental period to obtain % carbonate loss per day. Due to the slight variability in size of the natural rubble fragments, no abiotic dissolution correction factor from the bleached fragments could be applied to the living rubble fragments to separate abiotic dissolution from biogenic removal (Fang et al. 2013). Therefore, we report % change in carbonate mass for living rubble fragments as the rate of net carbonate loss (% g CaCO₃ d⁻¹) which integrates calcification and bioerosion, resulting from the presence of both bioeroders and secondary calcifiers (i.e., CCA), as well any abiotic dissolution. For simplicity, reported % change in carbonate mass per day is also referred to as the rate of net carbonate loss (% g CaCO₃ d⁻¹) for the bleached rubble fragments.

Data analysis

All data were analyzed using the free statistical software, R (R Development Core Team 2008). Due to the nature of the experimental design, tank means were analyzed for all treatments. One tank in the moderate acidification treatment was removed from the analysis due to unusually low pH levels resulting from a malfunction in the pH controller; therefore, the final number of tank means analyzed per treatment was $n = 5, 4,$ and 5 for the ambient, moderate, and high treatments, respectively. After ensuring that the assumptions of normality and homogeneity of variances were met, the rate of net carbonate loss (% g CaCO₃ d⁻¹)

of the bleached and living rubble fragments within tanks were each analyzed using a one-way ANOVA with pH as a factor; post hoc pairwise comparisons were made using the Tukey honestly significant difference (HSD) test.

Results

Water chemistry and treatment parameters

Treatment parameters were maintained successfully over the 53-d experimental period for each aquarium. Mean temperature (\pm SD hereafter, unless otherwise noted) was 29.6 ± 0.3 °C, but ranged 28.5–30.60 °C as it tracked both the daily and monthly (seasonal) fluctuations in ambient water temperatures of the bay where the organisms were collected. The mean pH (NBS scale) was 8.13 ± 0.01 , 7.78 ± 0.02 , and 7.57 ± 0.04 for the ambient, moderate, and high acidification treatments, which corresponded to mean $p\text{CO}_2$ values of 531 ± 62 , 1296 ± 107 , and 2194 ± 268 μatm , respectively. Although the resultant $p\text{CO}_2$ was slightly higher than anticipated based on the targeted pH levels, the acidification treatments still fell within the error range of anticipated values for the end of century and year 2300 according to the RCP 8.5 scenario extension (Meinshausen et al. 2011). Full carbonate chemistry parameters for each treatment are shown in Table 1. Levels of dissolved inorganic nutrients were not measured within the experimental system; however, a previous study characterizing nutrient levels near STRI reported that nitrite and nitrate levels ranged from 0.26 to 0.64 μM and phosphate levels ranged from 0.05 to 0.10 μM (D’Croz et al. 2005). While nutrient levels can fluctuate in wet laboratory systems, particularly those with unfiltered seawater, it is unlikely that nutrient levels varied among treatment tanks in this experiment, given the regular

cleaning of aquaria and relatively high turnover rates of the reservoirs (\sim 60–90 min) and experimental aquaria (\sim 10 min).

Net CaCO_3 loss: bleached rubble fragments

The bleached rubble fragments were evaluated within each aquarium for the percent change in CaCO_3 ; these data were also converted to rates ($\% \text{CaCO}_3 \text{d}^{-1}$) for ease of comparison to other studies. Overall, acidification increased the rate of net carbonate loss in the bleached coral rubble fragments. Bleached rubble within ambient tanks experienced 1.09 ± 0.43 $\% \text{CaCO}_3$ loss over the course of the experiment; however, there was no significant difference between the total $\%$ loss of CaCO_3 within the moderate and high acidification treatments (2.32 ± 0.60 and 2.27 ± 0.22 $\% \text{CaCO}_3$, respectively). The daily rate of net carbonate loss in bleached rubble found in the ambient treatments was 0.02 ± 0.01 $\% \text{CaCO}_3 \text{d}^{-1}$ which doubled in the moderate and high acidification treatments to 0.04 ± 0.01 and 0.04 ± 0.004 $\% \text{CaCO}_3 \text{d}^{-1}$, respectively (Fig. 1). The rate of net carbonate loss in the bleached rubble fragments was significantly different among acidification levels (one-way ANOVA: $F_{(2,11)} = 16.35$, $P < 0.01$; Table 2a); Tukey HSD pairwise comparisons (Table 2b) revealed that the rate of carbonate loss in both the moderate and high treatments significantly differed from the ambient treatment (Tukey HSD: $P < 0.01$ and $P < 0.01$, respectively), but not from each other.

Net CaCO_3 loss: living rubble fragments

Over the course of the experiment, all living rubble experienced a net loss of carbonate material, despite the presence of secondary calcifiers. Mean percent loss of CaCO_3 in the ambient acidification treatments was 3.21 ± 0.86 $\%$

Table 1 Summary of measured (*) and calculated (**) water chemistry parameters

	Treatment		
	Ambient acidification	Moderate acidification	High acidification
Temperature (°C)*	29.6 ± 0.2	29.7 ± 0.3	29.6 ± 0.3
Salinity*	35.1 ± 1.0	34.4 ± 1.3	34.7 ± 1.2
pH (NBS scale)*	8.14 ± 0.01	7.78 ± 0.02	7.57 ± 0.04
DIC ($\mu\text{mol kg}^{-1}$ seawater)*	2403 ± 185	2468 ± 176	2561 ± 161
Total alkalinity ($\mu\text{mol kg}^{-1}$ seawater)**	2684 ± 200	2563 ± 190	2583 ± 165
$p\text{CO}_2$ (μatm)**	531 ± 62	1297 ± 107	2194 ± 268
Ω_a **	3.4 ± 0.10	1.58 ± 0.18	1.06 ± 0.13

Mean (\pm SD) values of temperature, salinity, and pH (NBS scale) are reported from daily measurements. Dissolved inorganic carbon (DIC) was measured in treatment reservoirs at the beginning and end of the experiment; DIC and pH were used to calculate aragonite saturation state (Ω_a), $p\text{CO}_2$, and total alkalinity using the CO2SYS program (Pierrot et al. 2006)

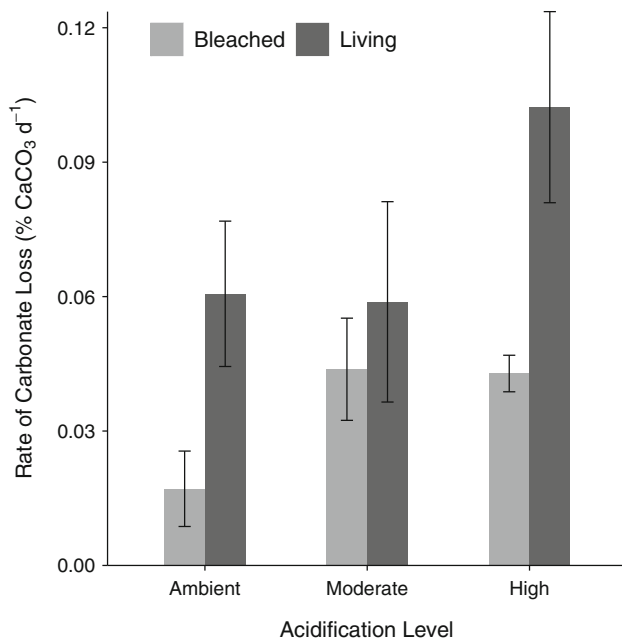


Fig. 1 Mean rates of net carbonate loss (% CaCO₃ d⁻¹; ±1 standard deviation of the mean) of bleached (light gray) and living (dark gray) coral rubble in ambient (pH 8.1), moderate (pH 7.8), and high (pH 7.6) acidification treatments

CaCO₃; the moderate treatment had a similar percent loss of $3.12 \pm 1.18\%$ CaCO₃. The highest acidification treatments experienced a $5.42 \pm 1.13\%$ reduction in CaCO₃ mass. A one-way ANOVA performed on the rates of net carbonate loss revealed a statistically significant difference due to acidification level ($F_{(2,11)} = 7.23$, $P < 0.01$; Table 2c). Rates of net carbonate loss in the highest acidification level ($0.10 \pm 0.02\%$ CaCO₃ d⁻¹) were significantly higher than both the moderate and ambient treatments (0.06 ± 0.02 and $0.06 \pm 0.016\%$ CaCO₃ d⁻¹; Tukey HSD: $P = 0.02$ and $P = 0.018$, respectively). There was no statistical difference in the rate of CaCO₃ loss between the ambient and moderate acidification treatments (Table 2d).

Discussion

Bioerosion is an essential component of a healthy reef ecosystem (Hutchings 1986), providing the destructive forces necessary for carbonate cycling, restructuring and changing reef surfaces (Goreau and Hartman 1963), and creating bare space for the settlement of new organisms (Williams et al. 1999). Environmental stresses often affect bioerosion, albeit indirectly, by disadvantaging calcifiers (primarily corals). For example, stressors such as over-fishing (Hughes 1994), disease (Aronson and Precht 2001),

Table 2 Statistical output from one-way ANOVA and post hoc comparisons on the rates of carbonate loss (% CaCO₃ d⁻¹) of bleached coral rubble (a, b) and the living rubble communities (c, d)

(a) ANOVA	df	SS	MS	F value	P
Bleached rubble: daily net carbonate loss					
Acidification	2	0.0022	0.0011	16.35	<0.001***
Residuals	11	0.00074	0.00007		
(b) Tukey's HSD	Difference	Lower 95% confidence interval	Upper 95% confidence interval	Adjusted P value	
Ambient versus moderate	-0.027	-0.042	-0.012	0.0011***	
Ambient versus high	-0.026	-0.040	-0.012	0.0014***	
High versus moderate	-0.001	-0.016	0.014	0.983	
(c) ANOVA	df	SS	MS	F value	P (perm)
Living rubble: daily net carbonate loss					
pH	2	0.005799	0.0023091	7.298	0.0096***
Residuals	11	0.004371	0.0003973		
(d) Tukey's HSD	Difference	Lower 95% confidence interval	Upper 95% confidence interval	Adjusted P value	
Ambient versus moderate	0.002	-0.034	0.038	0.99	
Ambient versus high	-0.042	-0.076	-0.0076	0.0178***	
High versus moderate	0.043	0.007	0.08	0.02***	

*** Significant results

eutrophication (Holmes 2000; Holmes et al. 2000), temperature stress (Glynn and D'Croz 1990), and acidification (Hoegh-Guldberg 2005) can lead to a reduction in live coral cover, which may facilitate the colonization of bioeroders (Glynn and Manzello 2015). Understanding that the balance between reef growth and bioerosion is largely dependent on the health of the calcifying community, Glynn (1997) suggested that relative increases in bioerosion occur when (1) the growth of bioeroders is favored over calcifying organisms or (2) conditions causing coral tissue death become more frequent. Unfortunately, both of these criteria will be increasingly met under projected ocean acidification scenarios (Hoegh-Guldberg et al. 2007; Anthony et al. 2011; Fang et al. 2013; DeCarlo et al. 2014);

the challenge lies in determining the relative contribution of each to the overall decline in reef function.

While the majority of studies have focused on determining the impact of acidification on coral calcification (e.g., Anthony et al. 2008; Marubini et al. 2008; Comeau et al. 2014), this study aimed to determine whether acidification altered rates of carbonate loss in a rubble community dominated by bioeroders over an 8-week experimental period. For both bleached and living rubble, net carbonate loss was highest in the acidification scenario expected for the year 2300 (Fig. 1). These findings are consistent with those of previous studies that have investigated bioerosion rates under acidification scenarios (Tribollet and Golubic 2005; Andersson and Gledhill 2013; Fang et al. 2013; Wisshak et al. 2013; DeCarlo et al. 2014; Stubler et al. 2014, 2015; Silbiger and Donahue 2015).

Bleached rubble carbonate loss

The rates of net carbonate loss for the bleached coral rubble in this study (Fig. 1; 0.02–0.04% $\text{CaCO}_3 \text{ d}^{-1}$) are comparable to those reported in Fang et al. (2013) where mean dissolution of bleached coral fragments evaluated over an 8-week period was approximately 0.02% $\text{CaCO}_3 \text{ d}^{-1}$ in ambient treatments, and 0.05% $\text{CaCO}_3 \text{ d}^{-1}$ under simultaneously increased acidification and temperature conditions. Interestingly, there was no significant difference in the rates of net carbonate loss between the moderate and high acidification treatments in the present study. Though Ω_a approached undersaturation, as it decreased from 1.58 in the moderate to 1.07 in the high acidification treatment (Table 1), it was never completely undersaturated. The water flow near the benthic boundary layer (carbonate–seawater interface) has been shown to play an important role in carbonate dissolution rates at reduced Ω_a , and may partially explain the similar rates of carbonate loss occurring in the bleached rubble assigned to moderate and high acidification treatments (Morse et al. 2007). However, we suspect that the carbonate loss observed may have been a form of chemical dissolution termed ‘metabolic dissolution,’ or dissolution as a result of the microbial breakdown of organic matter, a process that produces CO_2 and therefore changes the saturation state of microenvironments within a substrate (Andersson and Gledhill 2013). Therefore, although the saturation state of the overlying seawater was never truly undersaturated with respect to calcium carbonate ($\Omega < 1$), abiotic dissolution may have been enhanced by the microbial community that likely colonized the bleached rubble fragments over the course of the experiment. This could have contributed to the similarity in rates of carbonate loss of the moderate and high acidification treatments, despite the different saturation states. This may also explain the similarity in the rates of

carbonate loss reported in the present study ($\sim 0.04\% \text{CaCO}_3 \text{ d}^{-1}$) and those of Fang et al. (2013) under increased acidification and temperature (0.05% $\text{CaCO}_3 \text{ d}^{-1}$), despite a wide range of acidification between the two studies (1000 vs. 2400 μatm).

It is also worth considering that microbioeroder colonization of bleached rubble may have contributed to the net carbonate loss in the bleached rubble pieces. Multiple studies have shown that microbioerosion can have a substantial but often overlooked impact on net carbonate loss, particularly under acidified conditions (e.g., Tribollet et al. 2009; Reyes-Nivia et al. 2013). Although no microbioeroders were observed on the bleached rubble, many microbioeroders exist inconspicuously within the carbonate matrix (Chazottes et al. 1995). While the initial bleaching and subsequent drying processes would have undoubtedly eliminated any microbioeroders from the rubble, 8 weeks is ample time for new recruitment of endolithic microborers, particularly in an unfiltered seawater system. For this reason, it should be noted that microbioerosion cannot be dismissed as a contributor to the differences in net carbonate loss for the bleached rubble pieces.

Regardless, the rates of carbonate loss in the bleached rubble at acidification levels expected within the next century suggest that rates will double from what is currently experienced (loss of 0.02 vs. 0.04% $\text{CaCO}_3 \text{ d}^{-1}$). This will likely have profound implications for reef ecosystem function, as it will weaken foundation carbonate material, leaving reef structure at greater risk of storm and other physical damage. More alarmingly, the twofold increase in carbonate loss observed under projected acidification conditions is still an underestimation of actual CaCO_3 loss on a reef since carbonate substrates rarely remain uncolonized for prolonged periods, and many of the primary colonizers are likely to be bioeroding organisms. Therefore, understanding the effects of acidification on net carbonate loss will require a community-level approach.

Living rubble carbonate loss

In contrast to the bleached rubble, there was no statistical difference in rates of carbonate loss between the ambient and moderate acidification treatments for the living rubble (Table 2d). A potential explanation may be that the fragments in the moderate treatment experienced slightly increased calcification by CCA, which balanced any increased bioerosion occurring. There is experimental evidence that suggests CCA may up-regulate calcification in low-pH environments (Kamenos et al. 2013), although it should be noted that the majority of research investigating the response of CCA to acidification have found that CCA responds negatively to decreases in pH (Kuffner et al. 2007; Anthony et al. 2008; Diaz-Pulido et al. 2012). The

mutated response of the organisms within the moderate acidification level is not unprecedented; several studies have observed a wide range of responses from different organisms to moderate acidification (e.g., Ries et al. 2009; Kroeker et al. 2010).

In one of the only studies to date investigating a rubble community under acidification and warming conditions, Silbiger and Donahue (2015) evaluated the net calcification response over a 24-h period using the alkalinity anomaly technique and observed an increase in calcification in their moderate treatments mimicking projected carbonate chemistry for the year 2050 ($p\text{CO}_2 = 868$, $\text{pH} = 7.74$, $\Omega_a = 1.8$). They attributed this increase in calcification to one of three possible causes: up-regulation of calcification; acclimatization due to natural variability in environmental $p\text{CO}_2$ where rubble was collected; or a metabolic response to combined increases in temperature and $p\text{CO}_2$. Environmental acclimation may also be invoked in our study to explain the dampened response of the living rubble community to moderate acidification. The coral rubble collection site was near a mangrove island, where large diel variations in pH and $p\text{CO}_2$ often occur (Borges 2003; Zablocki et al. 2011). While in situ pH was not measured in this study, previous measurements from analogous reefs in the Bocas del Toro region suggest that ambient pH may range 7.8–8.1 (Stubler et al. 2014); thus, the rubble community may have already been slightly acclimated to the pH values applied in the moderate treatment, reducing the impact of the treatment altogether.

While this study did not aim to tease apart carbonate loss from abiotic dissolution or bioerosion as previous studies have done over a short (24-h) time period (e.g., Fang et al. 2013), a simple comparison of the rates of carbonate loss between bleached and living rubble suggests that the biogenic contribution is much greater than abiotic dissolution alone. Under ambient treatment conditions, the mean rate of carbonate loss in the bleached rubble was $0.02\% \text{ CaCO}_3 \text{ d}^{-1}$ compared to $0.06\% \text{ CaCO}_3 \text{ d}^{-1}$ for the living rubble; this suggests that over two-thirds of the carbonate loss occurring in a rubble community under present-day conditions may be attributed to bioeroders. This same relationship was found in the highest acidification treatment where the rate of carbonate loss was $0.04\% \text{ CaCO}_3 \text{ d}^{-1}$ in bleached rubble and $0.10\% \text{ CaCO}_3 \text{ d}^{-1}$ in living rubble. However, this trend does not hold for the moderate acidification level where daily carbonate loss was $0.04\% \text{ CaCO}_3 \text{ d}^{-1}$ vs. $0.06 \text{ CaCO}_3 \text{ d}^{-1}$ (only $0.02\% \text{ CaCO}_3 \text{ d}^{-1}$ is therefore attributed to biogenic dissolution). However, as previously discussed, the carbonate loss in the bleached rubble may not have been due to abiotic dissolution alone; therefore, if microbioeroders had, in fact, colonized the bleached rubble, the similar rates of daily carbonate loss between the bleached and living rubble in

the moderate treatments may be a reflection of increased microbioeroder activity.

This shift in the relative importance of biogenically driven carbonate loss from ambient to moderate, and then from moderate to high acidification treatments, may also represent a shift in the metabolic rates of the rubble community. Community metabolism has been shown to vary in response to acidification (Langdon et al. 2003). A meta-analysis by Hendriks et al. (2010) suggested that, in general, phototrophs display increased metabolic rates with acidification, while rates of metabolism in heterotrophs decrease. In a study by Tribollet et al. (2006), the metabolism of endolithic phototrophs was not affected by acidification, yet epilithic communities showed decreased respiration rates. In this study, no effort was made to measure metabolic rates of the rubble communities, as it was outside the scope of the study; therefore, the influence of any potential metabolic shifts on net carbonate loss remains largely speculative. Additionally, there was no qualitative change to suggest that the community composition itself changed. It is important to remember that the rubble communities would have been altered via attrition of species intolerant of acidification, and the experimental set-up, which limited any outside recruitment and colonization from a broader community that would naturally occur in situ, effectively hindered community turnover and succession of the rubble community. Thus, if the system had allowed for open recruitment and enabled the communities to experience a true shift in composition (by the loss and subsequent replacement of species), there may have been a more drastic change in bioerosion rates, as many of the new recruits would likely have been bioeroders.

Furthermore, this study investigated changes in carbonate chemistry alone, although temperature is likely to increase in tandem. Silbiger and Donahue (2015) investigated changes in calcification of rubble communities as a function of simultaneously increasing temperature and acidification and found that the rubble community switched to a state of net dissolution after an increase of $\sim 271 \mu\text{atm}$ and $0.75 \text{ }^\circ\text{C}$ over a 24-h period. Besides temperature, other stressors, such as eutrophication and general water quality degradation, have been correlated with elevated bioerosion rates on reefs (Holmes et al. 2000; Chazottes et al. 2002; Carreiro-Silva et al. 2005). In one of the few experimental studies assessing the potential for increased nutrient levels to directly accelerate carbonate removal rates, Carreiro-Silva et al. (2005) found that microbioerosion rates of shells were higher in fertilized treatments compared to unfertilized. While more experimental evidence is needed to confirm that elevated nutrients affect bioerosion rates in other groups of bioeroding taxa, there are a growing number of studies linking eutrophic conditions to increased

abundances of bioeroders (Rose and Risk 1985; Holmes 2000; Ward-Paige et al. 2005; DeCarlo et al. 2014). Greater abundances of endolithic bioeroders may further lower the threshold at which reefs switch from net growth to net erosion, as the increased presence of bioeroders will not only increase overall reef bioerosion rates, but also facilitate abiotic dissolution by increasing the exposed surface area of coral substrate.

As coastal systems become increasingly degraded at both regional and global scales, understanding the effects of stressors such as acidification on the carbonate budget balance will become even more important. This study adds to a growing body of evidence suggesting that bioerosion rates are likely to increase at both the species (Tribollet et al. 2009; Fang et al. 2013) and community levels (DeCarlo et al. 2014; Silbiger and Donahue 2015) as pH and Ω drop. However, more experimentation is necessary to tease apart the long-term response of abiotic and biogenic dissolution to projected conditions. Future studies should aim to incorporate multiple stressors, such as temperature and eutrophication, and broaden the complement and diversity of bioeroders examined. Finally, given the degradation of coral reefs in general, including dramatic reductions in reef complexity (Alvarez-Filip et al. 2009), the importance of carbonate rubble to reef resilience, recovery, and function should be investigated more thoroughly.

Acknowledgments This study was funded by a Smithsonian Pre-Doctoral Fellowship awarded to A. D. Stubler. Special thanks to the scientists and staff at the Smithsonian Tropical Research Institute's Bocas del Toro station. The authors would like to thank Dr. Chris Gobler and Ryan Wallace for their help with the carbonate chemistry analysis and Dr. Bradley Furman for his help with the experimental breakdown and manuscript comments. Dr. John Carroll provided additional comments that ultimately improved the quality of the manuscript.

References

- Alvarez-Filip L, Dulvy NK, Gill JA, Cote IM, Watkinson AR (2009) Flattening of Caribbean coral reefs: region-wide declines in architectural complexity. *Proc R Soc Lond B Biol Sci* 276:3019–3025
- Andersson AJ, Gledhill D (2013) Ocean acidification and coral reefs: effects on breakdown, dissolution and net ecosystem calcification. *Ann Rev Mar Sci* 5:321–348
- Anthony KR, Kline DI, Diaz-Pulido G, Dove S, Hoegh-Guldberg O (2008) Ocean acidification causes bleaching and productivity loss in coral reef builders. *Proc Natl Acad Sci U S A* 105:17442–17446
- Anthony KRN, Maynard JA, Diaz-Pulido G, Mumby PJ, Marshall PA, Cao L, Hoegh-Guldberg O (2011) Ocean acidification and warming will lower coral reef resilience. *Glob Chang Biol* 17:1798–1808
- Aronson RB, Precht WF (2001) White-band disease and the changing face of Caribbean coral reefs. *Hydrobiologia* 460:25–38
- Borges AV (2003) Atmospheric CO₂ flux from mangrove surrounding waters. *Geophys Res Lett* 30:1558–1562
- Carreiro-Silva M, McClanahan TR, Kiene WE (2005) The role of inorganic nutrients and herbivory in controlling microbioerosion of carbonate substratum. *Coral Reefs* 24:214–221
- Chan N, Connolly SR (2013) Sensitivity of coral calcification to ocean acidification: a meta-analysis. *Glob Chang Biol* 19:282–290
- Chazottes V, Le Campion-Alsumard T, Peyrot-Clausade M (1995) Bioerosion rates on coral reefs: interactions between macroborers, microborers and grazers (Moorea, French Polynesia). *Palaeogeogr Palaeoclimatol Palaeoecol* 113:189–198
- Chazottes V, Le Campion-Alsumard T, Peyrot-Clausade M, Cuet P (2002) The effects of eutrophication-related alterations to coral reef communities on agents and rates of bioerosion (Reunion Island, Indian Ocean). *Coral Reefs* 21:375–390
- Comeau S, Edmunds PJ, Spindel NB, Carpenter RC (2014) Fast coral reef calcifiers are more sensitive to ocean acidification in short-term laboratory incubations. *Limnol Oceanogr* 59:1081–1091
- Davies PS (1989) Short-term growth measurements of corals using an accurate buoyant weight technique. *Mar Biol* 101:389–395
- D'Croz LU, Del Rosario JB, Gondola P (2005) The effect of fresh water runoff on the distribution of dissolved inorganic nutrients and plankton in the Bocas del Toro Archipelago, Caribbean Panama. *Caribb J Sci* 41:414–429
- DeCarlo TM, Cohen AL, Barkley HC, Cobban Q, Young C, Shamberger KE, Brainard RE, Golbuu Y (2014) Coral macrobioerosion is accelerated by ocean acidification and nutrients. *Geology* 43:7–10
- Diaz-Pulido G, Anthony KRN, Kline DI, Dove S, Hoegh-Guldberg O (2012) Interactions between ocean acidification and warming on the mortality and dissolution of coralline algae. *J Phycol* 48:32–39
- Doney SC, Fabry VJ, Feely RA, Kleypas JA (2009) Ocean acidification: the other CO₂ problem. *Ann Rev Mar Sci* 1:169–192
- Duckworth AR, West L, Vansach T, Stubler A, Hardt M (2012) Effects of water temperature and pH on growth and metabolite biosynthesis of coral reef sponges. *Mar Ecol Prog Ser* 462:67–77
- Fang JK, Mello-Athayde MA, Schonberg CH, Kline DI, Hoegh-Guldberg O, Dove S (2013) Sponge biomass and bioerosion rates increase under ocean warming and acidification. *Glob Chang Biol* 19:3581–3591
- Glynn PW (1997) Bioerosion and coral reef growth: a dynamic balance. In: Birkeland C (ed) *Life and death of coral reefs*. Chapman and Hall, New York, pp 68–95
- Glynn PW, D'Croz L (1990) Experimental evidence for high temperature stress as the cause of El Niño-coincident coral mortality. *Coral Reefs* 8:181–191
- Glynn PW, Manzello DP (2015) Bioerosion and coral reef growth: a dynamic balance. In: Birkeland C (ed) *Coral reefs in the Anthropocene*. Springer, Netherlands, pp 67–97
- Goreau TF, Hartman WD (1963) Boring sponges as controlling factors in the formation and maintenance of coral reefs. In: Sognnaes RF (ed) *Mechanisms of hard tissue destruction*. American Association for the Advancement of Science, Washington D.C., pp 25–54
- Hendriks IE, Duarte CM, Álvarez M (2010) Vulnerability of marine biodiversity to ocean acidification: a meta-analysis. *Estuar Coast Shelf Sci* 86:157–164
- Hoegh-Guldberg O (2005) Low coral cover in a high-CO₂ world. *J Geophys Res* 110:C09S06
- Hoegh-Guldberg O, Mumby PJ, Hooten AJ, Steneck RS, Greenfield P, Gomez E, Harvell CD, Sale PF, Edwards AJ, Caldeira K, Knowlton N, Eakin CM, Iglesias-Prieto R, Muthiga N, Bradbury

- RH, Dubi A, Hatzios ME (2007) Coral reefs under rapid climate change and ocean acidification. *Science* 318:1737–1742
- Holmes KE (2000) Effects of eutrophication on bioeroding sponge communities with the description of a new West Indian sponges, *Cliona* spp. (Porifera: Hadromerida: Clionidae). *Invertebr Biol* 119:125–138
- Holmes KE, Edinger EN, Limmon GV, Risk MJ (2000) Bioerosion of live massive corals and branching coral rubble on Indonesian coral reefs. *Mar Pollut Bull* 40:606–617
- Hughes TP (1994) Catastrophes, phase shifts, and large-scale degradation of a Caribbean coral reef. *Science* 265:1547–1551
- Hurlbert SH (1984) Pseudoreplication and the design of ecological field experiments. *Ecol Monogr* 54:187–211
- Hutchings P (1986) Biological destruction of coral reefs. *Coral Reefs* 4:239–252
- Jokiel PL, Maragos JE, Franzisket L (1978) Coral growth: buoyant weight technique. UNESCO Monographs on Oceanographic Methodology 5:529–542
- Kamenos NA, Burdett HL, Aloisio E, Findlay HS, Martin S, Longbone C, Dunn J, Widdicombe S, Calosi P (2013) Coralline algal structure is more sensitive to rate, rather than the magnitude, of ocean acidification. *Glob Chang Biol* 19:3621–3628
- Kennedy EV, Perry CT, Halloran PR, Iglesias-Prieto R, Schönberg CH, Wisshak M, Form AU, Carricart-Ganivet JP, Fine M, Eakin CM, Mumby PJ (2013) Avoiding coral reef functional collapse requires local and global action. *Curr Biol* 23:912–918
- Kroeker KJ, Kordas RL, Crim RN, Singh GG (2010) Meta-analysis reveals negative yet variable effects of ocean acidification on marine organisms. *Ecol Lett* 13:1419–1434
- Kroeker KJ, Kordas RL, Crim R, Hendriks IE, Ramajo L, Singh GS, Duarte CM, Gattuso JP (2013) Impacts of ocean acidification on marine organisms: quantifying sensitivities and interaction with warming. *Glob Chang Biol* 19:1884–1896
- Kuffner IB, Andersson AJ, Jokiel PL, Ku'ulei SR, Mackenzie FT (2007) Decreased abundance of crustose coralline algae due to ocean acidification. *Nat Geosci* 1:114–117
- Langdon C, Broecker WS, Hammond DE, Glenn E, Fitzsimmons K, Nelson SG, Peng TH, Hajdas I, Bonani G (2003) Effect of elevated CO₂ on the community metabolism of an experimental coral reef. *Global Biogeochem Cycles* 17:1011
- Marubini F, Ferrier-Pagès C, Furla P, Allemand D (2008) Coral calcification responds to seawater acidification: a working hypothesis towards a physiological mechanism. *Coral Reefs* 27:491–499
- McCulloch M, Falter J, Trotter J, Montagna P (2012) Coral resilience to ocean acidification and global warming through pH up-regulation. *Nat Clim Chang* 2:623–627
- Meinshausen M, Smith SJ, Calvin K, Daniel JS, Kainuma MLT, Lamarque JF, Matsumoto K, Montzka SA, Raper SCB, Riahi K, Thomson A, Velders GJM, van Vuuren DPP (2011) The RCP greenhouse gas concentrations and their extensions from 1765 to 2300. *Clim Change* 109:213–241
- Moberg F, Folke C (1999) Ecological goods and services of coral reef ecosystems. *Ecol Econ* 29:215–233
- Morse JW, Arvidson RS, Lutge A (2007) Calcium carbonate formation and dissolution. *Chem Rev* 107:342–381
- Orr JC, Fabry V, Aumont O, Bopp L, Doney SC, Feely RA, Gnanadesikan A, Gruber N, Ishida A, Joos F (2005) Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms. *Nature* 437:681–686
- Perry CT, Spencer T, Kench PS (2008) Carbonate budgets and reef production states: a geomorphic perspective on the ecological phase-shift concept. *Coral Reefs* 27:853–866
- Pierrot D, Lewis E, Wallace DWR (2006) CO₂SYSDOS program developed for CO₂ system calculations. ORNL/CDIAC-105. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, US Department of Energy, Oak Ridge, TN
- R Development Core Team (2008) R: a language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria
- Reyes-Nivia C, Diaz-Pulido G, Kline D, Guldberg OH, Dove S (2013) Ocean acidification and warming scenarios increase microbioerosion of coral skeletons. *Glob Chang Biol* 19:1919–1929
- Ries JB, Cohen AL, McCorkle DC (2009) Marine calcifiers exhibit mixed responses to CO₂-induced ocean acidification. *Geology* 37:1131–1134
- Rose CS, Risk MJ (1985) Increase in *Cliona delerix* infestation of *Montastrea cavernosa* heads on an organically polluted portion of the Grand Cayman fringing reef. *Mar Ecol* 6:345–363
- Silbiger NJ, Donahue MJ (2015) Secondary calcification and dissolution respond differently to future ocean conditions. *Biogeosciences* 12:567–578
- Silbiger NJ, Guadayol Ò, Thomas FIM, Donahue MJ (2014) Reefs shift from net accretion to net erosion along a natural environmental gradient. *Mar Ecol Prog Ser* 515:33–44
- Stimson J, Kinzie RA (1991) The temporal pattern and rate of release of zooxanthellae from the reef coral *Pocillopora damicornis* (Linnaeus) under nitrogen-enrichment and control conditions. *J Exp Mar Bio Ecol* 153:63–74
- Stubler AD, Furman BT, Peterson BJ (2014) Effects of pCO₂ on the interaction between an excavating sponge, *Cliona varians*, and a hermatypic coral, *Porites furcata*. *Mar Biol* 161:1851–1859
- Stubler AD, Furman BT, Peterson BJ (2015) Sponge erosion under acidification and warming scenarios: differential impacts on living and dead coral. *Glob Chang Biol* 21:4006–4020
- Tribollet A, Golubic S (2005) Cross-shelf differences in the pattern and pace of bioerosion of experimental carbonate substrates exposed for 3 years on the northern Great Barrier Reef, Australia. *Coral Reefs* 24:422–434
- Tribollet A, Langdon C, Golubic S, Atkinson M (2006) Endolithic microflora are major primary producers in dead carbonate substrates of Hawaiian coral reefs. *J Phycol* 42:292–303
- Tribollet A, Godinot C, Atkinson M, Langdon C (2009) Effects of elevated pCO₂ on dissolution of coral carbonates by microbial euendoliths. *Global Biogeochem Cycles* 23:GB3008
- Ward-Paige CA, Risk MJ, Sherwood OA, Jaap WC (2005) Clionid sponge surveys on the Florida Reef Tract suggest land-based nutrient inputs. *Mar Pollut Bull* 51:570–579
- Williams EH, Bartels P, Bunkley-Williams L (1999) Predicted disappearance of coral-reef ramparts: a direct result of major ecological disturbances. *Glob Chang Biol* 5:839–845
- Wisshak M, Schonberg CHL, Form A, Freiwald A (2012) Ocean acidification accelerates reef bioerosion. *PLoS One* 7:e45124
- Wisshak M, Schönberg CHL, Form A, Freiwald A (2013) Effects of ocean acidification and global warming on reef bioerosion—lessons from a clionid sponge. *Aquatic Biology* 19:111–127
- Zablocki JA, Andersson AJ, Bates NR (2011) Diel aquatic CO₂ system dynamics of a Bermudian mangrove environment. *Aquat Geochem* 17:841–859