

1 **Secondary calcification and dissolution respond**
2 **differently to future ocean conditions.**

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8

9 **Abstract**

10 Climate change threatens both the accretion and erosion processes that sustain coral reefs.
11 Secondary calcification, bioerosion, and reef dissolution are integral to the structural
12 complexity and long-term persistence of coral reefs, yet these processes have received
13 less research attention than reef accretion by corals. In this study, we use climate
14 scenarios from RCP 8.5 to examine the combined effects of rising ocean acidity and sea
15 surface temperature (SST) on both secondary calcification and dissolution rates of a
16 natural coral rubble community using a flow-through aquarium system. We found that
17 secondary reef calcification and dissolution responded differently to the combined effect
18 of pCO₂ and temperature. Calcification had a non-linear response to the combined effect
19 of pCO₂-temperature: the highest calcification rate occurred slightly above ambient
20 conditions and the lowest calcification rate was in the highest pCO₂-temperature
21 condition. In contrast, dissolution increased linearly with pCO₂-temperature. The rubble
22 community switched from net calcification to net dissolution at +271 μatm pCO₂ and
23 0.75° C above ambient conditions, suggesting that rubble reefs may shift from net

24 calcification to net dissolution before the end of the century. Our results indicate that (i)
25 dissolution may be more sensitive to climate change than calcification and (ii) that
26 calcification and dissolution have different functional responses to climate stressors; this
27 highlights the need to study the effects of climate stressors on both calcification and
28 dissolution to predict future changes in coral reefs.

29

30 **1 Introduction**

31 In 2013, atmospheric carbon dioxide ($\text{CO}_{2(\text{atm})}$) reached an unprecedented
32 milestone of 400 ppm (Tans and Keeling, 2013), and this rising $\text{CO}_{2(\text{atm})}$ is increasing
33 sea-surface temperature (SST) and ocean acidity (Caldeira and Wickett, 2003; Cubasch et
34 al., 2013; Feely et al., 2004). Global SST has increased by 0.78°C since pre-industrial
35 times (Cubasch et al., 2013), and it is predicted to increase by another $0.8\text{--}5.7^{\circ}\text{C}$ by the
36 end of this century (Meinshausen et al., 2011; Van Vuuren et al., 2008; Rogelj et al.,
37 2012). The Hawai'i Ocean Time-series detected a 0.075 decrease in mean annual pH at
38 Station ALOHA over the past 20 years (Doney et al., 2009) and there have been similar
39 trends at stations around the world including the Bermuda Atlantic Time-series and the
40 European Station for Time-series Observations in the ocean (Solomon et al. 2007). pH is
41 expected to drop by an additional 0.14–0.35 pH units by the end of the 21st century (Bopp
42 et al., 2013). All marine ecosystems are at risk from rising SST and decreasing pH
43 (Doney et al., 2009; Hoegh-Guldberg et al., 2007; Hoegh-Guldberg and Bruno, 2010), but
44 coral reefs are particularly vulnerable to these stressors (reviewed in Hoegh-Guldberg et
45 al., 2007).

46 Corals create the structurally complex calcium carbonate (CaCO_3) foundation of
47 coral reef ecosystems. This structural complexity is at risk from climate-driven shifts
48 from high-complexity, branched coral species to mounding and encrusting growth forms
49 (Fabricius et al., 2011) and from increases in the natural processes of reef destruction,
50 including bioerosion and dissolution (Wisshak et al., 2012, 2013; Tribollet et al., 2006).
51 While substantial research attention has focused on the response of reef-building corals to
52 climate change (reviewed in Hoegh-Guldberg et al., 2007; Fabricius, 2005; Pandolfi et al.,
53 2011), secondary calcification (calcification by non-coral invertebrates and calcareous
54 algae), bioerosion, and reef dissolution that are integral to maintaining the structural
55 complexity and net growth of coral reefs has received less attention (Andersson and
56 Gledhill, 2013; Andersson et al., 2011; Andersson and Mackenzie, 2012). Bioerosion and
57 dissolution breakdown the reef framework while secondary calcification helps maintain
58 reef stability by cementing the reef together (Adey, 1998; Camoin and Montaggioni,
59 1994; Littler, 1973) and producing chemical cues that induce settlement of many
60 invertebrate larvae including several species of corals (Harrington et al. 2004; Price
61 2010). Coral reefs will only persist if constructive reef processes (growth by corals and
62 secondary calcifiers) exceed destructive reef processes (bioerosion and dissolution). In
63 this study, we examine the combined effects of rising ocean acidity and SST on both
64 calcification and dissolution rates of a natural community of secondary calcifiers and
65 bioeroders.

66 Recent laboratory experiments have focused on the response of individual taxa of
67 bioeroders or secondary calcifiers to climate stressors. For example, studies have
68 specifically addressed the effects of rising ocean acidity and/or temperature on bioerosion

69 by a *Clionid* sponge (Wisshak et al., 2012, 2013; Fang et al., 2013) and a community of
70 photosynthesizing microborers (Tribollet et al., 2009; Reyes-Nivia et al., 2013). These
71 studies found that bioerosion increased under future climate change scenarios. Several
72 studies have focused on tropical calcifying algae and have found decreased calcification
73 (Semese et al., 2009; Johnson et al., 2014; Comeau et al., 2013; Jokiel et al., 2008; Kleypas
74 and Langdon, 2006) and increased dissolution (Diaz-Pulido et al., 2012) with increasing
75 ocean acidity and/or SST. However, the bioeroding community is extremely diverse and
76 can interact with the surrounding community of secondary calcifiers: for example,
77 crustose coralline algae (CCA) can inhibit internal bioerosion (White, 1980; Tribollet and
78 Payri, 2001). To understand the combined response of bioeroders and secondary
79 calcifiers, we take a community perspective and examine the synergistic effects of rising
80 SST and ocean acidity on a natural community of secondary calcifiers and bioeroders.
81 Using the total alkalinity anomaly technique, we test for net changes in calcification
82 during the day and dissolution (most of which is caused by bioeroders; Andersson and
83 Gledhill, 2013) at night. Our climate change treatments are modelled after the
84 Representative Concentration Pathway (RCP) 8.5 climate scenario (Van Vuuren et al.,
85 2011; Meinshausen et al., 2011), one of the high emissions scenarios used in the most
86 recent Intergovernmental Panel on Climate Change (IPCC) report (Cubasch et al., 2013).
87 The RCP 8.5 scenario predicts an increase in temperature of 3.8 – 5.7°C (Rogelj et al.,
88 2012) and an increase in atmospheric CO₂ of 557 ppm by the year 2100 (Meinshausen et
89 al., 2011). We use the RCP 8.5 scenario because the current CO₂ concentrations are
90 tracking just above what this scenario predicts (Sanford et al., 2014). While prior studies
91 have focused on the contributions of individual community members to increased

92 temperature and CO₂; here, we examine the community response to the RCP 8.5 climate
93 scenario and measure calcification, dissolution, and net community production rates.

94 **2 Materials and Methods**

95 **2.1 Collection Site**

96 All collections were made on the windward side of Moku o Lo‘e (Coconut Island)
97 in Kāne‘ohe Bay, Hawai‘i adjacent to the Hawai‘i Institute of Marine Biology. This
98 fringing reef is dominated by *Porites compressa* and *Montipora capitata*, with occasional
99 colonies of *Pocillopora damicornis*, *Fungia scutaria*, and *Porites lobata*. Kāne‘ohe Bay
100 is a protected, semi-enclosed embayment; the residence time can be >1 month long in the
101 protected southern portion of the Bay (Lowe et al., 2009a;Lowe et al., 2009b) that is
102 coupled with a high daily variance in pH (Guadayol et al., 2014). The wave action is
103 minimal (Smith et al., 1981;Lowe et al., 2009a;Lowe et al., 2009b) and currents are
104 relatively slow (5cm s⁻¹ maximum) and wind-driven (Lowe et al., 2009a;Lowe et al.,
105 2009b).

106 **2.2 Sample Collection**

107 We collected pieces of dead *Porites compressa* coral skeleton (hereafter, referred to as
108 rubble) as representative communities of bioeroders and secondary calcifiers. Rubble was
109 collected with a hammer and chisel from a shallow reef flat (~1m depth) in November,
110 2012. Only pieces of rubble without any live coral were collected. The rubble community
111 in Kāne‘ohe Bay is comprised of secondary calcifiers, including CCA from the genera
112 *Hydrolithon*, *Sporolithon*, and *Peyssonnelia* and non-coral calcifying invertebrates (e.g.
113 boring bivalves (*Lithophaga fasciola* and *Barbatia divaricate*), oysters (*Crassostrea*

114 *gigas*), and small crustaceans); filamentous and turf algae; and internal bioeroders,
115 including boring bivalves (*L. fasciola* and *B. divaricate*), sipunculids (*Aspidosiphon*
116 *elegans*, *Lithacrosiphon cristatus*, *Phascolosoma perlucens*, and *Phascolosoma*
117 *stephensoni*), phoronids (*Phoronis ovalis*), sponges (*Cliona* spp.) and a diverse
118 assemblage of polychaetes (White, 1980). All rubble pieces were combined after
119 collection and maintained in a 100L flow-through tank with ambient seawater from
120 Kāneʻohe Bay until random assignment to treatments.

121 **2.3. Experimental Design**

122 The Hawaiʻi Institute of Marine Biology (HIMB) hosts a mesocosm facility with
123 flow-through seawater from Kāneʻohe Bay and controls for light, temperature, pCO₂, and
124 flow rate. The facility is comprised of 24 experimental aquaria split between four racks;
125 each rack has a 150L header tank which feeds 6 experimental aquaria, each 50L in
126 volume (Figure 1).

127 Before adding rubble to the experimental aquaria, we collected day and night
128 samples of pH, total alkalinity (TA), temperature, and salinity from all aquaria to
129 demonstrate the consistency of water conditions across aquaria without any rubble
130 present (Table 1). The long-term temporal stability of the mesocosm system is reported
131 in Putnam (2012). We then conducted “control” and “treatment” experiments to
132 determine how RCP 8.5 predictions affect daytime calcification and nighttime dissolution
133 rates in a natural rubble community. The first “control experiment” characterized baseline
134 calcification and dissolution in each aquarium caused by differences in rubble
135 communities. In the second “treatment experiment”, we manipulated pCO₂ and

136 temperature to simulate four climate scenarios (pre-industrial, present day, 2050, and
137 2100) and tested the response of calcification, dissolution, and net community
138 production. Each experiment used the TA anomaly method (Smith and Key, 1975;
139 Andersson et al., 2009). This method calculates net calcification from changes in total
140 alkalinity, and calculates net community production from changes in total dissolved
141 inorganic carbon adjusted for changes in carbon due to calcification. Because estimates
142 of calcification are based on changes in total alkalinity, this method does not account for
143 mechanical erosion (e.g., small chips of CaCO_3 produced by sponge erosion). However,
144 given the short duration of the experiment and the types of bioeroders present, we expect
145 that chemical dissolution captured a significant proportion of the erosion in the system.

146 Approximately 1.2L of rubble (3-4 pieces of weight 499 ± 148 g and skeletal
147 density 1.53 ± 0.1 g cm^{-3} (mean \pm SD, n=85)) were placed in each of the 24 experimental
148 aquaria and acclimated to tank conditions in ambient seawater for three days. On the
149 fourth day, we performed the control experiment, calculating daytime calcification and
150 nighttime dissolution for rubble in ambient seawater conditions using the TA anomaly
151 technique. The next day we manipulated seawater pCO_2 and temperature to replicate four
152 climate scenarios for the treatment experiment: pre-industrial ($-1 \pm 0.057^\circ\text{C}$ and -205 ± 11.9
153 μatm), present day (natural Kāneʻohe Bay seawater $24.8 \pm 0.09^\circ\text{C}$, 614 ± 15.6 μatm), 2050
154 ($+1.4 \pm 0.09^\circ\text{C}$ and $+255 \pm 31$ μatm), and 2100 ($+2.4 \pm 0.08$ and $+433 \pm 40$ μatm). Note that
155 all changes in temperature and pCO_2 were made relative to present day Kāneʻohe Bay
156 seawater conditions: pCO_2 in Kāneʻohe Bay is consistently high relative to the open
157 ocean and can range from 196-976 μatm in southern Kāneʻohe bay depending on
158 conditions (Drupp et al., 2013). The yearly average pCO_2 at our collection site ranged

159 from 565-675 μatm (Silbiger et al., 2014). After an acclimation time of seven days, we
160 sampled the treatment experiment, calculating daytime calcification and nighttime
161 dissolution over a 24 hour period.

162 During both experiments, TA, pH, salinity, temperature, and dissolved inorganic
163 nutrient (DIN) samples were collected every 12 hours over a 24 hour period: just before
164 lights-on in the morning (time 1) and just before lights-off at night (time 2) to capture
165 light conditions, and then again before lights-on the next morning (time 3) to capture dark
166 conditions. Flow into each aquarium was monitored and adjusted every three hours to
167 ensure a consistent flow rate over the 24 hour experiment. We calculated net ecosystem
168 calcification, dissolution, and net community production using a simple box model
169 (Andersson et al., 2009) and normalized all our calculations to the surface area of the
170 rubble in each tank. Surface area of the rubble was calculated using the wax dipping
171 technique (Stimson and Kinzie III, 1991) at the end of the experiment.

172 **2.4 Mesocosm Set-up**

173 The mesocosm facility (Figure 1) is supplied with ambient seawater from
174 Kāneʻohe Bay, which is filtered through a sand filter, passed through a water chiller
175 (Aqualogic Multi Temp MT-1 Model # 2TTB3024A1000AA), and then fed into one of
176 the four header tanks. pCO_2 was manipulated using a CO_2 gas blending system (see
177 Fangue et al., 2010; Johnson and Carpenter, 2012). Each target pCO_2 concentration was
178 created by mixing CO_2 -free atmospheric air with pure CO_2 using mass flow controllers
179 (C100L Sierra Instruments). Output pCO_2 was analyzed using a calibrated infrared
180 CO_2 analyzer (A151, Qubit Systems). CO_2 mixtures were then bubbled into one of the

181 four header tanks and water from each individual header tank fed into the six individual
182 treatment aquaria (Figure 1). The pCO₂ in each treatment aquarium was estimated with
183 CO2SYS (Van Heuven et al., 2009) using pH and TA as the parameters.

184 Temperature was manipulated in each treatment aquarium using dual-stage
185 temperature controllers (Aqualogic TR115DN). The temperature was continuously
186 monitored with temperature loggers (TidbiT v2 Water Temperature Data Logger,
187 sampling every 20 min) and point measurements were taken during every sampling
188 period with a handheld digital thermometer (Traceable Digital Thermometer, Thermo
189 Fisher Scientific; precision = 0.001 °C). Light was controlled by positioning an
190 oscillating pendant metal-halide light (250 W) over a set of three aquaria and was
191 programmed to emit an equal amount of light to each tank (~500μE of light). Lights were
192 set to a 12:12 hour photoperiod and were monitored using a LI-COR spherical quantum
193 PAR sensor. Flow rate was maintained at 115±1 ml min⁻¹, resulting in a residence time of
194 7.3±0.07 hours per tank. Each aquarium was equipped with a submersible powerhead
195 pump (Sedra KSP-7000 powerhead) to ensure that the tank was well-mixed.

196 **2.5 Seawater Chemistry**

197 All sample collection and storage vials were cleaned in a 10% HCl bath for 24 hours and
198 rinsed three times with MilliQ water before use and rinsed three times with sample water
199 during sample collection and processing.

200 **2.5.1 Total Alkalinity**

201 Duplicate TA samples were collected in 300 ml borosilicate sample containers with glass
202 stoppers. Each sample was preserved with 100μL of 50% saturated HgCl₂ and analyzed

203 within 3 days using open cell potentiometric titrations on a Mettler T50 autotitrator
204 (Dickson et al., 2007). A Certified Reference Material (CRM - Reference Material for
205 Oceanic CO₂ Measurements, A. Dickson, Scripps Institution of Oceanography) was run
206 at the beginning of each sample set. The accuracy of the titrator never deviated more than
207 $\pm 0.8\%$ from the standard, and TA measurements were corrected for these deviations. The
208 precision was 3.55 μEq (measured as standard deviation of the duplicate water samples).
209 During the 24-hour control experiment the average changes in TA were 37 μEq over the
210 day and 20 μEq over the night (day and night TA changes were of larger magnitude in the
211 treatment experiments): these are measurable changes given the precision and accuracy
212 of the TA measurements.

213 **2.5.2 pH_t (total scale)**

214 Duplicate pH_t samples were collected in 20ml borosilicate glass vials, brought to a
215 constant temperature of 25°C in a water bath, and immediately analyzed using an m-
216 cresol dye addition spectrophotometric technique (Dickson et al., 2007). Accuracy of the
217 pH was tested against a Tris buffer of known pH_t from the Dickson Lab at Scripps
218 Institution of Oceanography (Dickson et al., 2007). Our accuracy was better than
219 $\pm 0.04\%$, and the precision was 0.004 pH units (measured as standard deviation of the
220 duplicate water samples). *In situ* pH and the remaining carbonate parameters were
221 calculated using CO2SYS (Van Heuven et al., 2009) with the following measured
222 parameters: pH_t, TA, temperature, and salinity. The K1K2 apparent equilibrium constants
223 were from Mehrbach (1973) and refit by Dickson & Millero (1987) and HSO₄⁻
224 dissociation constants were taken from Uppström (1974) and Dickson (1990).

225 **2.5.3 Salinity**

226 Duplicate salinity samples were analyzed on a Portasal 8410 portable salinometer
227 calibrated with an OSIL IAPSO standard (accuracy = ±0.003, precision = ±0.0003).

228 **2.5.4 Nutrients**

229 Nutrient samples were collected with 60ml plastic syringes and immediately filtered
230 through combusted 25mm glass fiber filters (GF/F 0.7µm) and transferred into 50ml
231 plastic centrifuge tubes. Nutrient samples were frozen and later analyzed for Si(OH)₄,
232 NO₃⁻, NO₂⁻, NH₄⁺, and PO₄³⁻ on a Seal Analytical AA3 HR Nutrient Analyzer at the UH
233 SOEST Lab for Analytical Chemistry.

234 **2.6 Measuring Net Ecosystem Calcification**

235 We assumed that the mesocosms were well mixed systems; thus, we calculated net
236 ecosystem calcification and net community photosynthesis following the simple box
237 model presented in Andersson et al. (2009). TA was normalized to a constant salinity
238 (35) to account for changes due to evaporation and then corrected for dissolved inorganic
239 nitrogen and phosphate to account for their small contributions to the acid-base system
240 (Wolf-Gladrow et al., 2007). Net ecosystem calcification, or G, was calculated using the
241 following equation:

$$G = \left[F_{TAin} - F_{TAout} - \frac{dTA}{dt} \right] / 2 \quad \text{Eq. 1}$$

242 where F_{TAin} is the rate of TA flowing into an aquarium (= average TA in the header tank
243 times the inflow rate), F_{TAout} is the rate of TA flowing out of an aquarium (= average
244 TA in the aquarium times the outflow rate), and $\frac{dTA}{dt}$ is the change in TA in an aquarium

245 during the measurement period (change in TA normalized to the volume of water and the
 246 surface area of the rubble); specific calculations are given in the supplemental material.
 247 The equation is divided by two because one mole of CaCO₃ is precipitated or dissolved
 248 for every two moles of TA removed or added to the water column. Here, G represents the
 249 sum of all the calcification processes minus the sum of all the dissolution processes in
 250 mmol CaCO₃ m⁻² hr⁻¹; thus, all positive numbers are net calcification, and all negative
 251 numbers are negative net calcification (i.e., net dissolution). Net daytime calcification
 252 (G_{day}) is calculated from the first 12 hour sampling period in the light, net nighttime
 253 dissolution (G_{night}) is calculated from the second 12 hour sampling period in the dark, and
 254 total net calcification (G_{net}) is calculated from the full 24 hour cycle (G_{day} + G_{night}). G_{day},
 255 G_{night}, and G_{net} are converted from hourly to daily rates and presented as mmol CaCO₃ m⁻²
 256 d⁻¹.

257 **2.7 Measuring Net Community Production and Respiration**

258 Net community production (NCP) was calculated by measuring changes in DIC (Gattuso
 259 et al., 1999). DIC was normalized to a constant salinity (35) to account for any
 260 evaporation over the 24 hour period. We used a simple box model to calculate NCP:

$$NCP = \left[F_{DICin} - F_{DICout} - \frac{dDIC}{dt} \right] - G \quad \text{Eq. 2}$$

261 F_{DICin} , F_{DICout} , and $\frac{dDIC}{dt}$ are the rates of DIC flowing into the aquaria, flowing out of the
 262 aquaria, and the change in DIC in the aquaria per unit time in mmol C m⁻² hr⁻¹,
 263 respectively. To measure NCP, we subtract G to remove any change in carbon due to
 264 inorganic processes. NCP represents the sum of all the photynthetic processes minus the

265 sum of all the respiration processes, thus all positive numbers are net photosynthesis and
266 all negative numbers are negative net photosynthesis (i.e., net respiration). Net daytime
267 NCP (NCP_{day}) is calculated from the first 12 hour sampling period in the light, net
268 nighttime NCP (NCP_{night}) is calculated from the second 12 hour sampling period in the
269 dark, and total NCP (NCP_{net}) is calculated from the full 24 hour cycle ($NCP_{day} +$
270 NCP_{night}). All rates are presented as $mmol\ C\ m^{-2}\ d^{-1}$.

271 **2.8 Statistical Analysis**

272 Each aquarium contained a slightly different rubble community because of the
273 randomization of rubble pieces to each treatment. To ensure there were no systematic
274 differences in rubble communities between racks (rack effects) before the experimental
275 treatments were applied, we tested for differences in calcification and NCP between racks
276 in the control experiment using an ANOVA (Figure A2).

277 In the treatment experiment, we first tested for feedbacks in carbonate chemistry
278 due to the presence of rubble: using a paired t-test, we compared the day-night difference
279 in measured pCO_2 in each aquarium with rubble, $(pCO_{2,day} - pCO_{2,night})_{rubble}$, and
280 without rubble, $(pCO_{2,day} - pCO_{2,night})_{no\ rubble}$.

281 Although we imposed four discrete temperature- pCO_2 scenario treatments on
282 each tank (Table 1), random variation between treatments and the feedback between the
283 rubble communities and the water chemistry resulted in near-continuous variation in
284 temperature- pCO_2 treatments across aquaria (Figures 2 and A1). To capture this
285 continuous variation in temperature- pCO_2 in the analysis, we used the measured

286 temperature-pCO₂ seawater condition as a continuous independent variable in a
 287 regression rather than the four categorical treatment conditions in an ANOVA (an
 288 analysis of G and NCP using the ANOVA approach is included in Figures A3, A4 and
 289 Tables A1, A2). The regression approach allowed us to better capture the quantitative
 290 relationships between net calcification (G) or NCP and the temperature-pCO₂ treatment.
 291 We created a single, continuous variable, Standardized Climate Change (SCC), from a
 292 linear combination of temperature and pCO₂ values in each aquarium. A simple linear
 293 combination was used because pCO₂ increased linearly with temperature (Figure 2), as
 294 imposed by our treatments. We first calculated the relationship between ΔTemp (Eq 3)
 295 and ΔpCO₂ (Eq 4) using linear regression. The coefficients from this regression (slope: α
 296 = 0.0031; y-intercept: β = - 0.078) were used to combine pCO₂ and temperature onto the
 297 same scale, as a measure of Standardized Climate Change (Eq 5):

$$298 \quad \Delta Temp_i = Temp_{trt,i} - Temp_{cont,i} \quad \text{Eq. 3}$$

$$299 \quad \Delta pCO_{2i} = pCO_{2trt,i} - pCO_{2cont,i} \quad \text{Eq. 4}$$

$$300 \quad SCC_i = \Delta Temp_i + \alpha * \Delta pCO_{2i} + \beta \quad \text{Eq. 5}$$

301 This synthetic temperature-pCO₂ axis, SCC, is centered on the ambient (control)
 302 conditions such that a value of 0 corresponds to present day Kāne‘ohe Bay conditions, a
 303 negative value corresponds to water that is colder and less acidic (pre-industrial) and a
 304 positive value corresponds to water that is warmer and more acidic (future conditions)
 305 compared to background seawater. (The independent relationships between G and NCP
 306 with ΔTemp and ΔpCO₂ are shown in Figures A5 and A6 and are similar to the
 307 relationship with SCC.)

308 With SCC as a continuous, independent variable, we used a regression to test for
309 linear and non-linear relationships between day, night, and net calcification (G_{day} , G_{night} ,
310 and G_{net}) and NCP (NCP_{day} , NCP_{night} , and NCP_{net}) versus SCC. For a simple test of
311 nonlinearity in the response of calcification to SCC, we included a quadratic term (SCC^2)
312 in the model. For G_{day} , we used weighted regression (weight function: $w_i=1/(1+|r_i|)$,
313 where w_i = weight and r_i = residual, Fair, 1974) to account for heteroscedasticity. All
314 other data met assumptions for a linear regression. Lastly, we used a linear regression to
315 test the relationship between G and NCP.

316 **3 Results**

317 **3.1 Control Experiment**

318 For rubble in ambient seawater conditions, the average G_{day} , G_{night} , and G_{net} in the control
319 experiment were $3.4 \pm 0.16 \text{ mmol m}^{-2} \text{ d}^{-1}$, $-2.4 \pm 0.15 \text{ mmol m}^{-2} \text{ d}^{-1}$, and $0.96 \pm 0.20 \text{ mmol m}^{-2}$
320 d^{-1} , respectively. There was no significant difference in G_{day} ($F_{3,23}=0.68$, $p=0.58$), G_{night}
321 ($F_{3,23}=1.52$, $p=0.24$), or G_{net} ($F_{3,23}=1.38$, $p=0.28$) between racks in the control experiment
322 (Figure A2). NCP rates also did not show any racks effects. Average NCP rates were
323 $23.2 \pm 1.4 \text{ mmol m}^{-2} \text{ d}^{-1}$ ($F_{3,23}=0.07$, $p=0.94$) during the day, $-20.7 \pm 1.9 \text{ mmol m}^{-2} \text{ d}^{-1}$
324 ($F_{3,23}=1.95$, $p=0.15$) during the night, and $2.5 \pm 2.1 \text{ mmol m}^{-2} \text{ d}^{-1}$ ($F_{3,23}=1.5$, $p=0.25$) over
325 the entire 24 hour period.

326 **3.2 Treatment Experiment**

327 The rubble communities significantly altered the seawater chemistry, with higher $p\text{CO}_2$
328 than the applied $p\text{CO}_2$ manipulation, particularly at night (Figure A1). The mean

329 difference between day and night pCO₂ for all treatments was 134.4 ± 39 μatm without
330 rubble and was 438.5 ± 163.9 μatm when rubble was present (t₂₃ = -7.23, p < 0.0001;
331 Figure 2).

332 Standardized Climate Change was a significant predictor for G_{day}, G_{night}, and G_{net}
333 (Table 2; Figure 3). G_{day} had a non-linear relationship with Standardized Climate Change
334 (Table 2, Figure 3a), increasing to a threshold and then rapidly declining. G_{night}, however,
335 had a strong linear relationship with Standardized Climate Change (Table 2; Figure 3c),
336 suggesting that joint increases in ocean pCO₂ and temperature will increase nighttime
337 dissolution of coral rubble. Lastly, G_{net} had a strong negative relationship with
338 Standardized Climate Change (Table 2; Figure 3e) and the rubble community switched
339 from net calcification to net dissolution at an increase in pCO₂ and temperature of 271
340 μatm and 0.75° C, respectively. Standardized Climate Change was also a significant
341 predictor of NCP: Day, night, and net NCP rates all declined with standardized climate
342 change (Table 2; Figure 3b,d,f; Figure 3).

343 Net ecosystem calcification increased with net community production (F_{1,46} =
344 260, p < 0.0001, R² = 0.85; Figure 4). In general, communities were net photosynthesizing
345 and net calcifying during the day (Figure 4a: squares in the upper right quadrant) and
346 were net respiring and net dissolving at night (Figure 4a: circles in the lower left
347 quadrant). The exception was communities in the most extreme temperature-pCO₂
348 treatment: these communities were net respiring during the day while holding a positive,
349 yet very low, calcification rate (Figure 4a: squares in the upper left quadrant).

350

351 **4 Discussion**

352 **4.1 Carbonate Chemistry Feedbacks**

353 The rubble communities in the aquaria significantly altered the seawater
354 chemistry, particularly at night ($t_{23} = -7.23$, $p < 0.0001$; Figure 2, Figure A1). This day-
355 night difference in seawater chemistry increased under more extreme climate scenarios,
356 as predicted by Jury *et al.* (2013). This large diel swing in $p\text{CO}_2$ is not uncommon on
357 shallow coral reef environments. $p\text{CO}_2$ ranged from 480 to 975 μatm over 24 hours on a
358 shallow reef flat adjacent to our collection site (Silbiger *et al.* 2014) and from 450 to 742
359 μatm on a Moloka'i reef flat dominated by coral rubble (Yates and Halley, 2006). Here,
360 $p\text{CO}_2$ had an average difference of 438 μatm between day and night with a range of 412
361 μatm in the pre-industrial treatment to 854 μatm in the most extreme temperature- $p\text{CO}_2$
362 treatments (Figure 2). In our study, we incorporated these feedbacks into the statistical
363 analysis by using the actual, sampled $p\text{CO}_2$ (and temperature) in each aquaria (Figure 3)
364 rather than using the intended $p\text{CO}_2$ (and temperature) treatments in an ANOVA (Tables
365 A1, A2 and Figures A3, A4), better reflecting the $p\text{CO}_2$ experienced by organisms in
366 each aquarium.

367 **4.2 Calcification, Dissolution, and Net Community Production in a High** 368 **CO_2 and Temperature Environment**

369 Our results suggest that as $p\text{CO}_2$ and temperature increase over time, rubble reefs
370 may shift from net calcification to net dissolution. In our study, this tipping point
371 occurred at a $p\text{CO}_2$ and temperature increase of 271 μatm and 0.75° C. Further, our
372 results showed that G_{day} and G_{night} in a natural coral rubble community have different

373 functional responses to changing pCO₂ and temperature (Figure 3). The ranges in G_{day}
374 and G_{night} in our aquaria were similar to *in situ* rates on Hawaiian rubble reefs. Yates &
375 Halley (2006) saw G_{day} values between 3.3 to 11.7 mmol CaCO₃ m⁻² d⁻¹ and G_{night} values
376 between -2.4 to -24 mmol CaCO₃ m⁻² d⁻¹ on a Moloka'i reef flat with only coral rubble
377 (Note that Yates and Halley calculated G over a 4 hour timeframes and the data was
378 multiplied by 3 here to show G in mmol m⁻² d⁻¹. Also note that we normalized our rates to
379 the surface area of the rubble while Yates and Halley (2006) normalized their rates to
380 planar surface area.). G_{day} and G_{night} in our experiment ranged from 1.9 to 9.4 and -1.3 to
381 -10.5 mmol CaCO₃ m⁻² d⁻¹, respectively, across all treatment conditions. The higher
382 dissolution rates in the *in situ* study by Yates and Halley (2006) are likely due to
383 dissolution in the sediment, which was not present in our study.

384 G_{day} had a non-linear response to Standardized Climate Change. G_{day} increased
385 with temperature-pCO₂ until slightly above ambient conditions, and then decreased under
386 more extreme climate conditions (Figure 3a). This mixed response, increasing and then
387 decreasing with Standardized Climate Change, is reflected in prior experiments. We
388 suggest three possible mechanisms to explain why calcification increases in slightly
389 higher temperature-pCO₂ than ambient conditions. 1) Some calcifiers can maintain and
390 even increase their calcification rates in acidic conditions (Kamenos et al., 2013; Findlay
391 et al., 2011; Rodolfo-Metalpa et al., 2011; Martin et al., 2013) by either modifying their
392 local pH environment (Hurd et al., 2011) or partitioning their energetic resources towards
393 calcification (Kamenos et al., 2013). For example, in low, stable pH conditions the
394 coralline algae, *Lithothamnion glaciale*, increased its calcification rate relative to a
395 control treatment but, did not concurrently increase its rate of photosynthesis (Kamenos

396 et al., 2013). Kamenos et al (2013) suggest that the up-regulation of calcification may
397 limit photosynthetic efficiency. In the present study, the increase in G_{day} coincided with a
398 decrease in net photosynthesis (Figure 3a,b). Photosynthesizing calcifiers in the
399 community may be partitioning their energetic resources more towards calcification and
400 away from photosynthesis in order to maintain a positive calcification rate (Kamenos et
401 al., 2013). Notably, turf algae likely have a major control over the NCP in this
402 community which would not have any impact on calcification. 2) An alternative
403 hypothesis is that the calcifiers may be adapted or acclimatized to high $p\text{CO}_2$ conditions
404 (Johnson et al., 2014) and have not yet reached their threshold because the rubble was
405 collected from a naturally high and variable $p\text{CO}_2$ environment (Guadayol et al., 2014;
406 Silbiger et al. 2014). 3) In this study, the calcifiers experienced a combined increase in
407 both $p\text{CO}_2$ and temperature and, thus, the non-linear response in G_{day} may also be due a
408 metabolic response. In a typical thermal performance curve, organisms increase their
409 metabolism until they have reached a thermal maximum and then rapidly decline (Huey
410 and Kingsolver, 1989; Pörtner et al., 2006), and we see this response in our results. A
411 recent study found a similar nonlinear response to temperature and $p\text{CO}_2$ in the coral
412 *Siderastrea sidera* (Castillo et al. 2014). While they attribute the $p\text{CO}_2$ response to
413 photosynthesis being neutralized (we did not see this response in our non-coral
414 community), they suggest that the thermal response is due to both changes in metabolism
415 and thermally-driven changes in aragonite saturation state (Castillo et al. 2014).

416 We saw a decline in both calcification and NCP in the extreme temperature- $p\text{CO}_2$
417 condition (Figure 3). Calcification has been shown to decline with climate stressors and
418 the magnitude of decline differs across species (Kroeker et al., 2010; Pandolfi et al.,

419 2011;Ries et al., 2009;Kroeker et al., 2013). The concurrent decline in NCP and
420 calcification (Figure 3a,b & 4) suggests that non-photosynthesizing invertebrates in the
421 community (such as bivalves) might be dominating the calcification signal in these
422 conditions. This hypothesis would explain the pattern that we see in Figure 4, where
423 communities in the most extreme pCO₂ and temperature conditions are net respiring
424 during the day while still maintaining a small, positive calcification rate (Figure 4a: five
425 points in the upper left quadrant).

426 G_{night} rates are more straightforward, decreasing linearly with pCO₂ and
427 temperature (Figures 3c and 4). NCP_{night} rates also decreased linearly with pCO₂ and
428 temperature (Figure 3d). Similarly, Andersson et al. (2009) saw an increase in dissolution
429 under acidic conditions in a community of corals, sand, and CCA. Previous studies on
430 individual bioeroder taxa have also found higher rates of bioerosion or dissolution in
431 more acidic, higher temperature conditions (Wisshak et al., 2013;Fang et al., 2013;Reyes-
432 Nivia et al., 2013;Tribollet et al., 2009;Wisshak et al., 2012). There are several
433 mechanisms that could be mediating the increased dissolution rates in the high
434 temperature-pCO₂ treatments: 1) Higher temperatures could increase the metabolism of
435 the bioeroder community, thus increasing borer activity (e.g., Davidson et al. 2013). 2)
436 Because many boring organisms excrete acidic compounds to erode the skeletal structure
437 (Hutchings 1986), reduced pH in the overlaying water column may reduce the metabolic
438 cost to the organisms, making it easier for eroders to breakdown the CaCO₃. 3) Higher
439 dissolution rates could be mediated by an increase in the proportion of dolomite in the
440 skeletal structure of CCA on the rubble. A recent study found a 200% increase in
441 dolomite in CCA that were exposed to high pCO₂ and temperature conditions; this

442 increase in dolomite resulted in increased bioerosion by endolithic algae (Diaz-Pulido et
443 al., 2014). However, it is unlikely that changes in the mineralogy of the CCA indirectly
444 increased dissolution here given the short time-scale of our study. In the present study,
445 we used the TA anomaly method to calculate chemical dissolution as a proxy for
446 bioerosion. Future studies should also include measures of mechanical breakdown (e.g.
447 the production of sponge chips) in addition to chemical dissolution for a more complete
448 picture of the impacts of climate stress on reef breakdown. Studies, including the present
449 one, which focused on community-level responses, have consistently found that ocean
450 acidification will increase dissolution rates on coral reefs (Andersson and Gledhill, 2013).

451 Standardized Climate Change explained more of the variance in dissolution than
452 in calcification in our rubble community: ($R_{G_{night}}^2 = 0.64 > R_{G_{day}}^2 = 0.33$; Table 2) this
453 result is not surprising. Bioerosion, an important driver of dissolution, may be more
454 sensitive to changes in ocean acidity than calcification, leading to net dissolution in high
455 CO₂ waters. Many boring organisms excrete acidic compounds, which may be less
456 metabolically costly in a low pH environment. Erez et al. (2011) hypothesize that
457 increased dissolution, rather than decreased calcification, maybe be the reason that net
458 coral reef calcification is sensitive to ocean acidification. The results of this study support
459 this hypothesis. Although G_{net} declines linearly with pCO₂-temperature, calcification
460 (G_{day}) and dissolution (G_{night}) have distinct responses to Standardized Climate Change:
461 G_{day} had a non-linear response while G_{night} declined linearly with Standardized Climate
462 Change. Our results highlight the need to study the effects of climate stressors on both
463 calcification and dissolution.

464 **Author contributions:**

465 Conceived and designed the experiments: NJS MJD. Performed the experiments: NJS.

466 Analyzed the data: NJS MJD. Wrote the paper: NJS MJD.

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482

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706 Table 1: Means and standard errors of all measured parameters by rack. pCO_2 , HCO_3^- , CO_3^{2-} , DIC, and Ω_{arag} were all calculated from
707 the measured TA and pH samples using CO2SYS. Each table entry is the mean of 12 water samples: one daytime sample and one
708 nighttime sample for six aquaria within a rack. Data are all from the imposed treatment conditions with no rubble inside the aquaria.

Rack	Pre-industrial	Present Day	2050 prediction	2100 prediction
Temp (°C)	23.8±0.07	24.8±0.08	26.2±0.06	27.2±0.08
Salinity	35.65±0.01	35.71±0.02	35.62±0.02	35.71±0.02
Total Alkalinity ($\mu\text{mol kg}^{-1}$)	2137±1.7	2138±2.3	2139±2.0	2142±1.9
pH_t	8.02±0.02	7.87±0.01	7.74±0.02	7.67±0.02
pCO₂ (μatm)	409±20.0	614±15.6	868±33.0	1047±38.7
HCO₃⁻ ($\mu\text{mol kg}^{-1}$)	1692±16.9	1815±7.3	1894±7.8	1939±6.6
CO₃²⁻ ($\mu\text{mol kg}^{-1}$)	194.20±6.7	147.08±2.8	113.98±3.8	99.24±3.3
DIC ($\mu\text{mol kg}^{-1}$)	1898±10.9	1980±5.1	2032±5.0	2067±4.5
Ω_{arag}	3.06±0.1	2.32±0.04	1.80±0.06	1.57±0.05
NO₂⁻ ($\mu\text{mol L}^{-1}$)	0.082 ± 0.0028	0.078 ± 0.0045	0.074 ± 0.0047	0.070 ± 0.0051
PO₄³⁻ ($\mu\text{mol L}^{-1}$)	0.017 ± 0.014	0.0097 ± 0.0081	0.033 ± 0.016	0.018±0.0061
Si(OH)₄ ($\mu\text{mol L}^{-1}$)	3.60 ± 0.58	3.64 ± 0.61	3.88 ± 0.49	3.78 ± 0.52
NH₄⁺ ($\mu\text{mol L}^{-1}$)	0.45 ± 0.30	0.19 ± 0.067	0.23 ± 0.15	0.34 ± 0.14
NO₃⁻ ($\mu\text{mol L}^{-1}$)	2.13±0.20	2.25±0.21	2.55±0.10	2.48±0.11

709 Table 2: Regression results for the treatment experiments: G_{day} , G_{night} , and G_{net} versus
710 Standardized Climate Change (Figure 3a,c,e) and NCP_{day} , NCP_{night} , and NCP_{net} versus
711 Standardized Climate Change (Figure 3b,d,f). Bold values indicate a statistically significant
712 p-value at an $\alpha < 0.05$.

	SS	df	F	p	R ²
G_{day}					
Standardized Climate Change	3.79	1	1.45	0.06	
(Standardized Climate Change) ²	23.63	1	9.04	0.007	
Error	54.89	21			0.33
G_{night}					
Standardized Climate Change	67.80	1	39.14	<0.0001	
Error	38.11	22			0.64
G_{net}					
Standardized Climate Change	88.01	1	19.49	<0.001	
Error	99.35	22			0.47
NCP_{day}					
Standardized Climate Change	5687.2	1	57.36	<0.0001	
Error	2181.4	22			0.72
NCP_{night}					
Standardized Climate Change	3816.1	1	52.06	<0.0001	
Error	1612.6	22			0.70
NCP_{net}					
Standardized Climate Change	17925	1	121.47	<0.0001	
Error	3246.4	22			0.85

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715 **Figure legends:**

716 **Figure 1:** A schematic of the mesocosm system at the Hawai‘i Institute of Marine Biology.
717 Ambient seawater is pumped into the system from a nearby fringing reef in Kāne‘ohe Bay.
718 The seawater is filtered with a sand trap filter, passed through a water chiller and then fed into
719 one of four header tanks. pCO₂ is manipulated in each header tank by bubbling a mixture of
720 CO₂-free air and pure CO₂ to the desired concentration. The water from one header tank flows
721 into 6 aquaria (a rack). Light is controlled by rack with metal-halide lights. There are two
722 metal-halide lights per rack with each light oscillating over a set of three aquaria. Flow and
723 temperature are controlled in each individual aquarium with flow valves and aquarium heaters
724 and coolers, respectively.

725 **Figure 2:** pCO₂ and temperature in each aquarium (a) without any rubble present and (b) with
726 rubble present. Daily variability in pCO₂ was higher when rubble was present due to
727 feedbacks from the rubble community (note the different x-axis scales in panels a and b).
728 Panel (c) shows the mean difference between day and night pCO₂ with and without rubble
729 present with observations paired by aquarium (error bars are standard error) ($t_{23} = -7.23$,
730 $p < 0.0001$).

731 **Figure 3:** Net ecosystem calcification ((a) G_{day} , (c) G_{night} , (e) and G_{net}) and net community
732 production ((b) NCP_{day} , (d) $\text{NCP}_{\text{night}}$, and (f) NCP_{net}) versus Standardized Climate Change
733 (SCC). Each point represents net ecosystem calcification (left panel) or net community
734 production (right panel) calculated from an individual aquarium. Standardized Climate
735 Change was centered around background seawater conditions such that a value of 0 indicated
736 that there was no change in pCO₂ or temperature. Positive values indicate an elevated pCO₂
737 and temperature condition relative to background and negative values represent lower pCO₂
738 and temperature conditions. G_{day} had a non-linear relationship with Standardized Climate

739 Change ($y = -0.27x^2 + 0.59x + 5.7$), while G_{night} ($y = -0.63x - 3.6$) and G_{net} ($y = -0.76x + 1.1$)
740 each had a negative linear relationship with Standardized Climate Change (Table 2). NCP_{day}
741 ($y = -7.01x + 23.4$), NCP_{night} ($y = -35.76 - 4.74$), and NCP_{net} ($y = -12.07x - 10.85$) all had
742 significant negative relationships with Standardized Climate Change. Black lines are best fit
743 lines for each model with 95% confidence intervals in gray. The x's on the top panel represent
744 the imposed conditions for Pre-industrial, Present Day, 2050, and 2100. The black horizontal
745 line in panels (b), (e) and (f) shows the point where G and NCP = 0. Points above the line
746 are net calcifying (e) or net photosynthesizing (f) and points below the line are net dissolving
747 (e) or net respiring (f) over the entire 24 hour period.

748 **Figure 4:** (a) Calculated G and NCP rates for all treatment aquaria. Squares are data collected
749 during light (day) conditions and circles represent data collected during dark (night)
750 conditions, and the color represents Standardized Climate Change (color bar). There is a
751 strong positive relationship between G and NCP ($y = 0.14x + 1.9$, $p < 0.0001$, $R^2 = 0.85$).
752 Negative and positive y-values are net dissolution and net calcification, respectively; negative
753 and positive x-values are net respiration and net photosynthesis, respectively. (b) TA versus
754 DIC: There is a strong positive relationship between TA and DIC ($y = 0.31x + 1577.4$,
755 $p < 0.0001$, $R^2 = 0.85$). Black and gray lines represent the best-fit line and 95% confidence
756 intervals, respectively. As expected, the slope of TA versus DIC (0.31) is approximately twice
757 that of G versus NCP (0.14).

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