

1 Author Response to Reviewers

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3 *Note: All changes to the text are highlighted in blue.

4 5 Reviewer #1

6 **Comment:** However, the paper lacks general flow, appearing poorly written in some sections (e.g. the introduction is redundant).

7
8 **Answer:** We have re-worded several sections in the introduction for easier reading.

9 **Comment:** Because of the simplicity of the analyses, it would be interesting the addition of other
10 treatments and not only of the range ecologically relevant used. Extreme values of temperature and
11 pCO₂ could consolidate the conclusions that neither temperature nor pCO₂ affected mineralogy on
12 coral recruits.

13 **Answer:** This experiment was designed as part of a larger study looking at the impacts of
14 ecologically relevant temperature and pCO₂ treatments on larval and juvenile coral physiology. We
15 chose to use values that are relevant to what corals will be subjected to in the near future in order to
16 provide practical insights into their ability to adapt and survive. Although we chose to use only
17 ecologically relevant values for this study, Reviewer #1 is correct in suggesting that effects of
18 temperature and pCO₂ on mineralogy under extreme conditions could be investigated and perhaps a
19 change in mineralogy would be observed. We have added the following section to the Discussion to
20 acknowledge this: "Both the elevated temperature and elevated pCO₂ conditions applied in this
21 study were ecologically relevant values, chosen to correspond to future projections for atmospheric
22 CO₂ by 2100, under a business-as-usual (RCP 8.5) emissions scenario (Meinshausen et al., 2011;
23 IPCC, 2013). However, applying more extreme values for both temperature and pCO₂ could
24 potentially identify changes in the mineralogy under extreme conditions."

25 **Comment:** In the discussion not much debate is posed about ecologically implication for coral
26 recruits survival: how these organisms without the production of calcitic skeletons can face out to
27 future scenarios of "calcite sea" conditions?

28 **Answer:** We have added the following to the Discussion: "It is likely that new coral recruits will
29 continue to produce aragonitic skeletons under future emissions scenarios, however at reduced
30 calcification rates (Cohen et al., 2009; Anlauf et al., 2011; Foster et al., 2015a) and forming
31 skeletons that are smaller, malformed and show evidence of dissolution (Foster et al., 2015b).
32 Recruits require high calcification rates and robust skeletons to both maintain their position on the
33 substrate as they compete with other benthic organisms for space (Dunstan and Johnson 1998), and
34 also to rapidly outgrow the high mortality rates of the smallest and most vulnerable size classes
35 (Babcock 1991; Babcock and Mundy 1996; Doropoulos et al., 2012). Reduced calcification rates
36 and more soluble aragonitic skeletons will have implications for the longer-term survival of young
37 corals, as these factors will increase mortality rates in the early stages of growth and development
38 thereby reducing the numbers of recruits that survive into adulthood."
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40 Reviewer #2

41
42 The paper by Foster & Clode focuses on skeletal mineralogy of juvenile skeletons of scleractinian
43 corals (*Acropora spicifera*) grown under high temperature (elevated by +3°C) and high pCO₂ levels
44 (~900 μatm). The main rationale for using this experimental setting was to check if "modern
45 aragonitic corals, like their ancestors, are able to produce calcite in response to changing seawater
46 chemistry". Aragonite has higher solubility than calcite hence if corals would have plasticity to
47 adapt and produce calcite skeleton under high pCO₂ they would be less vulnerable to anthropogenic
48 ocean acidification. There are two aspects that should be better commented in the paper:
49

50 Comment 1

51 It is not clearly explained what are the values of pCO₂ and the temperature that could - theoretically
52 - induce inorganic calcite precipitation at modern 5.1 mol/mol Mg/Ca seawater ratio. Noteworthy,

53 the experiments with inorganic calcium carbonate precipitation (with noticeable effects on CaCO₃
54 polymorphism) were performed by Lee & Morse (2010: *Geology* 38:115-118) at different pCO₂
55 levels but at really low Mg/Ca values (1.2 mol/mol and 1.7 mol/mol). Also Balthasar and Cusack
56 (2015: *Geology* 43:99–102) showed that none of the carbonic acid parameters had a noticeable
57 systematic influence on CaCO₃ polymorph proportions, thus suggesting that these influences were
58 overprinted by Mg/Ca and temperature. In turn, Fine & Tchernov (2007: *Science* 315:1811) showed
59 that in highly acidic waters (pH values of 7.3 to 7.6 for 12 months) skeleton of *Oculina patagonica*
60 was completely dissolved but polyps maintained basic life functions as skeleton-less
61 ecophenotypes. This experiment points to a lack of strong functional significance of the skeleton for
62 the animal in experimental, aquarium conditions (opposite to real reef environment) and suggests
63 that corals in highly acidic waters will rather lose the skeleton (skeleton will be dissolved) than they
64 will keep it inducing its mineralogical change. The experiment would be perhaps more interesting
65 if the authors would test Mg/Ca and pCO₂ values as in Lee & Morse (2010) experiments that in
66 "inorganic world" promote calcite over aragonite precipitation.

67
68 **Answer 1:**

69 We agree with Reviewer #2 that we need to further discuss the role of Mg/Ca ratio and how our
70 high or modern Mg/Ca ratios would likely influence mineralogy. This experiment was part of a
71 larger experiment investigating the impacts of acidification and temperature on juvenile
72 calcification. In the other assays (Foster et al 2015a and 2015b) we saw a strong negative impact of
73 high pCO₂ on juvenile calcification. This is discussed further in the response to Comment 2.

74
75 As Reviewer #2 suggests, studies investigating inorganic CaCO₃ precipitation have found that
76 calcite is only produced at low seawater Mg/Ca ratios (Lee and Morse 2010, Balthasar and Cusack
77 2015), thus in the context of inorganic precipitation it was unlikely that our newly settled coral
78 recruits would produce calcite at modern Mg/Ca ratios, even under high pCO₂ conditions. However,
79 constraints on inorganic precipitation are only applicable to living organisms up to a point, as
80 animals such as corals (adults) are able to adjust their internal chemistry. Also, given the lack of
81 studies on the mineralogy of newly recruited corals, the confusion surrounding their mineralogy in
82 early works (Wainwright, 1963; Vandermeulen and Wantabe, 1973) and the body of recent studies
83 that have shown that corals (and other invertebrates) appear to have more plasticity in the early life
84 stages and thus a higher potential for coping with change (Byrne and Przeslawski 2013; Moya et al
85 2015; Foster et al 2015a), we thought it worthwhile to re-visit juvenile mineralogy and check if
86 calcite formation was possible under high pCO₂ alone *i.e* with unaltered Mg/Ca ratios. We have
87 added the following to consider inorganic calcite precipitation:

88 “The polymorphism of abiotically precipitated calcium carbonate varies with both temperature and
89 pCO₂, but occurs only at low Mg/Ca ratios (Lee and Morse, 2010; Balthasar and Cusack, 2015).
90 However less is known about the polymorphism of biologically precipitated CaCO₃.”

91
92 We have confirmed that high pCO₂ alone does not appear to impact juvenile skeletal mineralogy.
93 As Reviewer #2 suggests, it would be interesting to now test the impacts of both high pCO₂ and low
94 Mg/Ca ratio. We have made this suggestion in both our Abstract and Discussion sections:

95
96 **Abstract:**

97 “An important area for prospective research would be to investigate the combined impact of high
98 pCO₂ and reduced Mg/Ca ratio on coral skeletal mineralogy.”

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101 **Discussion:**

102 “While coral recruits exposed to extremely reduced Mg/Ca ratios still produced predominantly
103 aragonite skeletons (Higuchi et al., 2014), the combined impact of elevated pCO₂ and reduced
104 Mg/Ca ratio on the skeletal mineralogy of new recruits is yet to be tested. Since pCO₂ and Mg/Ca

105 ratio have varied approximately inversely proportionally to one another over geological time (Reis,
106 2010; 2011), this would be an interesting direction for future research. Certainly if elevated $p\text{CO}_2$
107 and concomitant reductions in Mg/Ca ratio are driving the ocean towards “calcite sea” conditions
108 (Andersson et al., 2008), then studying the impact of both acidified and low Mg/Ca ratio conditions
109 on skeletal mineralogy is necessary.”

110

111 **Comment 2**

112 Even if skeletal mineralogy of solitary Cretaceous coral *Coelosmilia* described by Stolarski et al.
113 (2007: *Science* 318: 92-94) was originally calcitic, there is no reason to believe that all corals share
114 “ancient ability (...) to produce entirely calcitic skeleton”. Especially *Acropora* which is
115 phylogenetically very distant from Cretaceous solitary “caryophyllid” *Coelosmilia*. There are many
116 coral lineages that in the Cretaceous formed aragonitic skeletons under highly reduced Mg/Ca ratio
117 conditions (e.g., Sorauf 1999: *J Paleontol* 73:1029–1041); it is therefore more likely that coral
118 response to environmental change is taxon-specific. Such taxon-specific response to ocean
119 acidification (skeleton dissolution not mineralogical change) was actually showed by Rodolfo-
120 Metalpa et al. (2011: *Nature Climate Change* 1:308–312): *Cladocora caespitosa* (large parts of the
121 skeleton exposed) showed clear marks of dissolution, whereas *Balanophyllia europaea* (skeleton
122 completely covered in tissue) was unaffected.

123

124 **Answer 2:**

125 We have revised the wording “ancient ability” in the Discussion. It now reads:

126 “...suggesting that the ability of some corals in the fossil record to produce entirely calcitic
127 skeletons (Stolarski et al., 2007), may not have been solely controlled by the Mg/Ca ratio of
128 seawater.”

129

130 We agree that the differences between taxa need to be considered and have added the following
131 sentence to the Discussion:

132 “However it should also be noted that other coral lineages in the Cretaceous formed entirely
133 aragonitic skeletons, even under highly reduced Mg/Ca ratios (Sorauf 1999).”

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135 We also agree with Reviewer #2 that dissolution and reduced skeletal deposition are more likely
136 outcomes than a change in mineralogy under elevated $p\text{CO}_2$. Indeed we have shown in other work
137 (Foster et al 2015b) that elevations in $p\text{CO}_2$ to 900 uatm can have severe impacts on calcification
138 and that skeletal surfaces show evidence of dissolution in newly settled coral recruits even when a
139 layer of tissue is present (as opposed to the adult corals in Rodolfo-Metalpa et al 2011, which only
140 showed signs of dissolution in species with sections of the skeleton exposed). Therefore we have
141 added the following section to the Discussion to highlight the likely reduction in skeletal deposition
142 under future $p\text{CO}_2$ scenarios:

143 “It is likely that new coral recruits will continue to produce aragonitic skeletons under future
144 emissions scenarios, however at reduced calcification rates (Cohen et al., 2009; Anlauf et al., 2011;
145 Foster et al., 2015a) and forming skeletons that are smaller, malformed and show evidence of
146 dissolution (Foster et al., 2015b). Recruits require high calcification rates and robust skeletons to
147 both maintain their position on the substrate as they compete with other benthic organisms for space
148 (Dunstan and Johnson 1998), and also to rapidly outgrow the high mortality rates of the smallest
149 and most vulnerable size classes (Babcock 1991; Babcock and Mundy 1996; Doropoulos et al.,
150 2012). Reduced calcification rates and more soluble aragonitic skeletons will have implications for
151 the longer-term survival of young corals, as these factors will increase mortality rates in the early
152 stages of growth and development thereby reducing the numbers of recruits that survive into
153 adulthood.”

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155

156 **Skeletal mineralogy of coral recruits under high temperature and $p\text{CO}_2$**

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184 **Abstract**

185 Aragonite, which is the polymorph of CaCO_3 precipitated by modern corals during skeletal
186 formation, has a higher solubility than the more stable polymorph calcite. This higher solubility
187 may leave animals that produce aragonitic skeletons more vulnerable to anthropogenic ocean
188 acidification. It is therefore important to determine whether scleractinian corals have the plasticity
189 to adapt and produce calcite in their skeletons in response to changing environmental conditions.
190 Both high $p\text{CO}_2$ and lower Mg/Ca ratios in seawater are thought to have driven changes in the
191 skeletal mineralogy of major marine calcifiers in the past ~540 Ma. Experimentally reduced Mg/Ca
192 ratios in ambient seawater have been shown to induce some calcite precipitation in both adult and
193 newly settled modern corals; however, the impact of high $p\text{CO}_2$ on the mineralogy of recruits is
194 unknown. Here we determined the skeletal mineralogy of one-month old *Acropora spicifera* coral
195 recruits grown under high temperature (+3°C) and $p\text{CO}_2$ (~900 μatm) conditions, using X-ray
196 diffraction and Raman spectroscopy. We found that newly settled coral recruits produced entirely
197 aragonitic skeletons regardless of the treatment. Our results show that elevated $p\text{CO}_2$ alone is
198 unlikely to drive changes in the skeletal mineralogy of young corals. Not having an ability to switch
199 from aragonite to calcite precipitation may leave corals and ultimately coral reef ecosystems more
200 susceptible to predicted ocean acidification. An important area for prospective research would be to
201 investigate the combined impact of high $p\text{CO}_2$ and reduced Mg/Ca ratio on coral skeletal
202 mineralogy.

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209 1 Introduction

210 Scleractinian corals are the major reef builders, with their skeletons providing the structural basis
211 for the habitats of many marine organisms. In modern adult corals, the skeletons are comprised of
212 aragonite, a polymorph of calcium carbonate (CaCO_3) whose stability is highly sensitive to changes
213 in ocean $p\text{CO}_2$ (Orr et al., 2005; Feely et al., 2009). However, examination of a 70 million year old
214 scleractinian coral fossil showed that some ancient corals were able to produce skeletons entirely of
215 calcite (Stolarski et al., 2007), the most stable and least soluble polymorph of CaCO_3 (de Leeuw et
216 al., 1998; Boulos et al., 2014). Throughout the Phanerozoic (past 540 Ma), there have been
217 oscillations between calcite and aragonite as the dominant polymorph precipitated by major reef
218 building organisms. During this time period there have been three aragonite-facilitating periods or
219 “aragonite seas” and two calcite-facilitating periods or “calcite seas”. The cause of these transitions
220 in mineralogy has been the topic of much debate over the past 30 years. One of the most important
221 factors affecting skeletal mineralogy is the magnesium to calcium ratio (Mg/Ca) of seawater
222 (Sandberg, 1983; Ries, 2010). If the Mg/Ca >2 , then aragonite is predominantly precipitated and if
223 the Mg/Ca <2 , then calcite is predominantly precipitated. Currently conditions favour aragonite
224 precipitation, with modern seawater having a Mg/Ca ratio of 5.2 (Lowenstein et al., 2001). A
225 recent study found CaCO_3 polymorph precipitation to be a function of both Mg/Ca ratio and
226 temperature, with aragonite precipitated at high temperature and Mg/Ca ratio and calcite
227 precipitated at low temperature and Mg/Ca ratio (Balthasar and Cusack, 2015). Changes in
228 atmospheric $p\text{CO}_2$ are also thought to contribute to changes in skeletal mineralogy (Sandberg, 1983;
229 Zhuravlev and Wood, 2009; Lee and Morse, 2010), with rising $p\text{CO}_2$ and subsequent reductions in
230 carbonate saturation state, potentially favouring the precipitation of minerals with higher stability
231 and lower Mg content, such as calcite (Morse et al., 2006; Zhuravlev and Wood, 2009). The
232 polymorphism of abiotically precipitated calcium carbonate varies with both temperature and $p\text{CO}_2$,
233 but occurs only at low Mg/Ca ratios (Lee and Morse, 2010; Balthasar and Cusack, 2015). However
234 less is known about the polymorphism of biologically precipitated CaCO_3 . If ocean acidification

235 favours the deposition of more stable carbonate minerals such as calcite (Mackenzie et al., 1983;
236 Morse et al., 2006; Andersson et al., 2008), then organisms producing less stable aragonite
237 skeletons will likely be more vulnerable to changes in ocean chemistry under high $p\text{CO}_2$.
238 Alternatively, organisms will be much less vulnerable if, under high $p\text{CO}_2$ conditions, they have the
239 ability to switch from predominantly aragonite to calcite precipitation, especially in their early
240 developmental stages.

241

242 It is therefore important to determine whether modern aragonitic corals, like their ancestors, are
243 able to produce calcite in response to changing seawater chemistry. Initial work on coral skeletal
244 mineralogy reported the presence of calcite in modern corals (Houck et al., 1975; Constanz and
245 Meike, 1990), however contamination by diagenetic recrystallization (Nothdurft and Webb, 2009)
246 and deposits from microboring organisms (Nothdurft et al., 2007) and coralline algae (Goffredo et
247 al., 2012) were later proposed to be the source of the calcite, rather than primary calcitic formation
248 by the coral. Adult corals grown under low Mg/Ca ratios simulating “calcite seas”, have been
249 shown to produce significant amounts of calcite (Reis et al., 2006), however again, some of this
250 calcite production may be due to secondary infilling of pore spaces (Reis et al., 2006; Ries, 2010).
251 Nevertheless it is accepted that modern adult corals grown under current ambient conditions have
252 entirely aragonitic skeletons (Cuif et al., 1999).

253

254 Much less is known about the mineralogy of corals in the early post-recruitment phases. Early work
255 on the mineralogy of new recruits reported the presence of calcite in only the very early post-
256 settlement stages (Wainwright, 1963; Vandermeulen and Wantabe, 1973), leading to the
257 assumption that unlike adults, newly settled recruits were able to precipitate both calcite and
258 aragonite under ambient conditions (Goffredo et al., 2012). However, new recruits of *Acropora*
259 *millepora* grown under carefully controlled ambient conditions did not show any evidence of calcite
260 in their skeleton (Clode et al., 2011) with these authors concluding that initial reports of calcite in

261 recruits was also likely to be artefactual. Similarly, an experiment growing new recruits under a
262 range of seawater Mg/Ca ratios, reported that even under the lowest Mg/Ca ratio (0.5), the skeletal
263 mineralogy was still dominated by aragonite and under current ambient conditions (Mg/Ca ratio =
264 5.3) skeletons were composed entirely of aragonite (Higuchi et al., 2014). Interestingly however,
265 this study confirmed that coral recruits are capable of producing some primary calcite in their
266 skeletons if the water chemistry is adjusted to “calcite sea” conditions (low Mg/Ca).

267

268 The impact of elevated $p\text{CO}_2$ on the skeletal mineralogy of new recruits is yet to be investigated.
269 Here we tested whether the treatment conditions of high temperature, high $p\text{CO}_2$, or a combination
270 of high temperature and high $p\text{CO}_2$, affected the skeletal mineralogy of newly settled corals.
271 Specifically, we question whether high $p\text{CO}_2$ and reduced carbonate saturation facilitate the
272 production of calcite within coral recruit skeletons.

273

274 **2 Methods**

275 **2.1 Treatment conditions**

276 A detailed description of the coral culturing methods and experimental set-up is given in Foster et
277 al. (2015a). Briefly, adult *Acropora spicifera* colonies were collected from the Houtman Abrolhos
278 Islands in Western Australia prior to spawning and maintained under ambient conditions ($\sim 24^\circ\text{C}$
279 and pH 8.1). Larvae were similarly cultured and maintained under ambient conditions until they
280 were motile, at which point they were transferred to treatment tanks. Treatment conditions were:
281 ambient temperature and $p\text{CO}_2$ (Control: 24°C , $\sim 250 \mu\text{atm}$), high temperature and ambient $p\text{CO}_2$
282 (high temperature: 27°C , $\sim 250 \mu\text{atm}$), ambient temperature and high $p\text{CO}_2$ (high $p\text{CO}_2$: 24°C , ~ 900
283 μatm) and high temperature plus high $p\text{CO}_2$ (high temperature + $p\text{CO}_2$: 27°C , $\sim 900 \mu\text{atm}$). See
284 Table 1 for more detail on the experimental conditions.

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286

287 **2.2 Processing of skeletons**

288 Once the coral larvae had settled, the recruits were grown for 4 weeks under treatment conditions,
289 before the experiment was concluded. To remove organic material, polyps were immersed in 3-7%
290 sodium hypochlorite (NaOCl) and rinsed three times in deionized water. The skeletons were then
291 stored in 100% ethanol until further examination and analysis were possible.

292

293 **2.3 X-ray diffraction analysis**

294 Bulk analysis of the skeletal mineralogy was conducted by obtaining X-ray diffraction (XRD)
295 patterns of the skeletal material. Subsets of 5 juvenile skeletons were randomly selected from each
296 treatment. Skeletons were removed from the ethanol and air dried, then detached from the
297 transparency paper using a scalpel and gently crushed. The crushed skeletal material from each
298 treatment was mounted on a low background holder (off angle piece of single crystal silicon) and
299 attached to a reflection spinner stage. A PANalytical Empyrean X-ray diffractometer was used with
300 $\text{CuK}\alpha$ radiation to record the XRD patterns. The scanning rate was 250 seconds per step in 2 Theta
301 ranging from 10° to 80° , with a step size of 0.006° . XRD patterns of skeletal material were
302 compared to the XRD peaks for ICDS aragonite and calcite standards.

303

304 **2.4 Raman spectroscopy**

305 XRD provides an average analysis for the entire sample, however for calcium carbonate samples
306 Raman spectroscopy has been shown to have lower detection limits and lower rates of errors,
307 though only the surfaces of selected fragments can be analysed at any one time (Kontoyannis and
308 Vagenas, 2000). Therefore, complementary Raman spectroscopy was also used to check the
309 skeletons for the presence of calcite within discreet skeletal fragments. A further 5 skeletons from
310 each treatment were randomly selected and each skeleton was individually analysed. Raman spectra
311 were collected from 10 random areas ($\sim 60 \times 60 \mu\text{m}$) in the crushed skeletal material of each
312 sample, using a 633 nm red Helium neon laser. Spectra were measured every $1 \mu\text{m}$ along the

313 gridded $\sim 60 \mu\text{m}^2$ area (Figure 1) for each of the 10 areas per sample ($\sim 36,000$ individual spectra
314 were taken per sample). Spectra were similarly taken of both a polished calcite standard and a
315 biogenic aragonite standard to use as references.

316

317

318 **3 Results**

319 Calcite was not detected in the XRD patterns of any of the skeletons, regardless of treatment.

320 Prominent peaks were observed at $2\theta \sim 26.2^\circ$ and 27.2° , corresponding with the aragonite

321 standard peaks, while no peaks were observed at $2\theta \sim 29.4^\circ$, the location of the primary calcite

322 peak (Figure 2). After analysing all of the skeletal material using XRD, the more sensitive Raman

323 spectrometry was employed to collect spectra from random fragments of the skeleton. Similarly, no

324 trace of calcite was detected in the spectra of any of the treatments. The calcite standard showed

325 peaks at $154, 281, 713, \text{ and } 1086 \text{ cm}^{-1}$ and the biogenic aragonite standard showed peaks at $154,$

326 $205, 704, \text{ and } 1086 \text{ cm}^{-1}$, which are typical of these polymorphs of CaCO_3 (Dandeu et al., 2006).

327 Since both calcite and aragonite peak at $\sim 154, \sim 710 \text{ and } \sim 1086 \text{ cm}^{-1}$, the peaks of interest were the

328 281 cm^{-1} peak typical of calcite and the 205 cm^{-1} peak typical of aragonite (Dandeu et al., 2006).

329 All spectra from all individuals, across all treatments, exhibited peaks typical of only aragonite

330 mineralogy (Figure 3), with prominent peaks at $\sim 207 \text{ cm}^{-1}$ and no peaks at $\sim 281 \text{ cm}^{-1}$. Both the

331 XRD patterns and Raman spectra collected indicate that neither temperature nor $p\text{CO}_2$ had any

332 effect on the skeletal mineralogy of 1-month old coral recruits, as all skeletons across treatments

333 formed entirely aragonitic skeletons.

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339 4 Discussion

340 Since aragonite is a more soluble polymorph of CaCO_3 than calcite, it would be advantageous for
341 modern corals in a rapidly acidifying ocean to be able to produce calcite. Production of calcite has
342 been shown to be a phenotypically plastic, with many marine calcifiers able to adjust both the
343 proportion of calcite in their shell or skeleton as well as the Mg/Ca ratio (Ries, 2010; 2011). In this
344 study both temperature and $p\text{CO}_2$ were manipulated to assess their impact on skeletal mineralogy of
345 newly settled coral recruits. Neither temperature nor $p\text{CO}_2$ affected mineralogy, with all coral
346 recruits analysed producing entirely aragonitic skeletons. Although temperature has been shown to
347 significantly affect abiotic polymorph precipitation (as a function of Mg/Ca), calcite co-
348 precipitation with aragonite is favoured at cooler temperatures and low Mg/Ca ratios ($<20^\circ\text{C}$,
349 Mg/Ca < 2 , Balthasar and Cusack, 2015). As such, temperature treatments applied in this study (24
350 and 27°C), were within the range of temperatures favouring aragonite production. These
351 temperatures were chosen because they are ecologically relevant to the sub-tropical corals used in
352 this study, under both present ambient and future elevated temperature regimes.

353
354 Predicting the impact of high $p\text{CO}_2$ on polymorph mineralogy is more complex. The extent to
355 which oscillations between “calcite seas” and “aragonite seas” throughout the Phanerozoic were
356 primarily driven by $p\text{CO}_2$ or Mg/Ca ratios has received a lot of attention (see review by Ries, 2010).
357 It is accepted that modern adult corals under current ambient conditions produce skeletons
358 comprised entirely of aragonite (Cuif et al., 1999). Furthermore, despite initial work suggesting that
359 new coral recruits were bimineralic (producing both calcite and aragonite), more recent studies have
360 shown that under ambient conditions recruits produce purely aragonitic skeletons (Clode et al.,
361 2011; Higuchi et al., 2014). However, under reduced Mg/Ca ratios, both adult and newly settled
362 corals are able to produce some calcite (Ries et al., 2006; Higuchi et al., 2014). Despite this ability
363 to switch to a bimineralic skeleton, corals still produce skeletons comprised mainly of aragonite,
364 even under extremely reduced Mg/Ca ratios (Higuchi et al., 2014), suggesting that the ability of

365 some corals in the fossil record to produce entirely calcitic skeletons (Stolarski et al., 2007), may
366 not have been solely controlled by the Mg/Ca ratio of seawater. However it should also be noted
367 that other coral lineages in the Cretaceous formed entirely aragonitic skeletons, even under highly
368 reduced Mg/Ca ratios (Sorauf 1999). The impact of elevated $p\text{CO}_2$ on mineralogy has also been
369 examined for a range of marine calcifiers (Ries, 2011). In bimineralic animals (*e.g.* whelks), the
370 proportion of calcite in the skeleton increased with increasing $p\text{CO}_2$, however in monomineralic
371 animals (entirely aragonitic skeletons), calcite was not incorporated into the skeleton as the $p\text{CO}_2$
372 increased. For the adult temperate coral *Oculina arbuscula*, a range of CO_2 treatments had no
373 impact on skeletal mineralogy, with corals in all treatments producing aragonitic skeletons (Ries et
374 al., 2010). Our study similarly observed no change in skeletal mineralogy under elevated $p\text{CO}_2$ for
375 newly settled corals.

376
377 Both the elevated temperature and elevated $p\text{CO}_2$ conditions applied in this study were ecologically
378 relevant values, chosen to correspond to future projections for atmospheric CO_2 by 2100, under a
379 business-as-usual (RCP 8.5) emissions scenario (Meinshausen et al., 2011; IPCC, 2013). However,
380 applying more extreme values for both temperature and $p\text{CO}_2$ could potentially identify changes in
381 the mineralogy under extreme conditions. Nevertheless, this study is part of a growing body of
382 evidence that indicates that corals do not produce calcite under current ambient or predicted near-
383 future high $p\text{CO}_2$ scenarios, regardless of their life stage. It is likely that new coral recruits will
384 continue to produce aragonitic skeletons under future emissions scenarios, however at reduced
385 calcification rates (Cohen et al., 2009; Anlauf et al., 2011; Foster et al., 2015a) and forming
386 skeletons that are smaller, malformed and show evidence of dissolution (Foster et al., 2015b).
387 Recruits require high calcification rates and robust skeletons to both maintain their position on the
388 substrate as they compete with other benthic organisms for space (Dunstan and Johnson 1998), and
389 also to rapidly outgrow the high mortality rates of the smallest and most vulnerable size classes
390 (Babcock 1991; Babcock and Mundy 1996; Doropoulos et al., 2012). Reduced calcification rates

391 and more soluble aragonitic skeletons will have implications for the longer-term survival of young
392 corals, as these factors will increase mortality rates in the early stages of growth and development
393 thereby reducing the numbers of recruits that survive into adulthood.

394

395 While coral recruits exposed to extremely reduced Mg/Ca ratios still produced predominantly
396 aragonitic skeletons (Higuchi et al., 2014), the combined impact of elevated $p\text{CO}_2$ and reduced
397 Mg/Ca ratio on the skeletal mineralogy of new recruits is yet to be tested. Since $p\text{CO}_2$ and Mg/Ca
398 ratio have varied approximately inversely proportionally to one another over geological time (Reis,
399 2010; 2011), this would be an interesting direction for future research. Certainly if elevated $p\text{CO}_2$
400 and concomitant reductions in Mg/Ca ratio are driving the ocean towards “calcite sea” conditions
401 (Andersson et al., 2008), then it will be important to examine the simultaneous impact of both
402 acidified and low Mg/Ca ratio conditions on coral skeletal mineralogy.

403

404 **Author contribution**

405 T.F. and P.C. designed the experiment, T.F. conducted the experiment, T.F. and P.C. conducted
406 laboratory work, T.F. wrote the manuscript and P.C. reviewed and commented on the manuscript.

407

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530 **Tables**

531

532 **Table 1.** Physical and chemical conditions maintained for the duration of the experiment (mean \pm
533 SD). Table from Foster et al., (2015a).

Treatment	Temperature (°C)	pH _T	TA ($\mu\text{mol kg}^{-1}$)	pCO ₂ (μatm)	Ω_{ar}
Control	24.4 \pm 0.5	8.22 \pm 0.05	2308 \pm 40	242 \pm 22	4.51 \pm 0.14
High temperature	27.6 \pm 0.8	8.18 \pm 0.05	2312 \pm 26	275 \pm 24	4.68 \pm 0.17
High pCO ₂	24.1 \pm 0.6	7.77 \pm 0.06	2307 \pm 30	872 \pm 58	1.93 \pm 0.08
High temperature + pCO ₂	27.4 \pm 0.9	7.75 \pm 0.08	2309 \pm 32	976 \pm 103	2.03 \pm 0.12

534 TA: total alkalinity; pCO₂: partial pressure of carbon dioxide; Ω_{ar} : aragonite saturation state.

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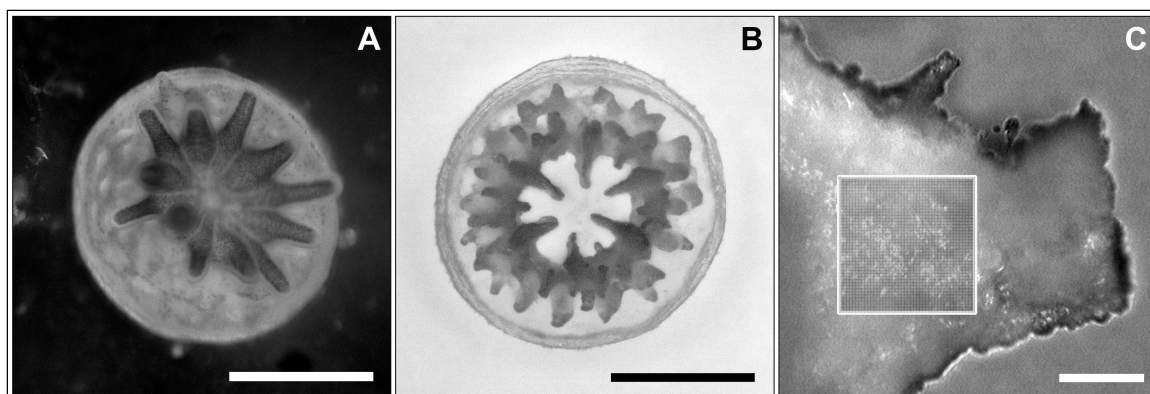
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538 **Figures**

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543 **Figure 1:** One month old living *Acropora spicifera* recruit (A), a typical *Acropora spicifera* recruit

544 skeleton with organic material removed (B) and crushed skeletal material showing a typical ~ 60

545 μm^2 scan area grid analysed by Raman spectroscopy (C). Scale bars for A and B = 500 μm and

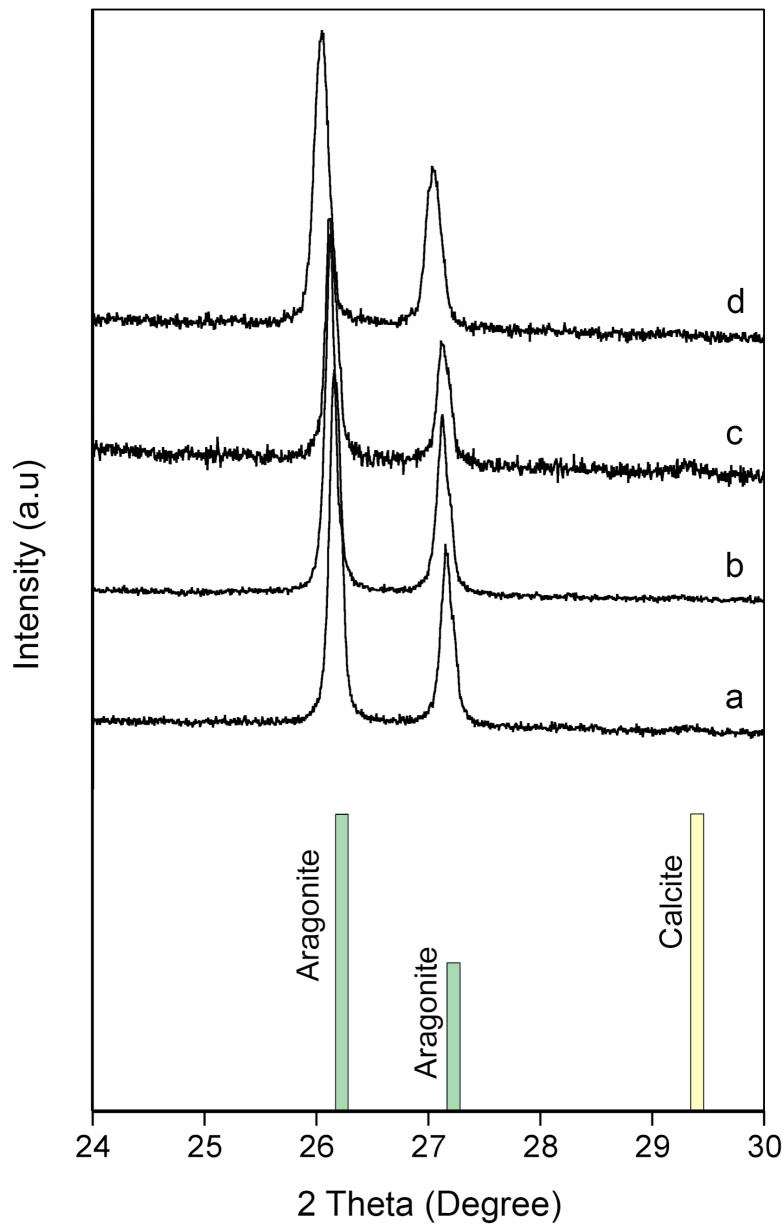
546 scale bar for C = 40 μm .

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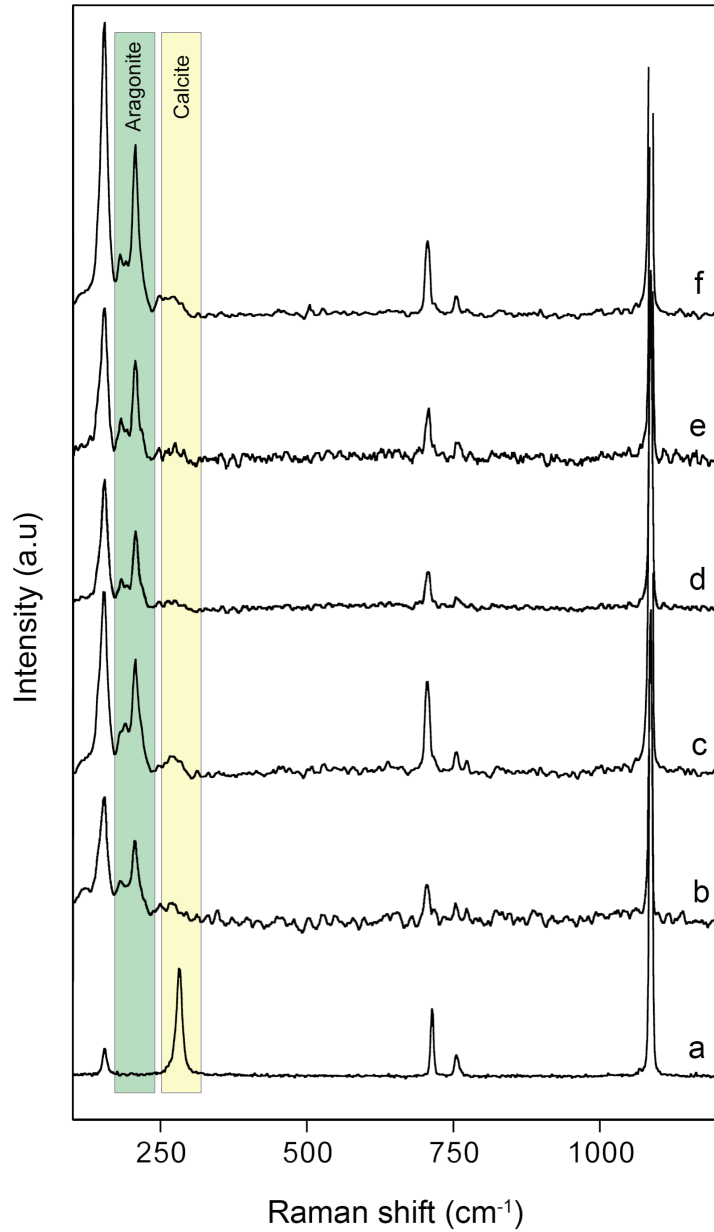
552 **Figure 2.** XRD patterns for *Acropora spicifera* coral recruit skeletons grown under control (a), high
 553 temperature (b), high $p\text{CO}_2$ (c) and high temperature + $p\text{CO}_2$ (d) conditions. Aragonite standard
 554 peaks occur at 26.2° and 27.2° (green bars), and the calcite standard peak occurs at 29.4° (yellow
 555 bar).

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561 **Figure 3:** Specific Raman shift of a calcite standard (**a**) and a biogenic aragonite standard (**b**) and
 562 skeletal material from control (**c**), high temperature (**d**), high $p\text{CO}_2$ (**e**), and high temperature +
 563 $p\text{CO}_2$ (**f**) treated *Acropora spicifera* coral recruits. The ~205 peak specific to aragonite is
 564 highlighted in green and the ~281 peak specific to calcite is highlighted in yellow.

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