

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

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

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Abstract

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

1 Introduction

Scleractinian corals are the major reef builders, with their skeletons providing the structural basis for the habitats of many marine organisms. The skeletons of modern adult corals are comprised of aragonite, a polymorph of calcium carbonate (CaCO_3) whose stability is highly sensitive to changes in ocean $p\text{CO}_2$ (Orr et al., 2005; Feely

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et al., 2009). Interestingly, examination of a 70 million year old scleractinian coral fossil showed that some ancient corals were able to produce skeletons entirely of calcite (Stolarski et al., 2007), the most stable and least soluble polymorph of CaCO_3 (de Leeuw et al., 1998; Boulou et al., 2014). Throughout the Phanerozoic (past 540 myr), there have been oscillations between calcite and aragonite as the dominant polymorph precipitated by major reef building organisms. During this time period there have been three aragonite-facilitating periods or “aragonite seas” and two calcite-facilitating periods or “calcite seas”. The cause of these transitions in mineralogy has been the topic of much debate over the past 30 years. One of the most important factors affecting skeletal mineralogy is the magnesium to calcium ratio (Mg/Ca) of seawater (Sandberg, 1983; Ries, 2010). If the $\text{Mg}/\text{Ca} > 2$, then aragonite is predominantly precipitated (modern seawater $\text{Mg}/\text{Ca} = 5.2$), and if the $\text{Mg}/\text{Ca} < 2$, then calcite is predominantly precipitated (Lowenstein et al., 2001). A recent study found CaCO_3 polymorph precipitation to be a function of both Mg/Ca ratio and temperature, with aragonite precipitated at high temperature and Mg/Ca ratio and calcite precipitated at low temperature and Mg/Ca ratio (Balthasar and Cusack, 2015). Changes in atmospheric $p\text{CO}_2$ are also thought to contribute to changes in skeletal mineralogy (Sandberg, 1983; Zhuravlev and Wood, 2009; Lee and Morse, 2010), with rising $p\text{CO}_2$ and subsequent reductions in carbonate saturation state, potentially favouring the precipitation of minerals with higher stability and lower Mg content, such as calcite (Morse et al., 2006; Zhuravlev and Wood, 2009). If ocean acidification favours the deposition of more stable carbonate minerals such as calcite (Mackenzie et al., 1983; Morse et al., 2006; Andersson et al., 2008), then organisms producing less stable aragonite skeletons will likely be more vulnerable changes in ocean chemistry under high $p\text{CO}_2$. Alternatively, organisms will be much less vulnerable if, under high $p\text{CO}_2$ conditions, they have the ability to switch from predominantly aragonite to calcite precipitation, especially in their early developmental stages.

It is therefore important to determine whether modern aragonitic corals, like their ancestors, are able to produce calcite in response to changing seawater chemistry.

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

Much less is known about the mineralogy of corals in the early post-recruitment phases. Early work on the mineralogy of new recruits reported the presence of calcite in only the very early post-settlement stages (Wainwright, 1963; Vandermeulen and Wantabe, 1973), leading to the assumption that unlike adults, newly settled recruits were able to precipitate both calcite and aragonite under ambient conditions (Goffredo et al., 2012). However, new recruits of *Acropora millepora* grown under carefully controlled ambient conditions did not show any evidence of calcite in their skeleton (Clode et al., 2011) with these authors concluding that initial reports of calcite in recruits was also likely to be artefactual. Similarly, a study (Higuchi et al., 2014) growing new recruits under a range of seawater Mg/Ca ratios, reported that even under the lowest Mg/Ca ratio (0.5), the skeletal mineralogy was still dominated by aragonite and under current ambient conditions (Mg/Ca = 5.3), skeletons were composed entirely of aragonite. Interestingly however, this study confirmed that coral recruits are capable of producing some primary calcite in their skeletons if the water chemistry is adjusted to “calcite sea” conditions (low Mg/Ca).

The impact of elevated $p\text{CO}_2$ on the skeletal mineralogy of new recruits is yet to be investigated. Here we tested whether the treatment conditions of high temperature, high $p\text{CO}_2$, or a combination of high temperature and high $p\text{CO}_2$, affected the skeletal mineralogy of newly settled corals. Specifically, we question whether high $p\text{CO}_2$

and reduced carbonate saturation facilitate the production of calcite within coral recruit skeletons.

2 Methods

2.1 Treatment conditions

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

15 2.2 Processing of skeletons

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

2.3 X-ray diffraction analysis

Bulk analysis of the skeletal mineralogy was conducted by obtaining X-ray diffraction (XRD) patterns of the skeletal material. Subsets of 5 juvenile skeletons were randomly

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selected from each treatment. Skeletons were removed from the ethanol and air dried, then detached from the transparency paper using a scalpel and gently crushed. The crushed skeletal material from each treatment was mounted on a low background holder (off angle piece of single crystal silicon) and attached to a reflection spinner stage. A PANalytical Empyrean X-ray diffractometer was used with $\text{CuK}\alpha$ radiation to record the XRD patterns. The scanning rate was 250 s per step in 2 Theta ranging from 10 to 80°, with a step size of 0.006°. XRD patterns of skeletal material were compared to the XRD peaks for ICDS aragonite and calcite standards.

2.4 Raman spectroscopy

XRD provides an average analysis for the entire sample, however for calcium carbonate samples Raman spectroscopy has been shown to have lower detection limits and lower rates of errors, though only the surfaces of selected fragments can be analysed at any one time (Kontoyannis and Vagenas, 2000). Therefore, complementary Raman spectroscopy was also used to check the skeletons for the presence of calcite within discreet skeletal fragments. A further 5 skeletons from each treatment were randomly selected and each skeleton was individually analysed. Raman spectra were collected from 10 random areas ($\sim 60\ \mu\text{m} \times 60\ \mu\text{m}$) in the crushed skeletal material of each sample, using a 633 nm red Helium neon laser. Spectra were measured every 1 μm along the gridded $\sim 60\ \mu\text{m}^2$ area (Fig. 1) for each of the 10 areas per sample ($\sim 36\ 000$ individual spectra were taken per sample). Spectra were similarly taken of both a polished calcite standard and a biogenic aragonite standard to use as references.

3 Results

Calcite was not detected in the XRD patterns of any of the skeletons, regardless of treatment. Prominent peaks were observed at 2 Theta ~ 26.2 and 27.2° , corresponding with the aragonite standard peaks, while no peaks were observed at 2 Theta $\sim 29.4^\circ$,

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the location of the primary calcite peak (Fig. 2). After analysing all of the skeletal material using XRD, the more sensitive Raman spectrometry was employed to collect spectra from random fragments of the skeleton. Similarly, no trace of calcite was detected in the spectra of any of the treatments. The calcite standard showed peaks at 154, 281, 713, and 1086 cm^{-1} and the biogenic aragonite standard showed peaks at 154, 205, 704, and 1086 cm^{-1} , which are typical of these polymorphs of CaCO_3 (Dandeu et al., 2006). Since both calcite and aragonite peak at ~ 154 , ~ 710 and $\sim 1086 \text{ cm}^{-1}$, the peaks of interest were the 281 cm^{-1} peak typical of calcite and the 205 cm^{-1} peak typical of aragonite (Dandeu et al., 2006). All spectra from all individuals, across all treatments, exhibited peaks typical of only aragonite mineralogy (Fig. 3), with prominent peaks at $\sim 207 \text{ cm}^{-1}$ and no peaks at $\sim 281 \text{ cm}^{-1}$. Both the XRD patterns and Raman spectra collected indicate that neither temperature nor $p\text{CO}_2$ had any effect on the skeletal mineralogy of 1 month old coral recruits, as all skeletons across treatments formed entirely aragonitic skeletons.

4 Discussion

Since aragonite is a more soluble polymorph of CaCO_3 than calcite, it would be advantageous for modern corals in a rapidly acidifying ocean to be able to produce calcite as their ancestors did. Production of calcite has been shown to be a phenotypically plastic, with many marine calcifiers able to adjust both the proportion of calcite in their shell or skeleton as well as the Mg/Ca ratio (Ries, 2010, 2011). In this study both temperature and $p\text{CO}_2$ were manipulated to assess their impact on skeletal mineralogy of newly settled coral recruits. Neither temperature nor $p\text{CO}_2$ affected mineralogy, with all coral recruits analysed producing entirely aragonitic skeletons. Although temperature has been shown to significantly impact abiotic polymorph precipitation (as a function of Mg/Ca), calcite co-precipitation with aragonite is favoured at cooler temperatures ($< 20^\circ\text{C}$, Balthasar and Cusack, 2015). As such, temperature treatments applied in this study (24 and 27°C), were within the range of temperatures favouring aragonite

production. These temperatures were chosen because they are ecologically relevant to the sub-tropical corals used in this study, under both present ambient and future elevated temperature regimes.

The impact of high $p\text{CO}_2$ on polymorph mineralogy is more complex. There has been much work focused on whether the oscillations between “calcite seas” and “aragonite seas” throughout the Phanerozoic were primarily driven by $p\text{CO}_2$ or Mg/Ca ratios (see review by Ries, 2010). It is accepted that modern adult corals under current ambient conditions produce skeletons comprised entirely of aragonite (Cuif et al., 1999). Similarly, despite initial work suggesting that new coral recruits were bimineralic (producing both calcite and aragonite), recent studies have shown that under ambient conditions recruits produce purely aragonitic skeletons (Clode et al., 2011; Higuchi et al., 2014). However, under reduced Mg/Ca ratio conditions, both adult and newly settled corals are able to produce calcite (Ries et al., 2006; Higuchi et al., 2014). Despite this ability to switch to a bimineralic skeleton, corals still produce skeletons comprised mainly of aragonite, even under extremely reduced Mg/Ca ratios (Higuchi et al., 2014), suggesting that the ancient ability of corals to produce entirely calcitic skeletons (Stolarski et al., 2007), is not solely controlled by the Mg/Ca ratio of seawater. The impact of elevated $p\text{CO}_2$ on mineralogy has also been tested for a range of marine calcifiers (Ries, 2011). In animals already bimineralic (e.g. whelks), the proportion of calcite in the skeleton increased with increasing $p\text{CO}_2$, however in monomineralic animals (entirely aragonitic skeletons), calcite was not incorporated into the skeleton as the $p\text{CO}_2$ increased. For the adult temperate coral *Oculina arbuscula*, a range of CO_2 treatments had no impact on skeletal mineralogy, with corals in all treatments producing aragonitic skeletons (Ries et al., 2010). Our study similarly observed no change in skeletal mineralogy under elevated $p\text{CO}_2$ for newly settled corals.

This study is part of a growing body of evidence that indicates that corals do not produce calcite under current ambient or predicted future high $p\text{CO}_2$ scenarios, regardless of their life stage. While coral recruits exposed to extremely reduced Mg/Ca ratios still produced predominantly aragonite skeletons (Higuchi et al., 2014), the com-

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

10 *Author contributions.* T. Foster and P. Clode designed the experiment, T. Foster conducted the experiment, T. Foster and P. Clode conducted laboratory work, T. Foster wrote the manuscript and P. Clode reviewed and commented on the manuscript.

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

| Treatment | Temperature (°C) | pH_7 | TA ($\mu\text{mol kg}^{-1}$) | $p\text{CO}_2$ (μatm) | Ω_{ar} |
|-----------------------------------|------------------|-----------------|--------------------------------|------------------------------------|----------------------|
| Control | 24.4 ± 0.5 | 8.22 ± 0.05 | 2308 ± 40 | 242 ± 22 | 4.51 ± 0.14 |
| High temperature | 27.6 ± 0.8 | 8.18 ± 0.05 | 2312 ± 26 | 275 ± 24 | 4.68 ± 0.17 |
| High $p\text{CO}_2$ | 24.1 ± 0.6 | 7.77 ± 0.06 | 2307 ± 30 | 872 ± 58 | 1.93 ± 0.08 |
| High temperature + $p\text{CO}_2$ | 27.4 ± 0.9 | 7.75 ± 0.08 | 2309 ± 32 | 976 ± 103 | 2.03 ± 0.12 |

TA: total alkalinity; $p\text{CO}_2$: partial pressure of carbon dioxide; Ω_{ar} : aragonite saturation state.

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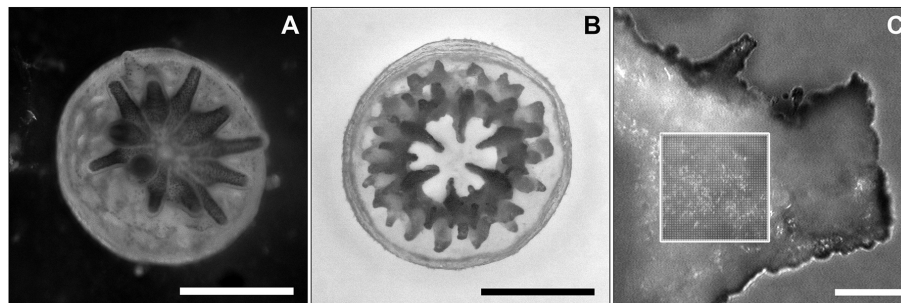


Figure 1. One month old living *Acropora spicifera* recruit **(a)**, a typical *Acropora spicifera* recruit skeleton with organic material removed **(b)** and crushed skeletal material showing a typical $\sim 60 \mu\text{m}^2$ scan area grid analysed by Raman spectroscopy **(c)**. Scale bars for **(a)** and **(b)** = 500 μm and scale bar for **(c)** = 40 μm .

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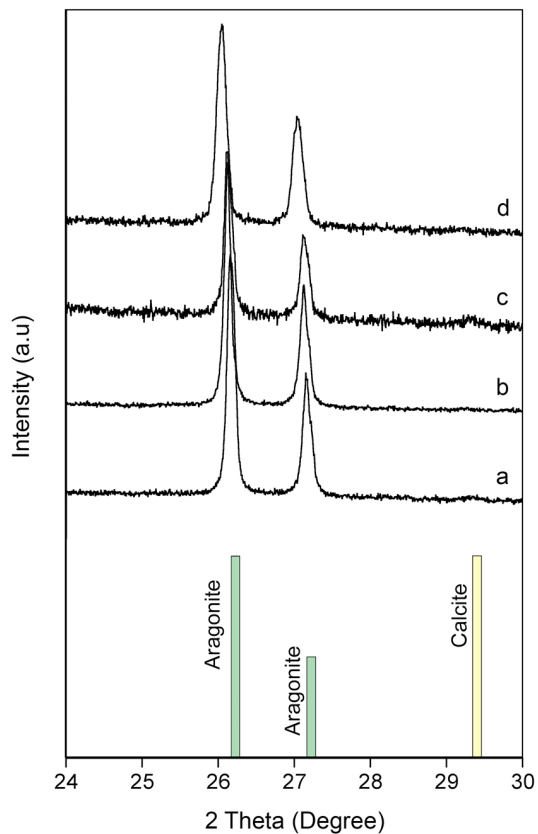


Figure 2. XRD patterns for *Acropora spicifera* coral recruit skeletons grown under control **(a)**, high temperature **(b)**, high $p\text{CO}_2$ **(c)** and high temperature + $p\text{CO}_2$ **(d)** conditions. Aragonite standard peaks occur at 26.2° and 27.2° (green bars), and the calcite standard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

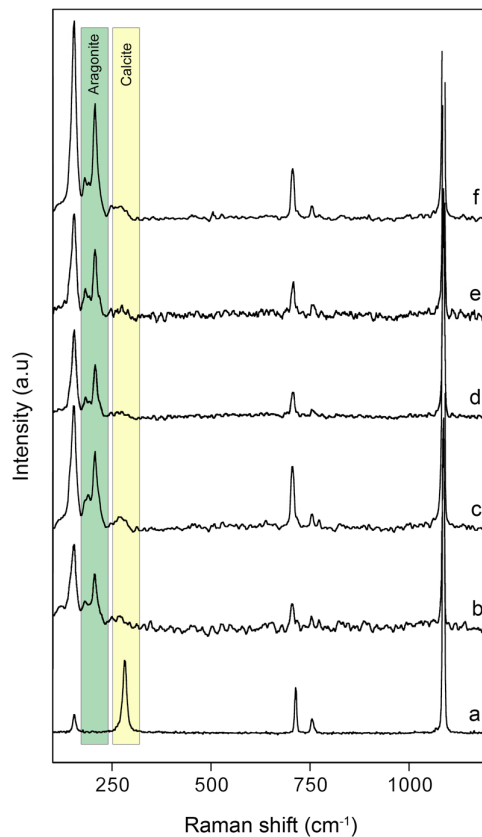


Figure 3. Specific Raman shift of a calcite standard (**a**) and a biogenic aragonite standard (**b**) and skeletal material from control (**c**), high temperature (**d**), high $p\text{CO}_2$ (**e**), and high temperature + $p\text{CO}_2$ (**f**) treated *Acropora spicifera* coral recruits. The ~ 205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