

# Temperature dependence of aragonite and calcite skeleton formation by a scleractinian coral in low $m\text{Mg}/\text{Ca}$ seawater

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## ABSTRACT

Temperature-dependent aragonite and calcite formation by scleractinian corals were examined in low molar ( $m$ )  $\text{Mg}/\text{Ca}$  seawater, the experimental conditions replicating the fluctuating  $m\text{Mg}/\text{Ca}$  levels prevailing throughout the Phanerozoic Eon. Incubation and skeletal growth monitoring of juveniles of the scleractinian coral *Acropora solitaryensis* for 4 months from the planula stage, in seawater with  $m\text{Mg}/\text{Ca}$  ratios of 5.2, 1.0, and 0.5, and temperatures of 19–28 °C, indicated that polymorphism of present-day scleractinian corals in low  $m\text{Mg}/\text{Ca}$  seawater is also influenced by seawater temperature. However, corals produced more aragonite than formed in inorganic  $\text{CaCO}_3$  precipitation experiments under the same conditions, except at 19 °C. Although the aragonite content reflected the results of the latter (abiotic) experiments at 19 °C, it is suggested that aragonitic scleractinian corals controlled skeletal formation biologically under low  $m\text{Mg}/\text{Ca}$  conditions at higher temperature, growth rates being faster at 25 °C and slower at 19 °C for all  $m\text{Mg}/\text{Ca}$  ratios. Compared with growth rates under the present-day-equivalent seawater  $\text{Mg}/\text{Ca}$  level of 5.2, juvenile growth decreased by  $62.8\% \pm 14.7\%$  and  $56.7\% \pm 6.7\%$  under  $m\text{Mg}/\text{Ca}$  levels of 1.0 and 0.5, respectively; the results suggest that growth of aragonitic scleractinian corals is suppressed throughout varying seasonal temperatures under low  $m\text{Mg}/\text{Ca}$  conditions. This supports previous findings from variable temperature perspectives that scleractinian corals grow more slowly in low  $m\text{Mg}/\text{Ca}$  (Cretaceous) seawater, interpreted as a possible explanation for the hiatus in scleractinian reef building in the Cretaceous Period.

## INTRODUCTION

The molar  $\text{Mg}/\text{Ca}$  ratio ( $m\text{Mg}/\text{Ca}$ ) of seawater has varied throughout the Phanerozoic Eon (541 Ma to the present day), including three episodes of aragonite/high-Mg calcite-facilitating conditions ( $m\text{Mg}/\text{Ca} > 2$ ) and two of calcite-facilitating conditions ( $m\text{Mg}/\text{Ca} < 2$ ), known as aragonite and calcite seas, respectively (Sandberg, 1983; Hardie, 1996; Ries, 2010). It has been proposed that the skeletal mineralogy of newly evolved calcifying organisms, such as the selection of aragonite versus calcite, was largely dictated by the  $m\text{Mg}/\text{Ca}$  in seawater at the time when mineralized skeletons were first acquired (Porter, 2007, 2010). The fossil record shows that the reign of scleractinian corals was interrupted during the mid-Cretaceous Period when  $m\text{Mg}/\text{Ca}$  dropped to its lowest levels, creating conditions that were unfavorable for corals with aragonitic skeletons (Stanley, 2003), a Cretaceous scleractinian fossil coral (*Coelosmilia* sp.) having been discovered with a calcitic skeleton (Stolarski et al., 2007). Nevertheless, aragonitic coral skeletons from this period have also been reported (Sorauf, 1999). In addition, Janiszewska et al. (2017) described a Cretaceous phase in the fossil coral record in which scleractinian micrabaciid corals appeared with aragonite skeletons, and Kiessling et al. (2008) reported that large-scale patterns of coral skeletal mineralogy have been affected by mass extinction events. Although confirmable amounts of calcite have been reported

in present-day coral skeletons grown in seawater of low  $\text{Mg}/\text{Ca}$  ( $m\text{Mg}/\text{Ca} < 1.5$ ), the major skeletal composition is aragonite, with maximum calcite levels of 20% in  $m\text{Mg}/\text{Ca}$  of 0.5 (Higuchi et al., 2014) and as much as 36% calcite in  $m\text{Mg}/\text{Ca}$  of 1.5 and 1.0 (Ries et al., 2006).

In the Cretaceous Period,  $m\text{Mg}/\text{Ca}$  levels dropped and temperatures increased simultaneously, seawater temperatures in the mid-Cretaceous being higher than in present-day oceans (Wilson and Norris, 2001; Forster et al., 2007). Experimental studies on bimineralic mussels showed that a 2 °C temperature increase with constant  $m\text{Mg}/\text{Ca}$  results in a decrease in aragonite secretion, with little change in that of calcite (Fitzer et al. 2014). De Choudens-Sanchez and Gonzalez (2009) showed that polymorph mineralogy is controlled by a combination of the saturation state of  $\text{CaCO}_3$  and the  $m\text{Mg}/\text{Ca}$  ratio in solution, abiotic precipitation experiments having suggested that polymorphism of  $\text{CaCO}_3$  is controlled by  $m\text{Mg}/\text{Ca}$  as well as temperature (Morse et al., 1997). Balthasar and Cusack (2015) showed experimentally that in the case of inorganic precipitation, aragonite content increased at a higher temperature with high  $m\text{Mg}/\text{Ca}$ , whereas calcite content increased at a lower temperature with low  $m\text{Mg}/\text{Ca}$ . However, the biological responses of skeletal organisms to environmental changes during the Phanerozoic Eon are still unknown; there have been no experimental studies on the effects of synergistic changes in both temperature and  $m\text{Mg}/\text{Ca}$  using skeletal organisms. As suggested by Kiessling (2015), studies on the skeletal formation of  $\text{CaCO}_3$  during manipulation of both temperature and  $m\text{Mg}/\text{Ca}$  are required. Here we report the temperature dependence of aragonite and calcite formation by scleractinian corals in low  $m\text{Mg}/\text{Ca}$  seawater.

## METHODS

### Incubation of Juvenile Corals

Planula larvae of *Acropora solitaryensis* were collected at the Biological Institute of Kuroshio, Kochi, Japan, and incubated in seawater with manipulated  $m\text{Mg}/\text{Ca}$  ratios under controlled temperatures. The larvae were maintained in each experimental condition for 3 days and then induced to metamorphose using the neuropeptide 2  $\mu\text{M}$  Hym 248 (Iwao et al., 2002), subsequently settling in plastic vessels as juveniles. After the introduction of symbiotic algae, *Symbiodinium* spp. (CCMP 2556, Clade D), to the juveniles (Yuyama and Higuchi, 2014), manipulated seawater was changed every 2–3 days, and juveniles were observed for 4 months under each experimental condition. Four electrically thermoregulated incubators (THS030PA; Advantec) with LED lighting (100  $\mu\text{mol m}^{-2} \text{s}^{-1}$ , light:dark = 12 h:12 h) were set to temperatures of 19, 22, 25, and 28 °C for the experiment, the average temperatures inside the incubators, recorded using a temperature logger, being  $19.3 \pm 0.5$  °C,  $21.7 \pm 0.4$  °C,  $25.1 \pm 0.5$  °C, and  $27.6 \pm 0.6$  °C.

Juvenile corals were incubated in manipulated seawater with three different concentrations of Mg and Ca ( $\text{Mg}/\text{Ca} = 5.2, 1.0, 0.5$ ), prepared by mixing filtered (pore size 0.22  $\mu\text{m}$ ) natural seawater and Mg-free water, the

TABLE 1. ARAGONITE AND CALCITE CONTENT IN BIOGENIC (CORAL *ACROPORA*) AND ABIOGENIC CALCIUM CARBONATE IN DIFFERENT TEMPERATURE AND MOLAR Mg/Ca REGIMES

	<i>Acropora solitaryensis</i> (this study)				<i>Acropora tenuis</i> (Higuchi et al., 2014)	Abiogenic formation (Balthasar and Cusack, 2015)			
Temperature (°C)	19	22	25	28	26	15	20	25	30
<i>mMg/Ca</i> = 5.2	A	A	A	A	A	A	A	A	A
<i>mMg/Ca</i> = 1.0	A + C (<10)	A + C (61.1 ± 0.5)	A + C (80.4 ± 4.8)	A + C (95.0 ± 2.8)	A + C (94.6)	A + C (5)	A + C (13)	A + C (39)	A + C (33)
<i>mMg/Ca</i> = 0.5	C (0)	A + C (<10)	A + C (<10)	A + C (44.8 ± 4.8)	A + C (80.0)	A + C (<1)	A + C (<1)	A + C (2)	A + C (8)

Note: *mMg/Ca* is MOLAR Mg/Ca. A is 100% aragonite, C is 100% calcite, A + C is mixture of aragonite and calcite. Numbers in brackets indicate aragonite content (%). Mean ± standard error (n = 3).

latter having been prepared by dissolving NaCl, Na<sub>2</sub>SO<sub>4</sub>, CaCl<sub>2</sub>, KCl, KBr, SrCl<sub>2</sub>, NaF, H<sub>3</sub>BO<sub>3</sub>, and NaHCO<sub>3</sub> in ultrapure water. The concentrations of major elements were manipulated to mimic those of natural seawater, excluding Mg (i.e., no addition of Mg). During incubation for 4 months, the *mMg/Ca* ratios were 5.15 ± 0.02, 0.94 ± 0.05, and 0.46 ± 0.01, as determined by inductively coupled plasma–mass spectrometry (ICP-MS). The measured values were compared to International Association for the Physical Sciences of the Oceans standard seawater (Ocean Scientific International Ltd, UK), the precision for *mMg/Ca* measurement being <0.7%. The pH of the manipulated seawater was 8.0–8.1, total alkalinity was 2.2–2.3 mmol kg<sup>-1</sup>, and salinity was 32.0–32.3 psu. After incubation, the juvenile corals were treated with NaClO to remove tissue and the skeletons were used for estimation of growth rate and determination of their crystal structure. Growth rates were estimated on a dry weight basis for 5–8 juveniles under each treatment condition at the end of the incubation, the initial skeletal weight being zero.

#### Determination of Crystal Structure

The crystal structure of CaCO<sub>3</sub> was determined by X-ray diffraction (XRD) with a low background silicon holder for quantitative determination of the calcite content. One to three juvenile skeletons were used for XRD measurements. To estimate aragonite and calcite content, a standard calibration curve was prepared by mixing pure aragonite and calcite powder (according to methods of Higuchi et al., 2014). As the calcite intensity was much stronger than that of aragonite, the specific peak of the latter (<10% wt%) was almost equivalent to the background and thus difficult to locate using XRD analysis (Fig. DR1 in the GSA Data Repository<sup>1</sup>). To confirm the presence of aragonite, Meigen's stain using 10% cobalt nitrate was conducted at 85 °C for 10 min (Hang et al., 2014).

#### RESULTS

XRD analysis showed that both calcite and aragonite were formed by scleractinian *Acropora* corals under the manipulated seawater conditions (Table 1). In *mMg/Ca* = 5.2 (equivalent to present-day natural seawater), pure aragonite skeletons were formed under all temperatures examined. The aragonite content became lower (i.e., calcite content higher) in lower *mMg/Ca* treatment groups, although still remaining high (even at *mMg/Ca* = 1.0), except at the lowest temperature (19 °C; Table 1). However, higher calcite content resulted under lower temperatures. Aragonite peaks following XRD analysis were obscured due to the strong calcite peaks with *mMg/Ca* = 1.0 at 19 °C, in addition to *mMg/Ca* = 0.5 at 22 °C and 25 °C (Fig. DR2); the presence of aragonite was confirmed with Meigen's stain (Fig. 1). These analyses indicated that calcite content was >90%, the corresponding aragonite content being <10% (Table 1). At *mMg/Ca* = 0.5, calcite formed the major skeletal component, although ~45% aragonite was coproduced at 28 °C. The skeletons were composed entirely of calcite at *mMg/Ca* = 0.5 (19 °C); aragonite was not evidenced by

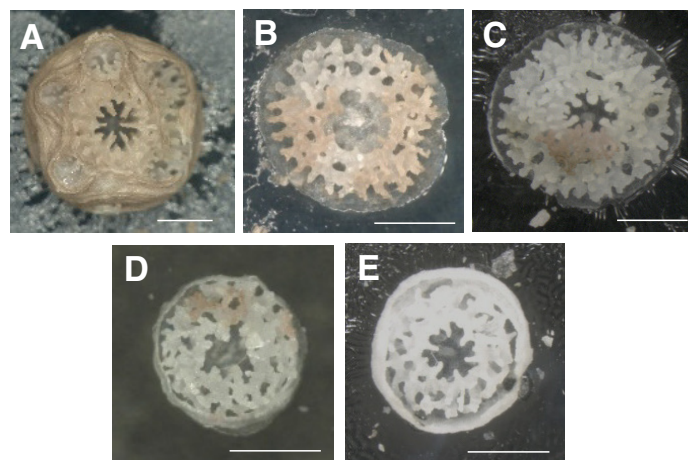


Figure 1. Juveniles of *Acropora solitaryensis* (Meigen's stain). Purple stained regions are aragonite; uncolored regions are calcite. A: 28 °C, *mMg/Ca* = 5.2. B: 28 °C, *mMg/Ca* = 0.5. C: 25 °C, *mMg/Ca* = 0.5. D: 22 °C, *mMg/Ca* = 0.5. E: 19 °C, *mMg/Ca* = 0.5. Scale bars are 0.5 mm.

either XRD or Meigen's stain (Fig. 1; Fig. DR2). However, the settlement success rate of planula larvae with decreased *mMg/Ca* at 19 °C was very low, especially with *mMg/Ca* = 0.5 (<1% success). Under the other experimental conditions, *A. solitaryensis* showed relatively high success rates for settlement and growth, even under conditions of low *mMg/Ca* or low temperature (e.g., *mMg/Ca* < 1 at 22 °C; *mMg/Ca* = 5.2 at 19 °C). However, juvenile coral growth rates decreased significantly at low *mMg/Ca* under each temperature condition examined ( $p < 0.05$ ; Table 2), being fastest at 25 °C and slowest at 19 °C for all *Mg/Ca* ratios. Compared with those in *mMg/Ca* = 5.2, the average juvenile growth rates decreased by 62.8% ± 14.7% and 56.7% ± 6.7% at *mMg/Ca* levels of 1.0 and 0.5, respectively, under all temperature conditions.

#### DISCUSSION

Growth rates were fastest at 25 °C for all *mMg/Ca* conditions examined. Although the precipitation rate of CaCO<sub>3</sub> (both aragonite and calcite) is theoretically faster at higher temperatures (Burton and Walter, 1987), in the case of corals biological processes also affect calcification. A temperature of 25 °C is considered optimal for growth of *A. solitaryensis*, which is distributed in temperate waters off Japan. The present growth

TABLE 2. GROWTH RATE OF JUVENILE *ACROPORA SOLITARYENSIS* IN DIFFERENT TEMPERATURE AND MOLAR Mg/Ca REGIMES

Temperature (°C)	19	22	25	28
<i>mMg/Ca</i> = 5.2 (n = 8)	39.0 ± 3.0 <sup>e</sup>	66.0 ± 3.2 <sup>c</sup>	135.9 ± 3.3 <sup>a</sup>	112.1 ± 6.1 <sup>b</sup>
<i>mMg/Ca</i> = 1.0 (n = 5)	9.9 ± 0.8 <sup>f</sup>	32.8 ± 2.5 <sup>e</sup>	52.1 ± 3.6 <sup>cd</sup>	39.9 ± 1.0 <sup>de</sup>
<i>mMg/Ca</i> = 0.5 (n = 5)	12.3 ± 1.4 <sup>f</sup>	41.0 ± 2.3 <sup>de</sup>	58.2 ± 5.0 <sup>cd</sup>	41.2 ± 1.3 <sup>de</sup>

Note: *mMg/Ca* is MOLAR Mg/Ca (μg juvenile<sup>-1</sup> month<sup>-1</sup>). Values are mean ± standard error. Superscript letters on growth rate values indicate significant difference (Tukey-Kramer honest significant difference test,  $p < 0.05$ ).

<sup>1</sup>GSA Data Repository item 2017386, Figure DR1 (standard of XRD pattern) and Figure DR2 (results of XRD pattern of corals), is available online at <http://www.geosociety.org/datarepository/2017/> or on request from editing@geosociety.org.

rate data for lower temperatures correspond to those of previous studies that indicated that the calcification rate of *A. solitaryensis* was lower at 18 °C than 23 °C (Higuchi et al., 2015).

As in a previous report on inorganic precipitation (Balthasar and Cusack, 2015), polymorphism of CaCO<sub>3</sub> by corals in low *mMg/Ca* seawater is shown here to be dependent upon seawater temperature. Kiessling's (2015) linear regression model to estimate temperature (*T*, in °C) from known percentages of abiogenic aragonite (*A*) and seawater *mMg/Ca* ( $R^2 = 0.73$ ), when converted to determine aragonite percentages [i.e.,  $A = (T + 8.5 \times mMg/Ca - 26.6)/0.18$ ], shows that most of the present results were above the line of theoretical inorganic precipitation of aragonite (Fig. 2). Thus, corals produced more aragonite than expected under inorganic conditions, for each experimental regime except at 19 °C. Polymorphism of CaCO<sub>3</sub> in biomineralizing organisms is controlled by organic matrix proteins (Belcher, 1996; De Yoreo and Dove, 2004; Goffredo et al., 2011), and the higher than expected aragonite proportions in corals for most experimental scenarios are most likely a reflection of this biological influence.

However, our experiments also demonstrate that at very low *mMg/Ca* (0.5) coral skeletal mineralogy is dominated by calcite or, at 19 °C, even exclusively calcitic. Although Higuchi et al. (2014) reported skeletons of modern *Acropora* composed of as much as 80% aragonite at *mMg/Ca* = 0.5 and 26 °C (Table 1), our data indicate that, when considering the *mMg/Ca* alone, calcite should have been more common among calcite-sea corals.

Most models of Phanerozoic seawater composition suggest that the *mMg/Ca* ratio did not drop below 1 during the Cretaceous (e.g., Demicco et al., 2005; Farkaš et al., 2007; but see Berner, 2004), and as such favored an increase in calcite secretion. However, at the same time seawater temperatures were above average during this time (Veizer and Prokoph, 2015). In our experiments aragonite forms the main polymorph in the coral skeleton at warm water (>19 °C) conditions of *mMg/Ca* >0.5, and thus supports the continued existence and appearance of aragonitic corals throughout the Cretaceous calcite sea (Janiszewska et al., 2017). This is further supported when considering that spawning of corals takes place at higher temperatures (mostly >25 °C) for both subtropical and high-latitude species (Hayashibara et al., 1993; Nozawa, 2012); this is likely

to result in the initial crystallization aragonite nuclei for shallow-water coral skeletons.

In addition to skeletal mineralogy, low *mMg/Ca* ratios also affect growth rates. In our experiments, coral growth rates decreased by >50% with low *mMg/Ca* under all temperature conditions examined, the results suggesting that natural growth of aragonitic scleractinian corals was suppressed throughout all seasons under low *mMg/Ca* conditions. Ries et al. (2006) also showed that growth rates of 3 species of scleractinian corals were much lower (60%–70%) under low *mMg/Ca* conditions at 25 °C. Although increased temperature induced aragonite skeleton production even under low *mMg/Ca*, higher temperatures, such as 31 °C, are not conducive for coral skeletal growth due to negative physiological responses (e.g., Higuchi et al., 2009). The paucity of fossilized corals in the geological record is associated with periods of unfavorable conditions for aragonite calcification, such as low *mMg/Ca* seas (Stanley, 2003), although *Acropora* corals may adapt to relatively slow changes in *mMg/Ca* over a long period (Stolarski et al., 2016). Present-day juvenile acroporid corals retain 90% of their growth ability at *mMg/Ca* = 1.5, compared with present seawater levels of *mMg/Ca* = 5.2 (Higuchi et al., 2014). When compared to the growth rates reported in our current experiments, we note a dramatic reduction in aragonitic skeletal growth between *mMg/Ca* ratios of 1.5 and 1. In addition to mass extinction events (Kiessling et al. 2008), low marine *mMg/Ca* ratios probably contributed to the paucity of scleractinian corals during the Cretaceous. Trends in seawater *mMg/Ca* determined not only productivity, but also the evolution of biomineralization (Stanley and Hardie, 1998). Although scleractinian corals may have acquired the ability to produce calcite skeletons during the Cretaceous calcite sea, these calcitic corals could not become dominant reef builders in calcite seas owing to the reduced growth rates at low *mMg/Ca* ratios.

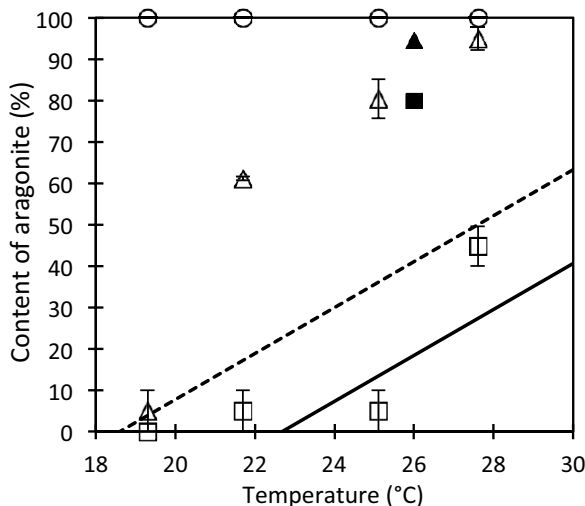
The present results show that skeletal polymorph mineralogy and growth rate of scleractinian corals are influenced by seawater temperature in addition to the effects of *mMg/Ca*. Beyond previous studies that showed that corals secrete calcite and grow slower at lower *mMg/Ca* ratios (Ries et al., 2006), our findings show that this pattern holds true even when corrected for the effect of temperature, as suggested for inorganic CaCO<sub>3</sub> precipitation (Balthasar and Cusack, 2015). Further growth experiments under varying temperature and *mMg/Ca* using other species are needed to see if our results reflect a more general pattern among calcifying organisms.

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**Figure 2. Aragonite content in *Acropora* cultured under different temperature and *mMg/Ca* regimes. Circle symbols—*mMg/Ca* = 5.2; open triangles—*mMg/Ca* = 1.0; open squares—*mMg/Ca* = 0.5, mean ± standard error (*n* = 3) (all *A. solitaryensis*; this study); solid triangle—*mMg/Ca* = 1.0; solid square—*mMg/Ca* = 0.5 (both *A. tenuis*; Higuchi et al., 2014). Dashed line indicates *mMg/Ca* = 1.0; solid line indicates *mMg/Ca* = 0.5 [by linear regression model  $A = (T + 8.5 \times mMg/Ca - 26.6)/0.18$  (*T* is temperature); modified from Kiessling, 2015]. Plots above lines indicate higher proportion of aragonite skeleton than inorganic precipitation of aragonite.**

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