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**Effects of secular  
variation in seawater  
Mg/Ca on marine  
biocalcification**

J. B. Ries

# Review: the effects of secular variation in seawater Mg/Ca on marine biocalcification

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## Abstract

Synchronized transitions in the polymorph mineralogy of the major reef-building and sediment-producing calcareous marine organisms and abiotic  $\text{CaCO}_3$  precipitates (ooids, marine cements) throughout Phanerozoic time is believed to have been caused by tectonically-induced variations in seawater molar Mg/Ca ( $>2$ ="aragonite seas";  $<2$ ="calcite seas"). Here, I review a series of experiments in which extant calcifying taxa were reared in experimental seawater formulated over the range of  $m\text{Mg}/\text{Ca}$  ratios (1.0 to 5.2) that occurred throughout their geologic history.

Aragonite-secreting bryopsidalean algae and scleractinian corals and calcite-secreting coccolithophores exhibited higher rates of calcification and growth in the experimental seawaters that favored their skeletal mineral. These results support the assertion that seawater Mg/Ca played an important role in determining which hypercalcifying marine organisms were the major reef-builders and sediment-producers throughout Earth history. The observation that primary production increased along with calcification in mineralogically-favorable seawater is consistent with the hypothesis that calcification promotes photosynthesis within autotrophs through the liberation of  $\text{CO}_2$ .

The Mg/Ca ratio of calcite secreted by the coccolithophores, coralline algae and reef-dwelling animals (crustacea, urchins, calcareous tube worms) declined with reductions in seawater Mg/Ca. Calcifying microbial biofilms varied their mineral polymorph with seawater Mg/Ca ( $m\text{Mg}/\text{Ca} < 2$ =low Mg calc;  $m\text{Mg}/\text{Ca} > 2$ =arag+high Mg calc), suggesting a nearly abiotic mode of calcification. These results indicate that biomineralogical control can be partially overridden by ambient seawater Mg/Ca and suggests that modern high Mg calcite organisms probably secreted low Mg calcite in calcite seas of the past. Notably, Mg fractionation in autotrophic organisms was more strongly influenced by changes in seawater Mg/Ca, a probable consequence of them inducing a less controlled mode of calcification simply through the removal of  $\text{CO}_2$  via photosynthesis.

This body of work also has implications for thermal-chemical reconstructions of seawater that are based upon skeletal Mg/Ca. And by identifying how marine calcifiers

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respond to changes in seawater Mg/Ca and absolute  $\text{Ca}^{2+}$  concentration, this work should enhance our interpretation of the parallel studies investigating the effects of  $\text{CO}_2$ -induced ocean acidification on marine calcification.

## 1 Introduction

5 Chemical analyses of fluid inclusions derived from ancient primary marine halite indicate that the molar Mg/Ca ratio (*mMg/Ca*) of seawater has varied between 1.0 and 5.2 throughout the Phanerozoic Eon (Lowenstein et al., 2001, 2003, 2005; Horita et al., 2002; Brennan et al., 2004; Timofeeff et al., 2006). These secular variations in seawater Mg/Ca are thought to be responsible for systematic changes in the poly-  
10 morph mineralogy of ooids and marine cements throughout Phanerozoic time (Sandberg, 1983). During intervals of low seawater *mMg/Ca* (<2), such as Early Cambrian through Late Mississippian time and Middle Jurassic through Middle Paleogene time, the predominant form of abiotically produced calcium carbonate ( $\text{CaCO}_3$ ) produced in shallow seas was low Mg calcite (i.e., “calcite seas”). During intervals of high seawater  
15 *mMg/Ca* (>2), such as during Early Cambrian time, Late Mississippian through Middle Jurassic time and Middle Paleogene through Modern time, aragonite and high Mg calcite were the predominant polymorphs (i.e., “aragonite seas”). For convention, I refer to Sandberg’s three aragonite sea intervals as Aragonite I, II, and III and his two calcite sea intervals as Calcite I and II.

20 Stanley and Hardie (1998, 1999) observed that the carbonate mineralogy of simple, hypercalcifying organisms has varied in concert with Sandberg’s (1983) aragonite and calcite seas throughout Phanerozoic time (Fig. 1). From this, they conclude that certain hypercalcifying organisms were only able to function as major reef builders (corals, sponges and algae) and carbonate sediment producers (algae) when their  
25  $\text{CaCO}_3$  polymorph mineralogy was favored by the Mg/Ca ratio of seawater. Here, I review experiments that explore the effects of seawater Mg/Ca on the biomineralization of extant representatives of the calcifying taxa that were subjected to the alternating

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calcite and aragonite seas of Phanerozoic time.

The experiments reviewed here investigate the effect of seawater Mg/Ca on: (1) algae that secrete aragonite in modern seas (three calcareous bryopsidalean algae *Penicillus capitatus* (Ries, 2005a), *Udotea flabellum* (Ries, 2006a), and *Halimeda incrassata* (Stanley et al., 2009)); (2) algae that secrete calcite in modern seas (the encrusting coralline red alga *Neogoniolithon* sp. (Ries, 2006b), three species of branching coralline red algae of the genus *Amphiroa* sp. (Stanley et al., 2002), and three species of coccolithophores *Pleurochrysis carterae*, *Ochrosphaera neopolitana*, and *Coccolithus neohelis* (Stanley et al., 2005)); (3) animals that secrete aragonite in modern seas (the scleractinian corals *Porites cylindrica*, *Montipora digitata*, and *Acropora cervicornis*; Ries et al., 2006); (4) animals that secrete calcite in modern seas (the echinoid *Eucidaris tribuloides*, the crab *Perchon gibbesi*, the shrimp *Palaemonetes pugio* and the calcareous serpulid worm *Hydroides crucigera*; Ries, 2004); and (5) microbial biofilms that secrete a mixture of aragonite and high Mg calcite in modern seas (Ries et al., 2008). The experiments on the bryopsidalean algae, the coccolithophores, and the scleractinian corals address mineralogy, Mg incorporation, and rates of calcification and growth, while the experiments on the coralline algae, calcite-secreting animals, and microbial biofilms focus solely on mineralogy and Mg incorporation.

## 1.1 Investigated organisms

### 1.1.1 Calcareous bryopsidalean algae (i.e., calcareous green algae)

Calcareous bryopsidalean algae have been primary sediment producers in tropical marine environments since the late Paleogene shift to Aragonite III seas (Fig. 1). Stanley and Hardie (1998, 1999) hypothesized that the dominance of these simple aragonitic hypercalcifiers was permitted by the transition to a seawater  $m\text{Mg}/\text{Ca}$  ratio greater than two in the oceans, which would have favored precipitation of their preferred skeletal mineral – aragonite.

Specimens of *Penicillus capitatus*, *Udotea flabellum*, and *Halimeda incrassata* were

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grown in experimental seawaters formulated at  $m\text{Mg}/\text{Ca}$  ratios of 1.0, 2.5 and 5.2, which correspond to calcite seawater, a boundary seawater, and aragonite seawater, respectively (Ries, 2005a, 2006a; Stanley et al., 2009). The effects of seawater  $\text{Mg}/\text{Ca}$  on algal growth and calcification, polymorph mineralogy, Mg fractionation, and crystal ultrastructure were investigated. Additionally, thallus stiffness was determined for the *Penicillus capitatus* specimens grown under the various seawater  $\text{Mg}/\text{Ca}$  ratios by subjecting them to a hydraulic stress-strain biomechanical analysis.

### 1.1.2 Coccolithophores

Coccolithophores flourished during the second half of Calcite II seas and were responsible for the deposition of the massive and widespread Cretaceous chalk deposits, from which the Cretaceous Period derives its name (“*Creta*” is Latin for “chalk”). Some of these calcareous nannoplankton secrete high Mg calcite while others secrete low Mg calcite in modern seas. The success of these algae in Late Cretaceous time has been attributed to the low  $\text{Mg}/\text{Ca}$  ratio of seawater at that time favoring the coccolithophores’ calcitic mineralogy (Stanley and Hardie, 1998, 1999)

To test this hypothesis, three species of coccolithophore (*Pleurochrysis carterae*, *Ochrosphaera neopolitana*, and *Coccolithus neohelis*) were cultured in seawater  $m\text{Mg}/\text{Ca}$  ratios of 0.5, 1.0, 1.5, 2.5, 3.5 and 5.2 (Stanley et al., 2005). The effects of seawater  $\text{Mg}/\text{Ca}$  on coccolithophorid population growth, chalk production, Mg fractionation, and skeletal ultrastructure were investigated.

### 1.1.3 Scleractinian corals

Stanley and Hardie (1998, 1999) suggest that aragonitic scleractinian corals have been major reef builders in Triassic, Jurassic, Early Cretaceous, Late Paleogene and Neogene time because, during these times in the history of the Earth, the oceans maintained  $\text{Mg}/\text{Ca}$  ratios favorable for the secretion of the coral’s inherently aragonitic skeleton. The reign of the scleractinian corals was interrupted during the Middle Cretaceous

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by the largely calcitic rudist bivalves, when Mg/Ca ratios dropped to their lowest levels of Phanerozoic time. The rudists retained their position as dominant reef builders through the end of Cretaceous time. Significantly, the scleractinian corals didn't resume their dominance until Late Eocene time, well after the extinction of the rudists at the end of the Cretaceous Period, when the Mg/Ca ratio of seawater had transitioned back into the aragonite domain.

To test Stanley and Hardie's hypothesis (1998, 1999) that scleractinian corals were able to flourish as reef builders only when oceanic Mg/Ca ratios supported their aragonitic skeletal mineralogy, three species of scleractinian corals (*Porites cylindrica*, *Montipora digitata*, and *Acropora cervicornis*) were grown in experimental seawaters formulated at mMg/Ca ratios of 0.5, 1.0–1.5, 1.5, 2.5, 3.5, 5.2 and 7.0 (Ries et al., 2006). The effects of seawater Mg/Ca on calcification rate, polymorph mineralogy, skeletal Mg-fractionation, and skeletal ultrastructure were determined. To differentiate between the effects of Mg/Ca ratio and absolute concentration of Ca on coral growth, three additional seawaters were formulated with fixed Ca concentrations at mMg/Ca ratios of 1, 3.5 and 5.2. This also permits the comparison of coral growth rates in two sets of seawaters with fixed mMg/Ca ratios (1.0 and 5.2) and different absolute Ca<sup>2+</sup> concentrations.

#### 1.1.4 Coralline red algae

Stanley and Hardie (1998, 1999) hypothesize that organisms that secrete high Mg calcite in modern seas (mMg/Ca=5.2) would have secreted low Mg calcite in ancient seas of lower Mg/Ca ratios. Füchtbauer and Hardie (1976, 1980) showed experimentally that the amount of magnesium incorporated into non-skeletal calcite is proportional to the ambient Mg/Ca ratio as well as to the temperature of the precipitating solution. Therefore, if simple organisms merely induce the precipitation of calcite, one would expect such skeletal carbonate to behave the same as Füchtbauer and Hardie's (1976, 1980) non-skeletal calcite, with respect to the incorporation of Mg<sup>2+</sup>. The application of this phenomenon to skeletal carbonates is further supported by Chave's (1954) work show-

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ing that the Mg/Ca ratio in the skeletons of many high Mg calcite organisms is indeed variable for a given organism, as it increases with ambient temperature.

To test this prediction, species of both encrusting and branching coralline red algae were grown over the range of seawater Mg/Ca ratios believed to have occurred throughout their geologic history (Stanley et al., 2002; Ries, 2006b). Magnesium fractionation curves for the various algae were developed from these experiments.

### 1.1.5 High Mg calcite-secreting animals

To investigate Stanley and Hardie's (1998, 1999) Mg-fractionation hypothesis for more complex organisms, four animals that secrete high Mg calcite in modern seas (the echinoid *Eucidaris tribuloides*, the crab *Perchon gibbesi*, the shrimp *Palaemonetes pugio* and the calcareous serpulid worm *Hydroides crucigera*) were grown in experimental seawaters formulated at Mg/Ca ratios believed to have existed throughout the animals' geologic histories (Ries, 2004). Mg fractionation curves were derived for the organisms and the Mg content of fossil echinoderms was used to reconstruct oceanic Mg/Ca throughout the Phanerozoic Eon.

Chave (1954) showed that the effect of temperature on skeletal Mg is greatest for taxonomically simple organisms. The experiments reviewed here (Ries, 2004) test whether the effect of seawater Mg/Ca on skeletal Mg incorporation is comparably correlated with taxonomic complexity.

### 1.1.6 Bacterial biofilms

Biofilms are highly diverse bacterial communities that can precipitate  $\text{CaCO}_3$  extracellularly within their mm-to-cm thick matrices through various redox reactions that alter the  $\text{CaCO}_3$  saturation state of the biofilm's intercellular fluid. Bacterial biofilms are the oldest biocalcifying systems on Earth, having been intimately involved in  $\text{CaCO}_3$  mineralization on the seafloor for at least the past ca. 3.45 Gy (Knoll and Semikhatov, 1998; Grotzinger and Knoll, 1999; Grotzinger and James, 2000; Riding, 2000). The ab-

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sence of grazing and bioturbation throughout most of Precambrian time enabled these biofilms to form laminated stromatolites, microbialites, and thrombolites throughout this interval (Awramik, 1971; Riding and Liang, 2005). Hardie's (2003) model of Precambrian seawater Mg/Ca – ultimately driven by the global rate of ocean crust production inferred from granitic pluton data – suggests that bacterial biofilms would have experienced six intervals of aragonite seas and five intervals of calcite seas between Late Archean and terminal Proterozoic time. If the polymorph mineralogy of the CaCO<sub>3</sub> precipitated within biofilms is strongly influenced by seawater Mg/Ca, then the original mineralogy of ancient microbial carbonates (i.e., stromatolites, microbialites, thrombolites) may prove to be a viable proxy for Precambrian seawater chemistry.

To evaluate the effect of Mg/Ca<sub>SW</sub> on microbial calcification (Ries et al., 2008), mixed-community marine sedimentary biofilms were cultured in experimental seawaters formulated over the range of *m*Mg/Ca ratios predicted to have occurred since Late Archean time (1.5, 2.5, 5.2; Hardie, 2003). Biofilm phylogenetic diversity, CaCO<sub>3</sub> polymorph mineralogy and distribution, and Mg fractionation in biofilm calcite were evaluated in response to these modifications in seawater Mg/Ca.

## 2 Background

### 2.1 Patterns of skeletal polymorph mineralogy throughout Phanerozoic time

Stanley and Hardie (1998, 1999) observed that the carbonate mineralogy of simple, hypercalcifying organisms has varied in concert with Sandberg's (1983) aragonite and calcite seas throughout Phanerozoic time. This led them to assert that certain taxa have been able to function as major reef builders and sediment producers only when their mineralogy was favored by the Mg/Ca ratio of seawater (Fig. 1). The general patterns that they identified are briefly reviewed in the following section.

In Calcite I (early-middle Paleozoic), calcitic tabulate, heliolitid and rugose corals, and stromatoporoids (possibly calcitic) were the dominant reef builders, while recep-



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taculitids (possibly calcitic) were the dominant sediment producers. As the Mg/Ca ratio increased in the middle Mississippian to cause the onset of Aragonite II (late Paleozoic-early Mesozoic), aragonitic groups of sponges, scleractinian corals and phylloid algae, and high Mg calcitic red algae, became major reef builders, while aragonitic dasycladaceans were important algal sediment producers. The Mg/Ca ratio then dropped again in the mid-Jurassic, shifting oceanic state to Calcite II (middle Jurassic-late Paleogene). During the peak of Calcite II (highest  $\text{Ca}^{2+}$  concentrations) in the mid-Cretaceous, the largely calcitic rudist bivalves replaced the aragonitic scleractinian corals as major reef builders, while calcitic nannoplankton (coccolithophores) became important chalk producers. Furthermore, as the absolute concentration of  $\text{Ca}^{2+}$  fell throughout Cenozoic time, the morphology of individual coccoliths became less robustly calcified (Stanley and Hardie, 1998, 1999). The most recent increase in seawater Mg/Ca, which commenced in late Paleogene time, has advanced the oceans into Aragonite III, where aragonitic scleractinian corals and high Mg calcitic red algae once again dominated reef construction and aragonitic green algae, such as *Halimeda*, *Penicillus*, and *Udotea*, control sediment production.

Stanley and Hardie (1998, 1999) investigated mineralogical trends in organisms that were hypercalcifiers and/or exhibited weak control over their calcification. Hypercalcifying organisms, defined either as individuals that produce massive calcium carbonate skeletons or as populations that produce excessive calcium carbonate material (e.g., reefs or sediment producers), probably require favorable seawater chemistry (i.e., Mg/Ca ratios that support their inherent mineralogy) to engage in such rapid calcification. Since hypercalcification is typically a warm-water phenomenon, most of the organisms analyzed in their study are warm-adapted taxa. Organisms that exhibit only minor control over their calcification, typically taxonomically simple organisms, are also likely to require favorable seawater chemistry to calcify. For example, Chave (1954) showed that the degree of correlation between skeletal Mg/Ca and temperature is inversely related to biological complexity. Therefore, one would expect the relationship between calcification rate and seawater Mg/Ca to be comparably linked to biological

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complexity.

In a recent study, Kiessling et al. (2008) identified a statistically relationship between oceanic state (aragonite vs. calcite seas) and the polymorph mineralogy of reef-building organisms throughout Phanerozoic time. Significantly, this relationship disappeared when their analysis was expanded to include all calcifying organisms – regardless of their inferred degree of biomineralogical control. However, an earlier study by Porter (2007) showed that the mineralogy of nearly all newly evolved CaCO<sub>3</sub> skeletons between Ediacaran and Ordovician time – for both hypercalcifying and non-hypercalcifying taxa – reflects the aragonite-calcite sea transition (Sandberg, 1983; Hardie, 1996) reported for that time. Thus, although most calcifying taxa appear to have been influenced by seawater Mg/Ca at the time of their skeletal evolution (Porter, 2007), only the major reef-building and sediment-producing organisms were affected by subsequent changes in oceanic state (Kiessling et al., 2008).

Van de Poel and Schlager (1994) had previously recognized a weak correspondence between skeletal and non-skeletal carbonates over the Mesozoic-Cenozoic interval. However, they were unable to illustrate that the shifts they observed were first-order changes in primary skeletal mineralogy, rather than second order oscillations imprinted upon Sandberg's (1975) one-time unidirectional shift from calcite to aragonite seas. The work by Kiessling et al. (2008) suggests that the reason Van de Poel and Schlager's (1994) skeletal data revealed only a weak correspondence with the non-skeletal data is because the latter included the skeletal remains of all calcifying taxa, including organisms whose biomineralization would not be expected to be strongly influenced by seawater chemistry, such as foraminifera and mollusks.

Sandberg (1975) originally suggested that the Phanerozoic Eon exhibited only a single transition (now known to be incorrect) from "calcite seas" to "aragonite seas," which occurred during the Cenozoic Era. Milliken and Pigott (1977) pointed to a similar shift during the Carboniferous. Wilkinson (1979), using the relative diversities and biomasses of various taxa, suggested a corresponding one-time shift in the dominant mineralogy of calcareous marine organisms. However, Wilkinson's erroneous miner-

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ological assessments of several groups of organisms and failure to distinguish between high Mg and low Mg calcite rendered his conclusions invalid.

## 2.2 Cause of calcite-aragonite seas: atmospheric $p\text{CO}_2$ vs. seawater Mg/Ca

### 2.2.1 Atmospheric $p\text{CO}_2$

5 Sandberg (1975) suggested that his observed single shift from calcite to aragonite seas was caused by an increase in the Mg/Ca ratio of seawater throughout Mesozoic time, resulting from the selective removal of calcium ions from the ocean via flourishing calcareous nannoplankton and planktonic foraminifera. As more ancient oolite and early marine cement data became available, Sandberg abandoned the single-shift hypothesis in favor of the currently accepted four-fold shift in carbonate mineralogy, consisting of 3 aragonite intervals (Late Precambrian to Early Cambrian; Late Mississippian to Late Triassic/Early Jurassic; early/middle Cenozoic to the present) and two calcite intervals (Cambrian to Late Mississippian; Late Triassic/Early Jurassic to Early/Middle Cenozoic; Sandberg, 1983; Lasemi and Sandberg, 2000). This oscillating trend in carbonate mineralogy also caused him to abandon his hypothesis that Mg/Ca ratios were driven by planktonic removal of calcium ions in favor of Mackenzie and Pigott's (1981) hypothesis that the observed mineralogical shifts were driven by tectonically induced shifts in atmospheric  $p\text{CO}_2$ .

10 However, atmospheric  $p\text{CO}_2$  would only be expected to cause a shift to calcite seas if  $p\text{CO}_2$  caused seawater to be simultaneously oversaturated with respect to calcite and undersaturated with respect to aragonite. Because the stoichiometric solubility coefficients ( $K_{\text{sp}}$ ) of aragonite ( $10^{-6.19}$ ) and calcite ( $10^{-6.37}$ ) are relatively close, the range of  $\text{CaCO}_3$  saturation states that yields simultaneous calcite oversaturation and aragonite undersaturation is correspondingly narrow ( $1 < \Omega_{\text{calcite}} < 1.5$ ;  $0.7 < \Omega_{\text{aragonite}} < 1$ ), and requires that seawater be near undersaturation with respect to calcite over protracted intervals of geologic time. Given the ubiquity and abundance of both biogenic and abiogenic limestone deposits throughout the calcite seas of Early Cambrian – Late

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Mississippian time and Late Jurassic – Middle Paleocene time, it seems improbable that the  $\text{CaCO}_3$  saturation state of seawater during these intervals was regularly constrained to such a narrow range, teetering on the edge of total  $\text{CaCO}_3$  undersaturation ( $\Omega_{\text{calcite}} < 1$ ).

Hardie (1996) also observed that the timing of Sandberg's transitions between aragonite and calcite seas are in phase with transitions between  $\text{MgSO}_4$  and KCl marine evaporites, respectively, throughout the Phanerozoic record. Hardie concluded that the synchronicity of these mineralogical shifts must have been caused by shifts in seawater chemistry that would have simultaneously influenced the mineralogy of both carbonate precipitates and marine evaporites. Atmospheric  $p\text{CO}_2$  is not capable of causing these synchronized mineralogical shifts because it bears no influence on the mineralogy of marine evaporites.

For these reasons, it is unlikely that atmospheric  $p\text{CO}_2$  is the primary link explaining the synchronicity between carbonate mineralogy and rates of ocean crust production (inferred from first order changes in eustatic sea level) throughout Phanerozoic time. Nonetheless, fluctuations in atmospheric  $p\text{CO}_2$  have surely modulated the effect of seawater Mg/Ca on oceanic state (calcite vs. aragonite seas) throughout Phanerozoic time. The effect of  $p\text{CO}_2$  would have been particularly pronounced during intervals in which seawater  $m\text{Mg}/\text{Ca}$  remained near the boundary between calcite and aragonite seas ( $m\text{Mg}/\text{Ca}=2$ ). For example, Zhuravlev and Wood (2008) attribute a short-lived aragonite sea interval that occurred shortly after the onset of Calcite I seas in middle Cambrian time (Late Atbadanian–Botoman) to seawater  $m\text{Mg}/\text{Ca}$  remaining near the boundary value of two over that interval. They assert that these conditions would have favored frequent transitions between calcite and aragonite sea intervals, since even minor changes in seawater Mg/Ca, atmospheric  $p\text{CO}_2$ , and/or temperature (Morse et al., 1997) could have caused a shift in oceanic state.

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## 2.2.2 Seawater Mg/Ca

Experimental work by Leitmeier (1910, 1915), Lippman (1960), Müller et al. (1972) and Folk (1974) have shown that the precipitation of aragonite and high Mg calcite, rather than low Mg calcite, is caused by elevated concentrations on  $Mg^{2+}$ .

Füchtbauer and Hardie (1976, 1980) showed that in laboratory experiments on the system  $MgCl_2-CaCl_2-Na_2CO_3-H_2O$ , the precipitation of calcite versus high Mg calcite and aragonite is determined by the solution's Mg/Ca ratio, ionic strength and temperature. Their experiments yielded an Mg/Ca mole ratio of 2 ( $\pm 0.5$ ) as the boundary between the low Mg calcite ( $mMg/Ca < 0.04$ ) and aragonite+high Mg calcite ( $mMg/Ca > 0.04$ ) nucleation fields for chloride solutions under laboratory conditions approximating modern values of ionic strength ( $I=0.7$ ), temperature ( $28^\circ C$ ), pressure (1 atm total pressure) and atmospheric  $pCO_2$ . Morse et al. (1997) have subsequently shown that for temperatures between  $6^\circ$  and  $35^\circ C$ , the carbonate polymorph precipitated (calcite vs. aragonite+high Mg calcite) will be primarily determined by the Mg/Ca ratio of the solution, rather than atmospheric  $pCO_2$ . These results are in excellent agreement with Müller et al.'s (1972) carbonate nucleation fields (Mg/Ca vs. salinity) that were determined from observations of natural lakes.

Experiments have also shown that the percentage of Mg incorporated into non-skeletal calcite precipitates increases in proportion to both the Mg/Ca ratio and temperature of the solution (Kitano and Kanamori, 1966; Glover and Sippel, 1967; Katz, 1973; Füchtbauer and Hardie, 1976, 1980; Devery and Ehlmann, 1981; Mucci and Morse, 1983; Rimstidt et al., 1998). Rushdi et al. (1992) also suggest that low Mg calcite is favored for  $mMg/Ca$  ratios less than 2.

Spencer and Hardie (1990) showed that the primary factors that control seawater chemistry are river water (input), mid-ocean ridge hydrothermal brine (input),  $CaCO_3$  precipitation (output) and  $SiO_2$  precipitation (output). Using mid-ocean ridge/river water flux ratios to calculate ancient seawater chemistry, Spencer and Hardie showed that small changes in the mid-ocean ridge flux can cause changes in the Mg/Ca, Na/K

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and  $\text{Cl}/\text{SO}_4$  ratios of seawater that would result in the observed synchronized shifts in limestone and marine evaporite mineralogy.

Hardie (1996) later proposed that such minor changes in mid-ocean ridge flux could be caused by changes in the rate of ocean crust production. Mid-ocean ridge basalt is converted to greenstone as it comes in contact with brine, thereby releasing  $\text{Ca}^{2+}$  and  $\text{K}^+$  to the seawater and removing  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  from it. Therefore, mid-ocean ridges act as massive ion exchange systems where high rates of ocean crust production result in relatively high concentrations of  $\text{Ca}^{2+}$  and low concentrations of  $\text{Mg}^{2+}$  in seawater (low  $\text{Mg}/\text{Ca}$  ratios). Using historical rates of ocean crust production (inferred from first order eustatic sea level changes), Hardie (1996) used his ocean chemistry model to calculate ancient  $\text{Mg}/\text{Ca}$  ratios. The combination of these historical  $\text{Mg}/\text{Ca}$  values with Füchtbauer and Hardie's (1976, 1980) experimentally determined carbonate polymorph nucleation fields predicts a pattern of aragonite and calcite seas over the Phanerozoic Eon that closely resembles Sandberg's (1983) pattern observed in the geologic record.

Hardie's (1996) Phanerozoic  $\text{Mg}/\text{Ca}$  curve can also be combined with empirically derived brine evaporite models to predict a temporal pattern of late stage evaporites throughout the Phanerozoic Eon (Fig. 1). Elevated rates of ocean crust production, which cause gypsum stage  $\text{CaCl}_2$  brines, would result in the dominance of  $\text{KCl}$  late stage evaporites. Depressed rates of ocean crust production, which cause gypsum stage  $\text{MgSO}_4$  brines, would result in the dominance of  $\text{MgSO}_4$  late stage evaporites. Hardie's model predicts a pattern of late stage marine evaporites that agrees very well with the pattern observed in the Phanerozoic record. The ability of the model to predict the synchronized variation in the mineralogies of both late stage marine evaporites (Hardie, 1983) as well as non-skeletal (Sandberg, 1983; Lasemi and Sandberg, 2000) and reef- and sediment-forming carbonates (Stanley and Hardie, 1998, 1999; Steuber, 2002; Porter, 2007; Kiessling et al., 2008) suggests that the principal assumptions of the model are correct. Hardie's model is further supported by ancient seawater  $\text{Mg}/\text{Ca}$  ratios estimated from fluid inclusions in primary marine halite (Lowenstein et

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al., 2001, 2003, 2005; Brennan and Lowenstein, 2002; Brennan, 2002; Horita et al., 2002; Brennan et al., 2004; Timofeeff et al., 2006); secular variation in the skeletal Mg/Ca ratio of fossil molluscs (Steuber and Rauch, 2005) and echinoderms (Dickson, 2002, 2004); and secular variation in concentrations of Br in marine halite (Siemann, 2003).

### 3 Calcareous bryopsidalean algae

Secular variation in seawater Mg/Ca would have subjected the sediment- and limestone-forming bryopsidalean algae (i.e., the calcareous green algae or the codiacean algae) to at least 3 transitions between intervals favoring the precipitation of low Mg calcite and intervals favoring the precipitation of aragonite (their preferred mineralogy) and high Mg calcite since Permian time, which is the age of the oldest fossils assigned to the bryopsidalean order (Hillis, 2000). However, despite reportedly existing since Permian time, the bryopsidalean algae (Fig. 2) did not assume their modern role as major contributors of aragonite sediments to carbonate platform environments until the Eocene, around the time that the oceans transitioned into the most recent aragonite sea interval ( $m\text{Mg}/\text{Ca} > 2$ ). Multiple studies have been published over the past several years investigating the effects of seawater Mg/Ca and absolute  $\text{Ca}^{2+}$  on the polymorph mineralogy, primary production, and calcification of calcareous bryopsidalean algae (Ries, 2005a, 2006a; Stanley et al., 2009).

Specimens of *Halimeda incrassata* (Stanley et al., 2009), *Penicillus capitatus* (Ries, 2005a), and *Udotea flabellum* (Ries, 2006a) were grown for up to 90 d in 10-gallon glass aquaria filled with 30 L of experimental seawater (Bidwell and Spotte, 1985) formulated with Mg/Ca ratios of 1.0–1.5, 2.5, and 5.2, corresponding to “calcite sea”, “boundary calcite-aragonite sea”, and “aragonite sea” conditions, respectively. In the experiments on *Halimeda*, an additional set of tanks was set up to investigate the effects of absolute  $[\text{Ca}^{2+}]$ . These aquaria were formulated with identical Mg/Ca ratios and differed only in absolute  $[\text{Ca}^{2+}]$ , which was fixed at 25.3, 18.1, and 10.2 mM, as

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well as  $[Mg^{2+}]$ , which was adjusted to maintain the prescribed Mg/Ca ratio, and  $[Na^{2+}]$ , which was adjusted to offset the prescribed variations in  $[Mg^{2+}]$  and  $[Ca^{2+}]$ , such that salinity was maintained at the modern value of 35 ppt.

### 3.1 Effect of seawater Mg/Ca on polymorph mineralogy of calcareous bryopsidalean algae

Powder X-ray diffraction (XRD) of the mineral precipitates (Fig. 3; Table 1) derived from the *Halimeda*, *Penicillus*, and *Udotea* offspring algae from the normal seawater treatments ( $mMg/Ca=5.2$ ) confirms that these algae produce the majority of their  $CaCO_3$  as aragonite (*Halimeda*=92% aragonite, 8% Mg-calcite; *Penicillus* and *Udotea*=100% aragonite) under these conditions. However, all three species of algae began producing a substantial portion of their  $CaCO_3$  as low Mg calcite (*Halimeda*=46%; *Penicillus*=22%; and *Udotea*=25%) under the experimental calcite sea conditions ( $mMg/Ca=1.0-1.5$ ; Table 1). The proportion of calcite produced by the *Halimeda* algae increased significantly ( $p \ll 0.001$ ) as the Mg/Ca ratio of the experimental seawater treatment decreased into the calcite stability field (Table 1). Furthermore, the Mg/Ca ratio of the calcite produced by the *Halimeda* specimens (*Halimeda* actually produced small amounts of high Mg calcite in the boundary and aragonite sea conditions, as well) increased proportionately ( $p \ll 0.001$ ) with the Mg/Ca ratio of the experimental seawater treatment (Fig. 4).

Backscatter electron images of the *Halimeda* (Fig. 5) and *Udotea* (Fig. 6) offspring algae from each of the seawater treatments reveal the distribution of aragonite and calcite precipitates within the intertricular space of the algae (Fig. 2). The aragonite crystals are acicular and euhedral, ranging in length from 1 to 10  $\mu m$ , and packed in apparently random orientations. The calcite crystals are rhombic and subhedral, less than one micron in diameter, and generally clustered between the aragonite bundles. The two mineral phases tend to exhibit clumped distribution amongst the algal tissue.

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### 3.2 Effect of seawater Mg/Ca on reproduction of calcareous bryopsidalean algae

The total number of offspring algae produced by the parent algae varied amongst the different experimental seawater treatments. In the calcite, boundary, and aragonite seawater treatments, *Halimeda* produced 18, 37, and 45 offspring algae, *Penicillus* produced 13, 29, and 16 offspring algae, and *Udotea* produced 16, 17, and 23 offspring algae, respectively. That the algae generally produced more offspring under increasingly elevated Mg/Ca ratios suggests that the algae were stressed by producing a large portion of their CaCO<sub>3</sub> as aragonite in the seawater favoring the nucleation of calcite. If the precipitation of aragonite under such conditions required extra energy to manipulate the composition of the algae's calcifying fluid (e.g., to elevate Mg/Ca) in order to produce aragonite under such conditions, then this energy may be diverted away from other physiological activities, such as reproduction and tissue growth.

### 3.3 Effect of seawater Mg/Ca on linear extension, calcification, and primary production of calcareous bryopsidalean algae

Rates of linear extension, calcification, and primary production for the *Halimeda*, *Penicillus*, and *Udotea* algae decreased significantly ( $p < 0.05$ ) with reductions in Mg/Ca of the experimental seawaters ( $p < 0.05$ ; Table 1). This observation is consistent with the assertion that the steady elevation of seawater mMg/Ca ratios (from 1.0 to 5.2) over the past 65 My, since the major diversification of the calcareous bryopsidalean algae (Fig. 1), has fostered their increasingly important role as contributors of CaCO<sub>3</sub> sediments to carbonate platform environments over this interval.

Although the observed relationship between seawater Mg/Ca and calcification within the *Halimeda*, *Penicillus*, and *Udotea* algae may be expected, it is less intuitive why seawater Mg/Ca would also affect primary production and linear extension of these algae.

It has been proposed that photosynthesis in some calcareous bryopsidalean algae

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and coccolithophores is enhanced by CO<sub>2</sub> liberated by calcification (Paasche, 1968; Borowitzka and Larkum, 1976b; Borowitzka, 1977; Sikes et al., 1980; Reiskind et al., 1988, 1989; Ries, 2005a, 2006a; Stanley et al., 2005, 2009). The equilibrium reactions that govern the aqueous carbonate system can be summarized as follows:



Reducing [CO<sub>3</sub><sup>2-</sup>] via calcification has the net effect of shifting the aqueous carbonate system towards elevated [CO<sub>2</sub>] and [H<sup>+</sup>]. Thus, elevated rates of calcification may increase CO<sub>2</sub> within the interutricular calcification space of the *Halimeda*, *Penicillus*, and *Udotea* algae (Fig. 2), thereby increasing the algae's rate of photosynthesis and primary production. Although calcification is certainly not the sole source of CO<sub>2</sub> for photosynthesis within calcareous bryopsidalean algae (as many non-calcifying bryopsidalean algae exist), its role in CO<sub>2</sub> liberation may be sufficient to explain the observed connection between calcification, primary production, and linear extension.

15 An alternative mechanism that explains why algal linear extension and primary production would track calcification is based upon the release of H<sup>+</sup> ions during calcification. In one model, H<sup>+</sup> ions complex with HCO<sub>3</sub><sup>-</sup> ions within the algae's interutricular space, thus facilitating CO<sub>2</sub> extraction by dehydration of H<sub>2</sub>CO<sub>3</sub> within the algal cell (McConnaughey and Whelan, 1997; Hellblom et al., 2001; Hellblom and Axelsson, 2003). In another model, H<sup>+</sup> ions liberated by calcification are utilized by the alga as symporters or co-transporters of HCO<sub>3</sub><sup>-</sup> and nutrients, such as NO<sub>3</sub><sup>-</sup> and PO<sub>4</sub><sup>-3</sup>, across the algal cell wall (Price and Badger, 1985; Price et al., 1985; McConnaughey and Whelan, 1997; Hellblom et al., 2001). Increased rates of assimilation of these typically limiting substrates could cause the algae's rate of photosynthesis and primary production to vary commensurately with their rate of calcification.

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### 3.4 Effect of absolute $[Ca^{2+}]$ on linear extension, calcification, and primary production of the *Halimeda* alga

Because variations in seawater Mg/Ca throughout the geologic past are thought to be partially driven by inverse changes in  $[Ca^{2+}]$ , there exists the potential that the positive effects of elevated seawater Mg/Ca favoring the nucleation of the algae's preferred aragonite mineral would have been outweighed by the corresponding negative effects of reduced  $CaCO_3$  saturation state resulting from reduced  $[Ca^{2+}]$ . To isolate the effects of  $[Ca^{2+}]$  and Mg/Ca, *Halimeda* algae were reared in an array of experimental seawaters, specifically formulated to test for the effects of  $[Ca^{2+}]$  when Mg/Ca is held constant, and vice versa (Fig. 7). When  $mMg/Ca$  was held constant (at 1.5, 2.5, and 5.2), increases in  $[Ca^{2+}]$  from 10.2, to 18.1, to 25.3 mM resulted in increases in rates of linear extension, calcification, and primary production (Fig. 7). And when  $[Ca^{2+}]$  was held constant (at 10.2, 18.1, and 25.3 mM), increases in  $mMg/Ca$  from 1.5, to 2.5, to 5.2 resulted in increased rates of linear extension, calcification, and primary production (Fig. 7).

Thus, the results of the study on *Halimeda* reveal that both elevated Mg/Ca ratios and elevated  $[Ca^{2+}]$  promote calcification, primary production, and linear extension within this alga. The elevated Mg/Ca ratios evidently translate to higher rates of calcification by creating ambient chemical conditions favorable for the precipitation of the alga's preferred aragonite biomineral. Elevated  $[Ca^{2+}]$  probably fosters higher rates of calcification by increasing the  $CaCO_3$  saturation state of the alga's ambient seawater.

Critically, over the range of  $mMg/Ca$  ratios (1.0–5.2) and absolute  $[Ca^{2+}]$  (10.2–25.3 mM) that are believed to have occurred throughout Phanerozoic time, the favorable effects of elevated Mg/Ca on bryopsidalean calcification were greater in magnitude than the unfavorable effects of reduced  $CaCO_3$  saturation state that resulted from corresponding reductions in  $[Ca^{2+}]$ . Thus, Mg/Ca ratio appears to be the primary determinant of how calcareous bryopsidalean algae would have responded to calcite-aragonite sea transitions. However, at least one scenario was identified in which increasingly

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favorable Mg/Ca ratios were concomitantly outweighed by increasingly unfavorable CaCO<sub>3</sub> saturation states (via decreasing [Ca<sup>2+</sup>]), in terms of their relative effects on calcification rate. This was evident (Fig. 7) when experimental seawater conditions shift from *mMg/Ca*=1.5, [Ca<sup>2+</sup>]=25.2 mM to *mMg/Ca*=2.5, [Ca<sup>2+</sup>]=10.2 mM.

### 5 3.5 Effect of seawater Mg/Ca on thallus stiffness in the *Penicillus* alga

Stress-strain curves were derived for the *Penicillus* specimens by plotting the stress exerted on the thallus against the resulting deflection or strain (Figs. 8–10). Strain was measured as thallus deflection because all deflection was due solely to current stress. The thallus stiffness for each *Penicillus* thallus was then calculated as the slope of the least squares linear regression through this stress-strain curve (Fig. 10a). Thallus stiffness was averaged for each of the seawater treatments and plotted against corresponding seawater *mMg/Ca* (Fig. 10b).

The stiffness of the *Penicillus* thalli increased significantly ( $p < 0.001$ ) with Mg/Ca ratio of the ambient seawater (Fig. 10b). Algae reared in the experimental seawater favoring their inherently aragonitic mineralogy were nearly twice as stiff as those reared in the experimental seawater that favored the nucleation of calcite.

### 3.6 Biomineralogical control within the calcareous byrpsidalean algae

The observation that the *Halimeda*, *Penicillus* and *Udotea* algae each precipitate the majority of their CaCO<sub>3</sub> as the aragonite polymorph in the experimental calcite seawater suggests that these algae exhibit some control over the Mg/Ca ratio of their intertricular calcifying fluid. However, since these algae commence producing a portion of their CaCO<sub>3</sub> as the kinetically favored calcite polymorph under these conditions, it is evident that their biomineralogical control can be partially overridden by ambient seawater Mg/Ca.

The distribution of aragonite and calcite precipitates within the *Halimeda* (Fig. 5), *Penicillus*, and *Udotea* (Fig. 6) algae grown in the experimental calcite seawater occurs

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on a spatial scale that is comparable to that of the purported acid and alkaline zones within these algae (De Beer and Larkum, 2001). Both conditions may reflect the algae's spatially limited control over the chemical milieu of their interutricular fluid.

It has been suggested that *Halimeda* algae control calcification solely through pH regulation (Borowitzka, 1987; De Beer and Larkum, 2001). If this assertion is correct, then *Halimeda* algae grown in the experimental calcite seawater should precipitate exclusively calcite – which they did not. DeBeer and Larkum's (2001) conclusion that  $\text{Ca}^{2+}$  is not actively transported into the interutricular space of *Halimeda* is based on their observation that the alga's rate of calcification is unaffected by inhibition of the Ca-ATPase enzyme. Although their findings show that *Halimeda* are not actively transporting  $\text{Ca}^{2+}$  into the calcifying space, it is conceivable that *Halimeda*, as well as *Penicillus* and *Udotea*, pump  $\text{Ca}^{2+}$  out of the interutricular space, thereby maintaining the Mg/Ca ratio of certain regions of the algae's interutricular space within the aragonite nucleation field ( $m\text{Mg}/\text{Ca} > 2$ ). This, of course, requires that the  $\text{CaCO}_3$  saturation state of the interutricular fluid is maintained at a level sufficient to promote calcification, even after  $\text{Ca}^{2+}$  is transported out, perhaps by increasing  $[\text{CO}_3^{2-}]$  by removing  $\text{CO}_2$  via photosynthesis (Borowitzka, 1982b, 1987) or by increasing pH through  $\text{H}^+$ -pumping (De Beer and Larkum, 2001). Alternatively, the same result could be achieved by actively transporting  $\text{Mg}^{2+}$  ions into the algae's interutricular space, thereby elevating the Mg/Ca ratio into the aragonite nucleation field. However, a mechanism capable of such rapid transport of  $\text{Mg}^{2+}$  across the algal cell wall has yet to be identified in the *Halimeda*, *Penicillus*, or *Udotea* algae.

### 3.7 Paleocological implications for the calcareous byropsidalean algae

The results of the experimental studies suggest that the predominant carbonate-producing bryopsidalean algae – *Halimeda*, *Penicillus*, and *Udotea* – would have been slower growing, smaller, and less calcified during calcite seas of the geologic past. Such geochemically induced reductions in the fitness of these algae would have had significant ecological implications for these algae and for carbonate platform environ-

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ments, in general. Their slower growth rates and smaller size would have reduced their ability to compete for space and sunlight on the substrate-limited shallow tropical seafloor. And their reduced calcification would have rendered them more susceptible to predation by grazing fish, which in modern aragonite seas are deterred by the algae's high  $\text{CaCO}_3$  content, as well as their secondary metabolic toxins (Wray, 1977; Paul and Fenical, 1984; Paul and Hay, 1986; Hay et al., 1988, 1994; Paul and Van Alstyne, 1988, 1992; Schupp and Paul, 1994). The algae's contribution of biogenic  $\text{CaCO}_3$  to shallow tropical carbonate platforms would have been comparably diminished by such reductions in calcification, primary production, and population density during calcite sea intervals.

### 3.8 Conclusions – calcareous bryopsidalean algae

1. Observed reductions in the calcification, primary production, and linear extension of *Halimeda*, *Penicillus*, and *Udotea* algae grown in experimental seawater that favors the calcite polymorph over the aragonite polymorph indicate that the fitness of these algae is reduced when grown in mineralogically unfavorable seawater. These experimental studies suggest that calcareous bryopsidalean algae would have been smaller, less abundant, less competitive for space on the seafloor, and less resistant to grazing when seawater Mg/Ca did not favor their inherently aragonitic mineralogy. This is consistent with the assertion (Stanley and Hardie, 1998, 1999) that a shift from calcite-to-aragonite seas in the early-to-middle Cenozoic enabled the aragonite-secreting bryopsidalean algae to flourish and to become the important producers of  $\text{CaCO}_3$  sediments that they are today.
2. Thallus stiffness decreased for specimens of *P. capitatus* grown in seawater that does not favor the aragonite polymorph. This physiological consequence of reduced Mg/Ca appears to result from decreased calcification and associated reductions in primary production.
3. Elevated Mg/Ca ratios and elevated  $[\text{Ca}^{2+}]$  both result in increased rates of calci-

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5 fication, primary production, and linear extension in *Halimeda* algae. Therefore, the inherently inverse relationship between Mg/Ca and  $[Ca^{2+}]$  causes their effects on *Halimeda* algal calcification, primary production, and linear extension to be interfering. However, over the range of coupled seawater Mg/Ca ratios and  $[Ca^{2+}]$  that are believed to have occurred throughout the geologic history of the bryopsidalean algae, these experiments reveal that seawater Mg/Ca is the dominant variable. Inverse variations in  $[Ca^{2+}]$  appear only to moderate the effects of seawater Mg/Ca.

- 10 4. The concomitant variations in calcification, primary production, and linear extension of the *Halimeda*, *Penicillus*, and *Udotea* algae suggest that there are important connections amongst these processes within the algae. Seawater Mg/Ca appears to directly influence calcification via  $CaCO_3$  polymorph compatibility. Calcification, in turn, may influence primary production and linear extension by supplying  $CO_2$  for photosynthesis and/or supplying  $H^+$  ions for various cellular functions that support photosynthesis, such as the transcellular proton-shuttling of nutrients or  $HCO_3^-$  and the formation of intracellular  $H_2CO_3$ , from which  $CO_2$  can be efficiently extracted via dehydration.
- 15 5. The precipitation of predominantly aragonite by *Halimeda*, *Penicillus*, and *Udotea* algae in experimental seawater that kinetically favors the precipitation of calcite ( $mMg/Ca < 2$ ) indicates that these algae actively specify nucleation of the aragonite polymorph. This may be accomplished by controlling internal Mg/Ca through cation pumping or with chemical and/or mechanical templates that specify nucleation of the aragonite polymorph (Borowitzka, 1987). However, the algae's partial precipitation of calcite in the experimental calcite seawater reveals that their biomineralogical control can be partially overridden by ambient seawater Mg/Ca.
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## 4 Coccolithophores

The formation of the massive, coccolithic chalk deposits in Late Cretaceous time (Hattin, 1988) has been attributed to the low oceanic Mg/Ca ratios reported for that interval (Stanley and Hardie, 1998, 1999), which would have favored the coccolithophores' inherently calcitic mineralogy. Experiments were conducted to evaluate the effect of seawater Mg/Ca on skeletal Mg/Ca, calcification, and growth rate of these calcifying nanoplankton (Stanley et al., 2005).

Coccolithophore strains (CCMP645, CCMP2119, CCMP298) of *Pleurochrysis carterae*, *Ochrosphaera neopolitana*, and *Coccolithus neohelis* were cultured for 15 d in 500 mL experimental seawaters (contained in 1 L beakers) formulated at mMg/Ca ratios of 0.5, 1.0, 1.5, 2.5, 3.5, and 5.2, thereby encompassing the range of values (Hardie, 1996) believed to have existed throughout the coccolithophores' existence. To differentiate between the effects of Mg/Ca ratio and absolute  $[Ca^{2+}]$  on the coccolithophores, three additional seawaters were formulated with fixed  $[Ca^{2+}]$  at mMg/Ca ratios of 1, 3.5 and 5.2 (see experimental design for experiments on calcareous bryopsidalean algae for details). The *Pleurochrysis carterae* and *Coccolithus neohelis* cultures were fertilized with  $8.8 \times 10^{-4}$  moles/L nitrogen (as nitrate),  $2.3 \times 10^{-4}$  moles/L phosphorus (as phosphate), and  $1.45 \times 10^{-5}$  moles/L iron (as  $Fe^{3+}$ ), as specified by the P-G CCMP f/2 culture medium. The *Ochrosphaera neopolitana* culture was fertilized with  $3.5 \times 10^{-5}$  moles/L nitrogen (as nitrate),  $9.2 \times 10^{-6}$  moles/L phosphorus (as phosphate), and  $5.8 \times 10^{-7}$  moles/L iron (as  $Fe^{3+}$ ), as specified by the P-G CCMP f/50 culture medium.

### 4.1 Effect of seawater Mg/Ca and $[Ca^{2+}]$ on population growth of coccolithophores

The rate of population growth for each of the three species of coccolithophore was greatest in the experimental seawaters that favored the nucleation of the coccolithophores' calcite skeletal mineral ( $mMg/Ca < 2$ ) and systematically decreased as sea-

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water Mg/Ca increased towards the aragonite stability field (Figs. 11, 12). Experiments that held the Mg/Ca ratio constant while varying  $\text{Ca}^{2+}$  concentrations (Fig. 13a–b), and the concentration of  $\text{Ca}^{2+}$  constant while varying Mg/Ca ratios (Fig. 13c–d), revealed that population growth rates increased with increasing absolute concentrations of  $\text{Ca}^{2+}$ , as well as with decreasing seawater Mg/Ca ratios.

## 4.2 Effect of seawater Mg/Ca on chalk production by coccolithophores

Chalk production increased significantly as seawater Mg/Ca decreased (Fig. 14), resulting in the greatest amount of chalk being formed in the experimental calcite seawater treatment. Significantly, the composition of this experimental calcite seawater treatment is believed to be representative of the oceans in Late Cretaceous time – when coccolithophores were producing the massive chalk deposits (e.g., White Cliffs of Dover) after which the Cretaceous Period is named. These results are consistent with the population data obtained from the daily turbidimeter measurements (Figs. 11, 12).

Backscatter electron images (Fig. 15) also reveal that individual coccoliths are more heavily calcified when grown in the low Mg/Ca seawater treatments, which favor nucleation of the coccolithophores' inherently calcitic biomineral. And like for the calcareous bryopsidalean algae, increased calcification apparently liberates more  $\text{CO}_2$ , which probably stimulates photosynthesis by the coccolithophores, thereby resulting in the elevated rates of population growth observed in the experimental calcite seawater treatments.

These results support the assertion that coccolithophore chalk production that was widespread throughout Cretaceous time was facilitated by the low seawater Mg/Ca ratios known to have existed throughout this interval, which would have supported precipitation of the coccolithophore's inherently calcitic skeletal mineral.

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### 4.3 Effect of seawater Mg/Ca on coccolithophorid mineralogy

The Mg/Ca ratios of the calcitic coccoliths secreted by the *Ochrosphaera neopolitana* and *Pleurochrysis carterae* coccolithophores (Fig. 16b–c) were directly correlated with the Mg/Ca ratio of their ambient seawater. The *Coccolithus neohelis* coccolithophores (Fig. 16a), however, produced low Mg calcite regardless of ambient seawater Mg/Ca. These results are particularly striking given that all coccolithophores are thought to secrete exclusively low Mg calcite in modern seas (Milliman, 1974).

The observation that two of the three species of coccolithophores incorporated Mg into their calcitic coccoliths in proportion to the Mg/Ca ratio of the seawater in which they were grown suggests that, despite their ability to dictate precipitation of highly intricate coccoliths, their mineralogical control is limited in its capacity to control Mg incorporation in the calcite crystal lattice. The third species, however, which precipitates low Mg calcite regardless of ambient seawater Mg/Ca, is apparently better able to regulate skeletal Mg incorporation.

### 4.4 Conclusions – coccolithophores

1. Increased rates of population growth and calcification exhibited by coccolithophores grown under low Mg/Ca ratios and high  $\text{Ca}^{2+}$  concentrations suggest that the existence of these conditions in Cretaceous time likely enabled coccolithophores to produce the massive chalk deposits from which that interval derives its name (*Creta-* is Latin for “chalk”). This is particularly striking given that the coccolithophores flourished in the most modified experimental seawaters, to which they were naturally the least accustomed.
2. Conversely, the high Mg/Ca ratio and low  $\text{Ca}^{2+}$  concentration of modern seawater probably prevents chalk production by most extant species.
3. The decrease in skeletal Mg/Ca in response to reduced seawater Mg/Ca for two of the species studied suggest that their biomineralogical control can be partially

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overridden by ambient seawater chemistry. That the third species did not exhibit a change in skeletal Mg/Ca in response to reduced seawater Mg/Ca may be evidence for stronger biomineralogical control.

- 5 4. Correlation between skeletal Mg/Ca and seawater Mg/Ca for two of the three species of coccolithophores, but not for the third species, suggests that the mineralogy (low Mg calcite vs. high Mg calcite) of some, but not all, species of coccolithophores has varied significantly with seawater Mg/Ca throughout their geological history.

## 5 Scleractinian corals

10 Scleractinian corals, which secrete massive aragonitic skeletons, have been major reef frame builders from Late Triassic (Stanton and Flügel, 1987; Bernecker, 1996) through Early Cretaceous time (Stanley and McRoberts, 1993) and from early Oligocene through to present time (Frost, 1977, 1981; Fig. 1). During these intervals, the Mg/Ca ratio of the oceans favored the inorganic precipitation of aragonite ( $mMg/Ca > 2$ , Hardie, 1996). The reign of the scleractinian corals was interrupted during Mid-Cretaceous time by the ascendance of the largely calcitic rudist bivalves (Scott, 1984; Kauffman and Johnson, 1988; Fig. 1) close to the time when the Mg/Ca ratio of seawater dropped to its lowest Phanerozoic level and favored the precipitation of calcite ( $mMg/Ca < 2$ ).

15 The rudists continued as primary reef builders through the end of the Cretaceous Period. Significantly, however, the scleractinian corals did not resume forming massive, widespread reefs until early in Oligocene time, just after the Mg/Ca ratio of seawater shifted back into the aragonite stability field (Fig. 1), despite the global climate cooling that had occurred at that time (Wolfe, 1978).

20 It has been proposed that shifts in the Mg/Ca ratio of seawater, which alternately favored the precipitation of calcite or aragonite throughout Phanerozoic time (Fig. 1), may have influenced the success of scleractinian corals as primary reef builders throughout

their existence (Stanley and Hardie, 1998, 1999). Experiments have been conducted (Ries et al., 2006) to evaluate the influence of seawater Mg/Ca on the mineralogy and growth rates of three species of modern scleractinian corals, *Acropora cervicornis*, *Porites cylindrica*, and *Montipora digitata*.

Sixty comparably sized individuals of each of the three species (180 total) were grown for 60 d in six experimental seawaters that were identical except for their *m*Mg/Ca ratios, which were formulated at 1.0, 1.5, 2.5, 3.5, and 5.2, thereby encompassing the range of values (Hardie, 1996) believed to have existed throughout the scleractinian corals' existence (Fig. 1). To differentiate between the effects of Mg/Ca ratio and absolute concentration of Ca<sup>2+</sup> on coral growth, three additional seawaters were formulated with fixed Ca<sup>2+</sup> concentrations at *m*Mg/Ca ratios of 1, 3.5 and 5.2. This simultaneously permits the comparison of coral growth rates in two sets of seawaters with fixed *m*Mg/Ca ratios (1 and 5.2) and different absolute Ca<sup>2+</sup> concentrations.

### 5.1 Effect of seawater Mg/Ca on scleractinian coral mineralogy

Backscatter electron imaging (Fig. 17) and X-ray diffraction of new skeletal growth revealed that the three species of corals each secreted approximately one-third of their skeleton as low Mg calcite (Fig. 18a) when grown in the low Mg/Ca experimental calcite seawater (*m*Mg/Ca=1.0). As seawater Mg/Ca increased towards the aragonite stability field, the proportion of calcite within the coral skeletons decreased (Fig. 18a). Concentrations of Sr and Mg in the corals' skeletons were mapped to approximate the distribution of aragonite and calcite, respectively (Fig. 17).

Notably, the Mg/Ca ratio of the calcite secreted by the corals increased proportionally with the Mg/Ca ratio of the experimental seawater, thereby producing low Mg calcite (*m*Mg/Ca<0.04) in seawater of *m*Mg/Ca<2, and high Mg calcite (*m*Mg/Ca>0.04) in seawater of *m*Mg/Ca>2 (Fig. 18b). This relationship is consistent with that observed for Mg incorporation in calcite secreted by four species of reef-dwelling animals (echinoids, crabs, shrimp, serpulid worms; Ries, 2004), coralline algae (Ries, 2006b; Stanley et al., 2002), some species of coccolithophores (Stanley et al., 2005), and the calcareous

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alga *Halimeda* (Stanley et al., 2009). The Mg/Ca ratio of the aragonite secreted by the corals, which was roughly one-tenth the magnitude of the Mg/Ca ratio of the calcite secreted by the corals, also increased with seawater Mg/Ca (Fig. 18b).

It has been proposed that organic matter detected within the centers of calcification of scleractinian corals (up to 1% by volume) is a vestige of the organic matrices and templates that specify nucleation of the aragonitic polymorph (Cuif et al., 1999). That the corals grown in the experimental seawater with an Mg/Ca ratio favoring the inorganic precipitation of low Mg calcite still precipitated two-thirds of their skeleton as aragonite supports the hypothesis that corals do exert significant control over their skeletal mineralogy (Cuif et al., 1999). However, the discovery that scleractinian corals precipitate approximately one-third of their skeleton as low Mg calcite, instead of aragonite, in the experimental calcite seawater suggests that CaCO<sub>3</sub> polymorph control within certain portions of the coral skeleton can be partially overridden by ambient seawater chemistry.

Additional evidence that scleractinians are limited in their mineralogical control is their tendency to incorporate Mg, as observed in this study, and other trace elements (Cohen and McConnaughey, 2003), into their skeletons in proportions that reflect their abundance in seawater. Furthermore, the acicular morphology and spherulitic organization of the aragontic crystals in the sclerodermites of coral skeletons closely resembles the spherulitic aragonite that forms inorganically in marine cements, suggesting that they could be deposited by abiotic precipitation (Barnes, 1970).

Seawater reaches the coral's region of calcification, beneath the calcicoblastic ectoderm, by moving through cells, between cells, and by diffusion through the porous skeleton. An ATPase pump elevates Ca<sup>2+</sup> in the region of calcification only slightly above the level of ambient seawater (Al-Horani et al., 2003), thereby suggesting that corals precipitate their skeletons from only slightly chemically modified seawater. The accelerated precipitation rate of the coral skeleton, nearly 100 times that of inorganic CaCO<sub>3</sub> precipitation (Cohen and McConnaughey, 2003), can instead be attributed to the pumping of protons from the calcification medium (Al-Horani et al., 2003). It there-

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fore seems reasonable that the Mg/Ca ratio of ambient seawater would have a significant effect on the chemistry of the coral's calcification medium, and therefore its skeletal polymorph mineralogy.

Additionally, there is a secondary mode of calcification in scleractinians that occurs beneath the coral's ectoderm-bounded calcification space that fills pore spaces formerly occupied by living tissue. In modern scleractinians, this secondary growth is aragonitic but its morphology, organization and trace element chemistry differs from that of the primary skeleton secreted (Enmar et al., 2000). Ries et al. (2006) hypothesized that the mineralogy of these secondary crystals is determined solely by the Mg/Ca ratio of the ambient seawater, and that these crystals may account for the relatively large amount of calcite produced by the scleractinians in the lower Mg/Ca experimental seawaters.

The discovery that coral skeleton polymorph mineralogy varies with the Mg/Ca of seawater suggests that the scleractinian corals may have secreted at least part of their skeleton as low Mg calcite in the calcite seas of Late Cretaceous and early Cenozoic time, when they existed as isolated colonies and did not build the massive, widespread reefs that they do today. This is supported by recent geochemical and petrographic analyses of fossil scleractinia from the Cretaceous Period, which suggest that some species of scleractinian corals produced largely calcitic skeletons during calcite seas of the geologic past (Stolarski et al., 2007).

The tendency for both the aragonitic and calcitic portions of the coral skeletons to incorporate Mg in proportion to its abundance in seawater suggests that the Mg/Ca of fossil corals ( $Mg/Ca_C$ ) may be a record of oceanic Mg/Ca ( $Mg/Ca_{sw}$ ) throughout their existence. Mg fractionation algorithms for coral calcite and aragonite were derived from the experiments on the three scleractinian species:

$$Mg/Ca_C = 0.002007(Mg/Ca_{sw}) \text{ (aragonite);} \quad (1)$$

$$Mg/Ca_C = 0.02129(Mg/Ca_{sw}) \text{ (calcite).} \quad (2)$$

These algorithms were combined with temperature-based Mg fractionation algorithms

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(species-normalized; Chave, 1954):

$$\text{Mg}/\text{Ca}_C = 0.0003227T + 0.002430 \text{ (aragonite);} \quad (3)$$

$$\text{Mg}/\text{Ca}_C = 0.004453T + 0.07004 \text{ (calcite)} \quad (4)$$

to yield single algorithms that define the Mg/Ca ratio of skeletal aragonite and calcite as a function of the Mg/Ca ratio ( $\text{Mg}/\text{Ca}_{\text{sw}}$ ) and temperature ( $T$ ) of seawater, and a species coefficient ( $S$ ) equal to the skeletal Mg/Ca of a wild representative of the given species in nature, which secreted  $\text{CaCO}_3$  at  $\text{Mg}/\text{Ca}_{\text{sw}}=5.2$  and some known temperature, divided by the skeletal Mg/Ca predicted by the algorithm for  $\text{Mg}/\text{Ca}_{\text{sw}}=5.2$  and the given temperature:

$$\text{Mg}/\text{Ca}_C = S \left[ 0.00006244(T) (\text{Mg}/\text{Ca}_{\text{sw}}) + 0.0004702 (\text{Mg}/\text{Ca}_{\text{sw}}) \right] \text{ (aragonite);} \quad (5)$$

$$\text{Mg}/\text{Ca}_C = S \left[ 0.0005227(T) \left( \text{Mg}/\text{Ca}_{\text{sw}}^{1.4628} \right) + 0.008222 \left( \text{Mg}/\text{Ca}_{\text{sw}}^{1.4628} \right) \right] \text{ (calcite).} \quad (6)$$

These algorithms could theoretically be used to calculate historical oceanic Mg/Ca ratios from the skeletal Mg/Ca and paleoenvironmental temperature of unaltered coral fossils. Likewise, paleotemperature reconstructions based on the Mg/Ca ratio of fossil coral skeletons must correct for the effect of seawater Mg/Ca on skeletal Mg/Ca (Hart and Cohen, 1996; Mitsuguchi et al., 1996).

## 5.2 Effect of seawater Mg/Ca on calcification rates within scleractinian corals

Each of the three species of scleractinian corals grew fastest in the aragonite sea water treatments (Fig. 19a). There was a significant decrease in growth rates when seawater crossed into the calcite nucleation field at  $m\text{Mg}/\text{Ca}<2$ . The slow growth rates for corals in the experimental calcite seawater is likely due to difficulties in precipitating aragonite, which still formed roughly two-thirds of their skeleton in this medium, from seawater that favors the nucleation of calcite (Hardie, 1996).

These results support the empirical evidence that the Early Cretaceous through early Oligocene hiatus of the aragontic scleractinians' reign as primary reef builders from

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Late Triassic through present time (Frost, 1977, 1981; Stanton and Flügel, 1987; Stanley and McRoberts, 1993; Bernecker, 1996), was caused at least in part by a drop in oceanic Mg/Ca over this interval such that seawater no longer favored the precipitation of the scleractinians' inherently aragonitic mineralogy (Stanley and Hardie, 1998, 1999). Such depressed growth rates over this interval would have opened the reef-building environments to the primarily calcitic rudists, which became the dominant reef builders throughout the Cretaceous Period (Scott, 1984; Kauffman and Johnson, 1988). However, the scleractinians did not resume their role as primary reef builders until early in the Oligocene (Frost, 1977, 1981), long after the decline of the rudists, when seawater  $m\text{Mg}/\text{Ca}$  ratios had risen into the aragonite stability field. Significantly, the highest growth rates for the scleractinians in this experiment occurred not in modern seawater ( $m\text{Mg}/\text{Ca}=5.2$ ), but rather in seawater with a  $m\text{Mg}/\text{Ca}=3.5$ . This is consistent with the dramatic resurgence of the scleractinians during the early Oligocene, when the  $m\text{Mg}/\text{Ca}$  of seawater was between 3 and 3.5. Ries et al. (2006) hypothesize that the occurrence of maximum growth rates in seawater with  $m\text{Mg}/\text{Ca}=3.5$  resulted from the optimal combination of elevated  $[\text{Ca}^{2+}]$ , relative to modern seawater, along with Mg/Ca ratios that were well within the aragonite stability field.

### 5.3 Effect of absolute $[\text{Ca}^{2+}]$ on calcification rates within scleractinian corals

Experimental seawater treatments were formulated at  $m\text{Mg}/\text{Ca}$  ratios of 1.0, 3.5, and 5.2 with absolute  $\text{Ca}^{2+}$  concentrations fixed at 14 mM to differentiate between the effects of Mg/Ca and absolute  $\text{Ca}^{2+}$  on coral growth rates. Again, the corals exhibited maximum growth rates in seawater formulated at  $m\text{Mg}/\text{Ca}=3.5$ , slightly decreased growth rates in seawater formulated at  $m\text{Mg}/\text{Ca}=5.2$ , and minimum growth rates in seawater formulated at  $m\text{Mg}/\text{Ca}=1.0$  (Fig. 19b). The similarity between these results and those from the experiments with variable absolute  $\text{Ca}^{2+}$  suggests that, regardless of the absolute concentration of  $\text{Ca}^{2+}$ , 3.5 is the optimal  $m\text{Mg}/\text{Ca}$  ratio of seawater for the production of scleractinian coral skeleton.

In pioneering experiments on the influence of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  concentrations on



coral biomineralization (Swart, 1980), specimens of *Acropora aquamosa*, *Pocillopora damicornis*, *Acropora cuneata* and *Porites lutea* were grown for 10 d in seawater with  $Mg^{2+}$  concentrations 100 and 200 mg/L higher than modern values and  $Ca^{2+}$  concentrations 100, 200, and 400 mg/L higher than modern values. Seawater  $Mg^{2+}$  concentrations significantly higher than that of modern seawater prevented new skeletal growth, while  $Ca^{2+}$  concentrations twice those of modern seawater resulted in reduced rates of growth. These results are consistent with the findings that coral growth rates decreased significantly in experimental seawaters with low *mMg/Ca* ratios, relative to modern values. However, the short duration of these experiments and the anomalously high concentrations of  $Mg^{2+}$  and  $Ca^{2+}$  used – higher than have ever characterized Phanerozoic seawater – preclude interpretation of the results in the context of actual past marine conditions.

Other experiments on specimens of *Acropora* sp., *Stylophora pistillata*, *Acropora cervicornis* and *Acropora formosa* show that calcification rates increase as  $Ca^{2+}$  concentrations are elevated from approximately 20% to 80% of normal marine values (Chalker, 1976; Gattuso et al., 1998). At  $Ca^{2+}$  concentration above 80%, calcification rates level out and, in some cases, decline. However, these experiments do not adjust  $Mg^{2+}$  concomitantly with  $Ca^{2+}$ , and therefore do not control for the kinetic effects of ambient seawater *Mg/Ca*. When the observed variation in calcification rate is correlated with the implicit variation in the *Mg/Ca* ratio of the experimental seawaters, the results conform to those observed in this study. Furthermore, the short durations (2–2.5 h) of the experiments did not allow sufficient time for the corals to fully equilibrate to the substantially altered ambient conditions, thereby limiting the biological significance of the results.

Experiments have also shown that the  $CO_3^{2-}$  concentration of seawater can limit the rate of coral calcification (Langdon et al., 2000; Marubini et al., 2003). Therefore, it is conceivable that the rapid ocean crust production and accompanying volcanism that characterized the Cretaceous Period would have elevated  $pCO_2$  in the atmosphere and oceans and reduced the aragonite saturation state of seawater. One could therefore

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deduce that it was the reduced aragonite saturation state of seawater during Cretaceous time, and not the low oceanic Mg/Ca favoring the precipitation of calcite over aragonite, which resulted in the scleractinian hiatus over this interval. However, as discussed above, the rapid ocean crust production of the Cretaceous Period resulted in an enrichment in oceanic  $\text{Ca}^{2+}$  that would have mostly offset the accompanying decline in  $\text{CO}_3^{2-}$  (Hardie, 1996; Berner, 1997; Demicco et al., 2005), thereby maintaining seawater near the 3–4 times aragonite supersaturated state that exists today.

#### 5.4 Paleocological implications of reduced and bi-mineralic calcification

The apparent lability of coral skeletal polymorph mineralogy begs the question whether there is a biomechanical advantage for a coral skeleton built from aragonite needles versus one built from calcite rhombs. The obvious difference between the two skeletons concerns crystal packing and can be likened to the advantages of trabecular (low density) and cortical (high density) bone in vertebrates. Assuming that calcitic rhombs would be more closely packed than aragonitic needles, the calcitic skeletons would presumably be denser and, therefore, less successful at taking up space on the seafloor, which could be a significant disadvantage in the highly competitive, substrate-limited tropical reef environment. The increased density of the close-packed calcitic skeleton would likely make the coral's surface more resistant to abrasion from minor impact, such as that delivered by grazing parrotfish, while its overall skeleton would probably be more susceptible to major impacts, such as that associated with hurricane surf, which would result in cross-skeletal fractures propagating along the calcite rhombs' perfect cleavage planes. Alternatively, coral skeletons built from aragonite would be more resistant to major fracturing, as propagating fractures would be interrupted by the spherulitic organization of the aragonitic sclerodermites, and less resistant to minor surficial abrasion, due to lower skeletal density.

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## 5.5 Conclusions – scleractinian corals

1. Scleractinian corals changed their skeletal mineral from aragonite in modern aragonite seawater to a mixture of one-third low Mg calcite and two-thirds aragonite when grown in experimental calcite seawater – indicating that although corals do specify nucleation of the aragonite polymorph, this mineralogical control can be partially overridden by ambient seawater chemistry.
2. The polymorph mineralogy of portions of scleractinian corals' skeletons may have varied with seawater Mg/Ca throughout geologic time. It now seems conceivable that they would have produced at least part of their skeleton from low Mg calcite during the calcite seas of mid-Late Cretaceous time.
3. Scleractinian corals exhibit reduced rates of calcification relative to the control when grown in experimental calcite seawaters that do not favor precipitation of the coral's preferred aragonite mineral.
4. These results support the hypothesis that the scleractinia's hiatus from primary reef building during the Early Cretaceous through early Oligocene may have been caused, at least in part, by the transition to calcite seawater over this interval. Likewise, their reappearance in the early Oligocene and continued dominance as reef builders through to the present may have been facilitated by the concomitant transition back to aragonite seawater, which favors the scleractinians' preferred aragonitic mineralogy.

## 6 Coralline red algae

Coralline algae have been important producers of  $\text{CaCO}_3$  in the oceans throughout Phanerozoic time (Wray, 1977). Branching corallines have been major contributors of carbonate sediments to lower energy back-reef and fore-reef environments while encrusting corallines have been important cementers of reefs on the high-energy reef

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crest (Alexandersson, 1977; James et al., 1988; Berner, 1990; Aguirre et al., 2000; Littler, 1973; Macintyre, 1997; Wray, 1977; Chisholm, 2003). In modern seawater with a  $m\text{Mg}/\text{Ca}$  of 5.2, these algae produce exclusively high Mg calcite. However, it has been asserted that the Mg/Ca ratio of the calcite secreted by these algae may have varied throughout geologic time in lock-step with secular variations in seawater chemistry (Stanley and Hardie, 1998, 1999). This assertion was based on two sets of earlier observations: (1) that the Mg/Ca ratio of calcite secreted by coralline algae, along with a wide range of other calcite-secreting organisms, is strongly influenced by seawater temperature (Chave, 1954); and (2) that the Mg/Ca ratio of abiotically-precipitated calcite is determined by the temperature and Mg/Ca ratio of the precipitating solution (Berner, 1975; Füchtbauer and Hardie, 1976, 1980; Mucci and Morse, 1983; Morse et al., 1997). Here, I review two sets of experiments that were conducted to investigate the effects of seawater Mg/Ca on Mg incorporation in the encrusting (Ries, 2006b) and branching (Stanley et al., 2002) coralline red algae.

Specimens of three branching species of coralline algae of the genus *Amphiroa* (*A. fragilissima* and two unknown species, A and B) and one encrusting species of the genus *Neogoniolithon* were grown for 100 d in experimental seawaters that were identical (Bidwell and Spotte, 1985) except for their  $m\text{Mg}/\text{Ca}$  ratios, which were formulated at 1.0, 1.5, 2.5, 2.5, 5.2 and 7.0, thereby encompassing the range of values shown to have existed throughout the algae's geologic history (1.0–5.2; Fig. 1; Hardie, 1996). To differentiate between the effects of Mg/Ca ratio and absolute  $\text{Mg}^{2+}$  concentration on skeletal Mg fractionation in the encrusting coralline algae, a second set of experimental seawaters were formulated with  $m\text{Mg}/\text{Ca}$  ratios of 1.0 and 5.2 and corresponding absolute concentrations of  $\text{Mg}^{2+}$  (and  $\text{Ca}^{2+}$ ) that were lower and higher, respectively, than those employed in the first set of experimental seawaters with the same Mg/Ca ratios.

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## 6.1 Mg fractionation in coralline algal calcite

Specimens of the branching and encrusting specimens of coralline algae precipitated exclusively the calcite polymorph in each of the experimental seawaters. Significantly, however, the Mg/Ca of the calcite secreted by each of the four species of coralline algae declined proportionately with the Mg/Ca of the experimental seawater in which they were grown (Fig. 20). Specimens grown in the lowest seawater  $m\text{Mg}/\text{Ca}$  ratio of 1.0 changed their mineralogy from high Mg to low Mg calcite ( $m\text{Mg}/\text{Ca} < 0.04$ ). Encrusting coralline algae grown in the experimental seawaters with  $m\text{Mg}/\text{Ca}$  ratios of 1.0 and 5.2 with reduced and elevated absolute  $\text{Mg}^{2+}$  concentrations, respectively, showed no significant differences in skeletal Mg/Ca ratios from the algae grown in seawater treatments formulated with corresponding Mg/Ca ratios and normal absolute  $\text{Mg}^{2+}$  concentrations (Fig. 20a).

Critically, Mg fractionation coefficients ( $D_c\text{Mg}$ ) calculated for both encrusting and branching coralline algae grown in the various experimental seawaters varied with seawater Mg/Ca (Fig. 21). Excluding the lowest seawater Mg/Ca condition ( $m\text{Mg}/\text{Ca} = 1$ ),  $D_c\text{Mg}$  generally decreased as  $\text{Mg}/\text{Ca}_{\text{sw}}$  increased.

The proportionality between the Mg/Ca of the algal calcite and the Mg/Ca of experimental seawater indicates that the Mg content of the calcite produced by both branching and encrusting coralline red algae is variable, and that this variability can be driven by ambient seawater chemistry (Fig. 20). The similarity between the Mg/Ca ratios of algae grown in the two sets of experimental seawaters of identical  $m\text{Mg}/\text{Ca}$  ratios (1.0 and 5.2) and differing absolute concentrations of  $\text{Mg}^{2+}$  reveals that the incorporation of Mg in algal calcite is, in fact, determined by the Mg/Ca ratio of seawater, rather than the absolute concentration of  $\text{Mg}^{2+}$  in seawater.

This proportionality between the Mg/Ca of the algal calcite and the Mg/Ca of the experimental seawaters (Fig. 20) also suggests that the Mg content of branching and encrusting coralline algae has fluctuated along with seawater Mg/Ca throughout Phanerozoic time. Furthermore, the production of low Mg calcite in experimental seawater with

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$m\text{Mg}/\text{Ca}=1$  suggests that these algae, which produce exclusively high Mg calcite in modern seawater ( $m\text{Mg}/\text{Ca}=5.2$ ), probably produced low Mg calcite in middle and Late Cretaceous seas, when  $m\text{Mg}/\text{Ca}$  ratios are believed to have been near unity.

A backscatter electron image of a longitudinal section through the tip of the branching coralline alga *Amphiroa* sp. (Fig. 22) reveals that skeletal %  $\text{MgCO}_3$  progressively declined from 19%  $\text{MgCO}_3$  (i.e., high Mg calcite) to 2%  $\text{MgCO}_3$  (i.e., low Mg calcite) over a four day period following immersion of the alga in the experimental calcite seawater ( $m\text{Mg}/\text{Ca}=1.0$ ).

Backscatter electron images of the *Neogoniolithon* sp. algae reveal that specimens grown in the low Mg/Ca experimental seawater ( $m\text{Mg}/\text{Ca}=1.5$ ; Fig. 23a–i) produced a more heavily calcified and less organized skeleton than algae grown in the high Mg/Ca experimental seawater ( $m\text{Mg}/\text{Ca}=5.2$ ; Fig. 23j–l), which produced well-defined cell layers that were so weakly calcified that they frequently appear to be shattered. The elevated rates of calcification evident for algae grown in the experimental calcite seawaters (Fig. 23a–i) may disrupt their normally well ordered daily growth bands, resulting in a more chaotic skeletal ultrastructure. Backscatter images of algae grown in experimental seawaters formulated at a fixed  $m\text{Mg}/\text{Ca}$  ratio (1.5) and differing absolute concentrations of  $\text{Ca}^{2+}$  (10, 18, 25 mM; Fig. 23a–i) revealed no major differences in either skeletal organization or thickness.

The *Neogoniolithon* and *Amphiroa* genera investigated in the studies reviewed here belong to the Corallinacean family, a member of the Rhodophyte phylum that is believed to have originated in Early Cretaceous time (Fig. 1). However, a closely related family of coralline Rhodophytes, known as the Solenoporacean algae, was an important contributor to shelf, reefal, and bioherm carbonates throughout Paleozoic and Mesozoic time. In fact, the Solenoporaceae's similar morphology, environmental distributions, and mineralogy (calcitic) to the Corallinaceae (Wray, 1977) has led to them being invoked, somewhat controversially (Aguirre et al., 2000), as potential ancestors of the Corallinaceae. Regardless of the phylogenetic relationship between the more recent Corallinaceae and the older Solenoporaceae, their similar morphologies, modes of

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calcification, and mineralogies suggest that the findings of these experiments on Mg fractionation within the *Amphiroa* and *Neogoniolithon* algae can probably be extrapolated back for most calcite-secreting benthic marine macroalgae, and the limestones that they formed, throughout Phanerozoic time.

## 6.2 Implications for biomineralogical control within the coralline red algae

The Mg fractionation curves derived for the encrusting (*Neogoniolithon*) and branching coralline red algae (*Amphiroa*) are strikingly similar to that for abiotic calcite (Füchtbauer and Hardie, 1976; Mucci and Morse, 1983; Fig. 24), thereby suggesting that these algae are merely inducing the precipitation of calcite by removing CO<sub>2</sub> via photosynthesis. However, the algae's precipitation of high Mg calcite from the experimental seawater formulated at a mMg/Ca ratio of 7.0, which favors the abiotic precipitation of the aragonitic polymorph (Füchtbauer and Hardie, 1976), suggests that the algae are actively specifying nucleation of the calcitic polymorph. However, the algae's abiotic pattern of Mg incorporation suggests that its mineralogical control is limited to polymorph specification and that it is unable to regulate Mg fractionation, which appears to be driven by ambient seawater chemistry and temperature.

It is intriguing that the Mg fractionation curve for the branching coralline algae *Amphiroa* sp. (Stanley et al., 2002) appears to be slightly lower than the Mg fractionation curve generated in this study for the encrusting coralline algae (Fig. 24). This suggests that the branching *Amphiroa* algae are slightly more adept at excluding Mg from their skeletal calcite crystal lattice than the encrusting *Neogoniolithon* algae, which is perhaps indicative of enhanced biomineralogical control within the *Amphiroa* genus.

The relationship between Mg/Ca ratios of the coralline algal calcite and the experimental seawater is also generally consistent with the experiments reviewed above regarding Mg fractionation within calcite secreted by the *Halimeda* algae (Stanley et al., 2009), by two species of coccolithophores (Stanley et al., 2005), and by three species of scleractinian corals (Ries et al., 2006).

The inverse relationship observed between  $D_c\text{Mg}$  and  $\text{Mg}/\text{Ca}_{\text{sw}}$  (when the  $D_c\text{Mg}$

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value at  $m\text{Mg}/\text{Ca}_{\text{sw}}=1.0$  is excluded) is also consistent with other studies on Mg fractionation in biotic calcite (Füchtbauer and Hardie, 1976; Mucci and Morse, 1983; Stanley et al., 2002; Ries, 2004). This relationship suggests that the algae are less efficient at excluding Mg in their skeletal calcite when the ambient concentration of  $\text{Mg}^{2+}$  is low relative to  $\text{Ca}^{2+}$ . As the relative  $\text{Mg}^{2+}$  concentration increases, the organisms appear to become more efficient at excluding it. However, the identification of this inverse proportionality between  $D_c\text{Mg}$  and  $\text{Mg}/\text{Ca}_{\text{sw}}$  in abiotic Mg-calcite (Füchtbauer and Hardie, 1976; Mucci and Morse, 1983) suggests that the comparable relationship observed in the algae may simply be an abiotic consequence of calcification and, therefore, of little biological significance.

The biological consequences of Mg incorporation in the calcite of encrusting coralline algae are not well understood (Milliman et al., 1971). The size differences between the  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  cations in the Mg calcite crystal lattice may reduce crack propagation, relative to the homogeneous crystal lattice of pure calcite (Magdans and Gies, 2004). However,  $\text{Mg}^{2+}$  has been shown to slow abiotic calcite crystal growth (Davis et al., 2000) and reduce the unit cell volume of skeletal calcite (Bischoff et al., 1983).

### 6.3 Paleoenvironmental reconstructions from fossil coralline red algae

The branching and encrusting coralline algae's well-defined growth bands, widespread distribution, long life spans and ubiquity in carbonate rocks throughout Phanerozoic deposits (Wray, 1977) have identified them as potential paleoenvironmental indicators (Halfar et al., 2000). Specifically, the relationship observed in this study between the Mg/Ca ratio of coralline algal calcite and ambient seawater suggests that fossil coralline algae may be an archive of oceanic Mg/Ca.

The relationship between seawater Mg/Ca ( $\text{Mg}/\text{Ca}_{\text{sw}}$ ) and algal Mg/Ca ( $\text{Mg}/\text{Ca}_C$ ) can be quantified with the following algorithms (Fig. 24):

$$\text{Mg}/\text{Ca}_C = 0.0582\text{Mg}/\text{Ca}_{\text{sw}}^{0.904} \quad (\text{branching coralline algae}) \quad (7)$$

$$\text{Mg}/\text{Ca}_C = 0.0421\text{Mg}/\text{Ca}_{\text{sw}}^{1.01} \quad (\text{encrusting coralline algae}) \quad (8)$$



However, the Mg/Ca of coralline algal calcite is also known to vary as a function of ambient seawater temperature (Chave, 1954). This relationship, when calibrated for *Amphiroa* sp. and *Neogoniolithon* sp., can be quantified as follows:

$$\text{Mg/Ca}_C = 0.0825e^{0.0457T} \text{ (branching coralline algae)} \quad (9)$$

$$5 \quad \text{Mg/Ca}_C = 0.0709e^{0.0457T} \text{ (encrusting coralline algae)} \quad (10)$$

The Mg/Ca<sub>sw</sub>- and *T*-based Mg fractionation algorithms can be solved simultaneously at *m*Mg/Ca<sub>sw</sub> = 5.2 to yield unified Mg fractionation algorithms for the branching and encrusting coralline algae that vary as a function of both temperature and seawater Mg/Ca:

$$10 \quad \text{Mg/Ca}_C = 0.0186e^{0.0457T} \text{Mg/Ca}_{\text{sw}}^{0.904} \text{ (branching coralline algae)} \quad (11)$$

$$\text{Mg/Ca}_C = 0.0134e^{0.0457T} \text{Mg/Ca}_{\text{sw}}^{1.01} \text{ (encrusting coralline algae)} \quad (12)$$

Therefore, as long as one of these paleoenvironmental variables is known for the fossil alga, then the other variable (temperature or seawater Mg/Ca) can be calculated.

High Mg calcite is notorious for its rapid loss of Mg during even the early stages of diagenesis. Therefore, one of the greatest challenges in using fossil Mg/Ca to infer oceanic Mg/Ca is the identification of carbonate material that has retained its original Mg content. Petrographic conditions do exist that stabilize high Mg calcite, as demonstrated in recent studies that deduced ancient oceanic Mg/Ca ratios from the Mg content of well preserved fossil echinoderms from throughout Phanerozoic time (Dickson, 2002, 2004; Ries, 2004). Additionally, the closed-system diagenetic conversion of coralline algae's high Mg calcite to low Mg calcite frequently results in the local precipitation of dolomite rhombs within the fossil algae (Schlanger, 1957). Therefore, assuming that all of the Mg in the original skeleton is retained in the precipitation of the dolomite, the volume of that dolomite relative to the volume of the original fossil should provide an approximation of the original Mg content of the encrusting coralline algae.

It should be noted that the accuracy of ancient chemical and temperature reconstructions from the Mg content of fossil encrusting coralline algae will be reduced by factors

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such as open system diagenesis (in which Mg is lost), species-specific Mg fractionation, variations in algal growth rates, and fluctuations of other cations in seawater that influence Mg partitioning in the algal calcite.

#### 6.4 Conclusions – coralline red algae

1. The Mg/Ca ratio of calcite produced by coralline algae of the genera *Neogoniolithon* and *Amphiroa* varies proportionally with the Mg/Ca ratio of ambient seawater. Therefore, the skeletal Mg/Ca ratios of these important reef cementing algae should have tracked secular changes in the Mg/Ca ratio of seawater throughout the Phanerozoic Eon. First-order reconstructions of oceanic Mg/Ca ratios or paleotemperatures can be made from the Mg content of well-preserved fossils of these coralline algae, given that one of these variables is known for the seawater in which the fossilized algae originally lived.
2. The Mg fractionation curves for calcite produced by the *Neogoniolithon* and *Amphiroa* algae are nearly identical to the Mg fractionation curve for abiotically precipitated calcite. This suggests that the *Neogoniolithon* and *Amphiroa* algae exercise little or no influence over the incorporation of Mg into their skeletons. Their biomineralogical control is apparently limited to the specification of the calcite polymorph over the aragonite polymorph, as evidenced by their exclusive production of calcite even in experimental seawater that favors the abiotic precipitation of aragonite ( $m\text{Mg}/\text{Ca}=7.0$ ).
3. The coralline algae *Neogoniolithon* and *Amphiroa* change their skeletal composition from high Mg calcite to low Mg calcite when transplanted from experimental seawater with a  $m\text{Mg}/\text{Ca}$  ratio of 5.2 to experimental seawater with a  $m\text{Mg}/\text{Ca}$  ratio of 1.0. This suggests that these coralline algae, which produce exclusively high Mg calcite in modern seas ( $m\text{Mg}/\text{Ca}=5.2$ ), probably produced low Mg calcite during middle to Late Cretaceous time, when seawater  $m\text{Mg}/\text{Ca}$  ratios were near unity (Lowenstein et al., 2001, 2003). This assertion may also be applicable to the

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solenoporacean algae, possible ancestors of the Corallinaceae, which have geologic ranges spanning the calcite seas of both the Cretaceous and the Cambrian through middle Mississippian intervals.

## 7 High Mg calcite-secreting animals

5 The coralline red algae and coccolithophores are not the only modern, high Mg calcite secreting organisms whose Mg content may have fluctuated in synchronicity with seawater Mg/Ca. Chave (1954) observed that the Mg content of more than twenty species of high Mg calcite secreting marine organisms varied proportionally with seawater temperature. This observation led Stanley and Hardie (1998, 1999) to hypothesize that  
10 the Mg content of most high Mg calcite secreting marine organisms has varied with seawater Mg/Ca throughout the geologic past. Anticipating empirical support for this hypothesis, Dickson (2002, 2004) used the skeletal Mg/Ca of fossil echinoderms to reconstruct seawater Mg/Ca ratios throughout Phanerozoic time. This reconstruction assumed (1) that skeletal Mg/Ca varies with seawater Mg/Ca and (2) that this variation is linear and can therefore be defined with a single fractionation coefficient. Here,  
15 I review a series of experiments (Ries, 2004) that were conducted to investigate the relationship between seawater Mg/Ca and skeletal Mg/Ca for four species of high Mg calcite-secreting marine animals.

Four types of marine invertebrates that secrete high Mg calcite in modern seas –  
20 echinoids (*Eucidaris tribuloides*), crabs (*Perchon gibbesi*), shrimps (*Palaemonetes pugio*) and calcareous serpulid worms (*Hydroides crucigera*) – were reared for 160 d in six experimental seawaters (Bidwell and Spotte, 1985) formulated with *m*Mg/Ca ratios of 1.0, 1.5, 2.9, 4.4, 5.4, and 6.7. Temperature of the experimental seawaters was maintained at  $25 \pm 1^\circ\text{C}$ . After growth in the experimental seawaters, the Mg/Ca ratios of the  
25 spines and coronal plates of the pencil urchins, claws of the sally lightfoot crabs, tails of the grass shrimp, and tube sections of the serpulid worms (portions grown exclusively in the experimental seawaters) were measured with energy dispersive spectroscopy

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and confirmed with X-ray diffractometry.

## 7.1 Mg fractionation within shells of calcitic animals

Each of the four organisms incorporated less Mg into their skeletal calcite as the Mg/Ca of the experimental seawater decreased (Fig. 25a, c, e). Organisms grown in the experimental seawater of lowest  $m\text{Mg}/\text{Ca}$  (1.0) changed their mineralogy to low Mg calcite ( $m\text{Mg}/\text{Ca}_C < 0.04$ ), while organisms grown in the experimental seawater of highest  $m\text{Mg}/\text{Ca}_{\text{sw}}$  (5.2; i.e., “modern” seawater) produced high Mg calcite – remaining within 3% of their pre-experimental  $\text{Mg}/\text{Ca}_C$  ratios.

The production of low Mg calcite by each of the four organisms in the experimental seawater with  $m\text{Mg}/\text{Ca}=1.0$  suggests that these organisms, which produce high Mg calcite in modern seas, probably produced low Mg calcite in middle and Late Cretaceous seas, when  $m\text{Mg}/\text{Ca}$  ratios are thought to have been near unity. This trend was also observed in similar studies on coccolithophorids (Stanley et al., 2005), coralline red algae (Stanley et al., 2002; Ries, 2006b), *Halimeda* algae (Stanley et al., 2009) and scleractinian corals (Ries et al., 2006). The wide variety of organisms that exhibit this proportionality between skeletal and seawater Mg/Ca suggests that this is a general trend for modern high Mg calcareous organisms.

Each type of organism investigated in this study produced a unique Mg fractionation curve. Even the spines and coronal plates within the same echinoid yielded unique fractionation curves (Fig. 24a). And each of these curves was lower than the experimentally determined curve for abiotic magnesian calcite (Füchtbauer and Hardie, 1976). This deviation of the biotic fractionation curves from the abiotic curve suggests that these organisms influence, to varying degrees, the incorporation of Mg in their calcitic skeletons. However, ranking the organisms by increasing Mg content – echinoid spine, shrimp, crab-echinoid plate-worm – suggests that the degree of Mg fractionation is not, as previously suggested, linked to taxonomic complexity (Chave, 1954).

Calculation of Mg fractionation coefficients [ $D_C\text{Mg}=(\text{Mg}/\text{Ca}_C)/(\text{Mg}/\text{Ca}_{\text{sw}})$ ] at various  $\text{Mg}/\text{Ca}_{\text{sw}}$  ratios revealed that this coefficient varied with ambient  $\text{Mg}/\text{Ca}_{\text{sw}}$  for each of

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the organisms investigated (Fig. 25b, d, f).  $D_c\text{Mg}$  decreased for the echinoid spines–coronal plates and crabs as  $\text{Mg}/\text{Ca}_{\text{sw}}$  increased (Fig. 25b, d). This result is consistent with the experiments on the coralline red algae (Stanley et al., 2002; Ries, 2006b) and abiotic magnesian calcite (Füchtbauer and Hardie, 1976; Mucci and Morse, 1983). However,  $D_c\text{Mg}$  values increased for the grass shrimps as  $\text{Mg}/\text{Ca}_{\text{sw}}$  increased (Fig. 25d) and were scattered for the serpulid worm tubes (Fig. 25f). The discrepancies amongst the organisms may be attributable to differences amongst the organic templates thought to control crystal growth and/or differences in the mechanisms that transport  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions into or out of the organisms' calcifying fluids.

The high survival rate for these organisms in each of the seawater treatments suggests that the organisms were not severely stressed by the prescribed variations in concentrations of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ . Bellis et al. (1987) showed that reduced levels of ambient  $\text{Mg}^{2+}$  (from 50 to 0 mM) did not have significant effects on amino acid retention in sea urchin larvae, whereas Hayashi and Motokawa (1986) demonstrated that elevated  $\text{Mg}^{2+}$  levels increased tissue viscosity in echinoderms. However, this increase was observed at  $\text{Mg}^{2+}$  concentrations 2–5 times greater than modern values, well above the range of concentrations evaluated in these experiments.

## 7.2 Ocean chemistry reconstructions from skeletal Mg/Ca of calcitic animals

The proportionality between the Mg/Ca of these animals' skeletons and the Mg/Ca of the seawater in which they were reared suggests that such animals should have recorded oceanic Mg/Ca throughout Phanerozoic time. Dickson (2002, 2004) innovatively employed a fixed  $D_c\text{Mg}$ , derived from echinoderms in modern seawater at 25°C, to reconstruct paleoceanic Mg/Ca from the Mg/Ca of fossil crinoid ossicles and echinoid plates. The presently reviewed study showed that this reconstruction can be improved by employing a Mg fractionation curve, instead of a fixed  $D_c\text{Mg}$ , to convert skeletal Mg/Ca to seawater Mg/Ca. The effect of ancient seawater temperature on fossil Mg/Ca can also be corrected for in the reconstruction by using Chave's (1954) observations on the relationship between skeletal Mg fractionation and temperature.

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Mg fractionation curves for echinoid plates, echinoid spines, crabs, serpulid worm tubes, coralline algae (Stanley et al., 2002), and nonskeletal calcite (Füchtbauer and Hardie, 1976) were species-normalized with a factor equal to Chave's (1954) average skeletal Mg/Ca of the given higher taxon at  $m\text{Mg}/\text{Ca}_{\text{sw}}=5.2$ ,  $T=25^\circ\text{C}$  divided by the skeletal Mg/Ca of the species in that taxon evaluated in this study at  $m\text{Mg}/\text{Ca}_{\text{sw}}=5.2$ ,  $T=25^\circ\text{C}$  (Table 2). The species-normalization factors for the echinoid plates, echinoid spines, crabs, serpulid worm tubes, and coralline algae are 0.913, 1.708, 0.868, 1.140, and 1.3297, respectively.

Temperature-dependent Mg fractionation curves were determined from Chave's (1954) and Füchtbauer and Hardie's (1976) data using least squares regressions (Table 2). The species-normalized  $\text{Mg}/\text{Ca}_{\text{sw}}$ -dependent Mg fractionation curves and temperature-dependent Mg fractionation curves were solved simultaneously at  $m\text{Mg}/\text{Ca}_{\text{sw}}=5.2$ , thus yielding a single Mg fractionation algorithm varying as a function of temperature and  $\text{Mg}/\text{Ca}_{\text{sw}}$  (Table 2).  $R^2$ -coefficients for the Mg fractionation algorithms for the echinoid plates, echinoid spines, crabs, serpulid worm tubes, coralline algae, and nonskeletal precipitates are 0.66, 0.77, 0.93, 0.94, 0.88, and 0.98, respectively.

The derived Mg fractionation algorithms can be used to calculate paleoceanic Mg/Ca ratios from unaltered fossils of the investigated taxa. Although these Mg fractionation algorithms are normalized for the investigated species, they can be calibrated for other extant species with a species coefficient ( $S$ ) equal to the skeletal Mg/Ca ratio of that species in the wild divided by the skeletal Mg/Ca ratio predicted by the algorithm for the temperature and  $m\text{Mg}/\text{Ca}$  ratio (5.2) of the seawater in which the wild specimen lived (Table 2). However, the accuracy of the ancient seawater Mg/Ca calculations will be inherently limited for fossils whose Mg fractionation algorithms cannot be calibrated with extant representatives. The accuracy of the algorithms may also be limited by other factors that may have influenced biogenic Mg fractionation in the past, yet are not incorporated into the model (e.g., variations in growth rates, fluctuations of other ions in seawater).

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Dickson's (2002, 2004) paleo-seawater Mg/Ca ratios were recalculated using the echinoid plate Mg fractionation algorithm (calibrated for crinoid ossicles when applicable) that accounts for ambient temperature and variable  $D_c$ Mg values (Fig. 1). Paleotemperatures were estimated by Dickson (see Dickson's (2002) supplementary data) from paleogeographic and paleotemperature maps (Golonka et al., 1994). The resulting Mg/Ca ratios are consistent with other estimates and models of paleoceanic Mg/Ca over Phanerozoic time (Hardie, 1996; Lowenstein et al., 2001; Siemann, 2003; Demicco et al., 2005).

### 7.3 Ocean temperature reconstructions from skeletal Mg/Ca of calcitic animals

The correlation between temperature and skeletal Mg incorporation (Chave, 1954) also permits the reconstruction of ancient seawater temperatures from skeletal Mg/Ca ratios. However, such reconstructions must correct skeletal Mg/Ca for the effect of varying  $Mg/Ca_{sw}$ . A recent temperature reconstruction from the  $Mg/Ca_C$  of fossil foraminifera (Lear et al., 2000) has, like the echinoderm reconstruction (Dickson, 2002, 2004), employed a fixed  $D_c$ Mg to make this correction. This paleotemperature reconstruction can be improved by using an empirically derived Mg fractionation algorithm, which accounts for  $D_c$ Mg varying with  $Mg/Ca_{sw}$  (Table 2).

### 7.4 Conclusions – calcite-secreting animals

1. The Mg/Ca ratio in the calcite secreted by echinoids, shrimp, crabs, and serpulid worms varies proportionally with the Mg/Ca ratio of the seawater in which they are grown. Organisms grown in experimental seawaters formulated with the calcite sea  $mMg/Ca$  ratio of 1 began secreting low Mg calcite, as opposed to their normal high Mg calcite, under these conditions. This suggests that the organisms evaluated in this study, which all produce high Mg calcite in modern seas, probably produced low Mg calcite in middle and Late Cretaceous seas, when Mg/Ca values are thought to have been near their lowest.

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2. The Mg/Ca of unaltered fossils of these organisms may be a reliable monitor of changes in oceanic Mg/Ca throughout Phanerozoic time. However, given the variation in Mg fractionation curves amongst closely related organisms, such as crabs and shrimps, and between different skeletal components within the same organism, such as echinoid spines and coronal plates, these reconstructions should employ only anatomically and taxonomically appropriate Mg fractionation algorithms.

3. Mg fractionation coefficients ( $D_c\text{Mg}$ ) were shown to vary with  $\text{Mg}/\text{Ca}_{\text{sw}}$  for each of the four organisms. Prior reconstructions of paleoceanic  $\text{Mg}/\text{Ca}_{\text{sw}}$  from echinoderms and temperature from foraminifera, which employed a fixed  $D_c\text{Mg}$  over a range of ambient  $\text{Mg}/\text{Ca}_{\text{sw}}$  ratios, would be improved by employing Mg fractionation algorithms that account for variations in  $D_c\text{Mg}$  with ambient  $\text{Mg}/\text{Ca}_{\text{sw}}$  and temperature.

## 8 Bacterial biofilms

15 The same mechanism reported to be responsible for secular variation in seawater Mg/Ca ratios throughout Phanerozoic time – ion exchange along zones of newly formed ocean crust driven by global rates of ocean crust production – has also been hypothesized as the primary mechanism controlling this ratio throughout Precambrian time (Hardie, 2003). A hydrothermal brine-river water mixing model (Hardie, 1996, 2003) driven by global rates of ocean crust production inferred from secular variation in the frequency of granite-pluton production in North America (Engel and Engel, 1970) predicts that Precambrian seawater  $m\text{Mg}/\text{Ca}$  would have been constrained to the same range of values that existed throughout Phanerozoic time (1-to-5.2) and would have caused six intervals of aragonite seas and five intervals calcite seas between Late Archean and terminal Proterozoic time (Fig. 26). The observed distribution of aragonite seafloor precipitates in the form of crystal fans, early marine cements, and ooids,



as compiled by Hardie (2003, see references therein), is consistent with the predictions of his Precambrian seawater Mg/Ca model (Fig. 26).

Marine calcification throughout Precambrian time – unlike throughout Phanerozoic time – was generally dominated by bacterial biofilms (Riding, 2000). Such bacterially induced calcification is recorded in the geologic record in the form of microbialites, stromatolites, and thrombolites. Although the distribution and abundance of these bacterially induced carbonates has varied substantially throughout Precambrian time, most likely due to fluctuations in the  $\text{CaCO}_3$  saturation state of seawater (Grotzinger and Knoll, 1999; Arp et al., 2001; Sumner and Grotzinger, 2004; Riding and Liang, 2005) and the evolution of grazing eukaryotes (Awramik, 1971; Riding and Liang, 2005), these deposits are well-represented from Late Archean through Cambrian time (Riding, 2000). Experiments were conducted to investigate the effects of varied seawater Mg/Ca on calcification within marine bacterial biofilms (Ries et al., 2008). The results of these experiments have important implications for our understanding of the mechanisms of calcification within bacterial biofilms, for the history of biofilm calcification throughout Precambrian time, and for the viability of microbial carbonates (e.g., microbialites, stromatolites, thrombolites) as a proxy record of Precambrian ocean chemistry.

Mixed-community marine sedimentary biofilms were cultured in experimental seawaters formulated over the range of  $m\text{Mg}/\text{Ca}$  ratios predicted to have occurred since Late Archean time (1.5, 2.5, 5.2; Hardie, 2003), corresponding to a calcite sea, a boundary calcite-aragonite sea, and an aragonite sea interval. Biofilm phylogenetic diversity,  $\text{CaCO}_3$  polymorph mineralogy and distribution, and Mg fractionation in biofilm calcite were evaluated in response to these modifications in seawater Mg/Ca.

## 8.1 $\text{CaCO}_3$ distribution within biofilms

Backscatter electron images of biofilms cultured in the three experimental seawaters (Fig. 27) reveals that  $\text{CaCO}_3$  is generally precipitated between the biofilm's microbial cells. This is particularly evident in Fig. 27c, where bacterial cells were cross-sectioned during sample preparation, thus revealing the intercellular, void-filling  $\text{CaCO}_3$  matrix.

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The biofilms, including the control, showed no significant ( $p < 0.05$ ) differences in their percent calcification. Average wt-percent calcification for biofilms grown in the three seawater treatments was  $64 \pm 4\%$ . SEM imaging revealed that the non-biofilm control plates contained no trace of  $\text{CaCO}_3$  precipitation.

## 8.2 Effect of $\text{Mg}/\text{Ca}_{\text{sw}}$ on polymorph mineralogy and Mg content of biofilm $\text{CaCO}_3$

Powder X-ray diffraction analysis of  $\text{CaCO}_3$  precipitated within the biofilms revealed that the calcite:aragonite ratio increased as  $\text{Mg}/\text{Ca}_{\text{sw}}$  decreased towards the calcite stability field ( $m\text{Mg}/\text{Ca}_{\text{sw}} < 2$ ; Fig. 28a). Biofilms cultured in the modern, aragonite seawater ( $m\text{Mg}/\text{Ca}_{\text{sw}} = 5.2$ ) produced the majority ( $57 \pm 1.0\%$ ) of their  $\text{CaCO}_3$  as aragonite with lesser amounts as magnesian calcite ( $43 \pm 1.0\%$ ; Fig. 3b). Biofilms cultured in the aragonite-calcite boundary seawater ( $m\text{Mg}/\text{Ca}_{\text{sw}} = 2.5$ ) produced the majority of their  $\text{CaCO}_3$  as magnesian calcite ( $85 \pm 1.1\%$ ) with lesser amounts as aragonite ( $15 \pm 1.1\%$ ). And biofilms cultured in the experimental calcite seawater ( $m\text{Mg}/\text{Ca}_{\text{sw}} = 1.5$ ) produced exclusively magnesian calcite (Fig. 28).

The  $\text{Mg}/\text{Ca}$  ratio of the biofilm calcite ( $\text{Mg}/\text{Ca}_{\text{calcite}}$ ) varied proportionally with  $\text{Mg}/\text{Ca}_{\text{sw}}$  (Fig. 28b). Biofilms cultured in the experimental seawaters formulated at  $m\text{Mg}/\text{Ca}_{\text{sw}}$  of 5.2, 2.5, and 1.5 yielded  $m\text{Mg}/\text{Ca}_{\text{calcite}}$  of  $0.16 \pm 0.01$ ,  $0.08 \pm 0.01$ , and  $0.06 \pm 0.01$ , respectively. The observed relationship between  $\text{Mg}/\text{Ca}_{\text{sw}}$  and  $\text{Mg}/\text{Ca}_{\text{calcite}}$  observed for the biofilms ( $0.16 < m\text{Mg}/\text{Ca}_{\text{calcite}} < 0.17$  in  $m\text{Mg}/\text{Ca}_{\text{sw}} = 5.2$  at  $25^\circ\text{C}$ ) generally mimics Mg fractionation in abiotically precipitated calcite cements ( $0.14 < m\text{Mg}/\text{Ca}_{\text{calcite}} < 0.18$  in modern shallow seawater; Morse et al., 2006) and is consistent with Mg fractionation in calcite produced by corals (Ries et al., 2006), calcareous bryopsidalean algae (Stanley et al., 2009), coralline red algae (Stanley et al., 2002; Ries, 2006b), some species of coccolithophores (Stanley et al., 2005), echinoids, crabs, shrimp, and calcareous serpulid worm tubes (Ries, 2004).

It should also be noted that although Mg fractionation in biofilm calcite appears to mimic that of abiotic calcification, the observation that calcification occurred exclusively

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on the biofilm plates, and not at all on the non-biofilm control plates, indicates that the calcification observed in the biofilms required biological forcing, and should thus be considered biogenic in nature.

### 8.3 Effect of seawater Mg/Ca on the bacterial community

5 Clone library estimates of the microbial diversity (Table 3) and phylogenetic structure of the biofilms cultured in the artificial aragonite ( $m\text{Mg}/\text{Ca}=5.2$ ) and calcite ( $m\text{Mg}/\text{Ca}=1.0$ ) seawaters, and of the control biofilm, were highly similar. The biofilm communities from each of the seawater treatments were dominated by cyanobacteria, alpha proteobacteria, bacteroidetes, and gamma proteobacteria, which collectively comprise greater  
10 than 70% of the biofilms' bacterial community. Cyanobacteria were more abundant in the control biofilm than in either of the experimental biofilms that were subjected to artificial seawater. This may be attributable to the lower irradiance of laboratory conditions affecting growth of these phototrophs. The biofilms grown in the artificial seawaters also had greater abundances of gamma proteobacteria than bacteroidetes, while the  
15 control biofilm had a greater abundance of bacteroidetes than gamma proteobacteria. There were also slight differences in the representation of the low-abundance bacterial groups, including the planctomycetes, chloroflexi, actinomycetes, verrucomicrobia, legionella, acidobacteria, chlamydiales, delta proteobacteria, and gemmatimonadetes. Such minor differences in the relative abundances of bacterial groups amongst the one  
20 control and two experimental biofilms may be attributable to subtle differences between laboratory and natural conditions and/or stochastic variations in cloning or sampling efficiency.

It is improbable that the minor differences in bacterial diversity and abundance that were observed between the biofilms cultured in the experimental aragonite and calcite  
25 seawaters could account for the significant differences in their  $\text{CaCO}_3$  polymorph ratios. The more parsimonious explanation for the observed variation in  $\text{CaCO}_3$  polymorphism and  $\text{Mg}/\text{Ca}_{\text{calcite}}$  within biofilms cultured in the various seawater treatments is the prescribed difference in seawater Mg/Ca. While specific sulfate reducing bacteria may

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dictate CaCO<sub>3</sub> polymorph mineralogy in pure culture (Van Lith et al., 2003), the results of the present study suggest that this ability is lost in natural, normal-salinity mixed-culture biofilms, where such polymorph-specifiers apparently constitute only a small portion of the total calcifying bacterial community.

Furthermore, the similarity of the composition and structure of the experimental biofilms to that of the control biofilm (Table 3), which was not subjected to the experimental seawater conditions, as well as to other natural calcifying microbial communities (Burns et al., 2004; Lopez-Garcia et al., 2005; Papineau et al., 2005), indicates that the experimental biofilms are essentially representative of natural, calcifying microbial communities and, therefore, reasonable systems from which to extrapolate about microbial calcification throughout the geologic past. Barring phylogenetic reconstruction of fossilized DNA from lithified microbial communities, these modern, normal-salinity, calcifying biofilm systems are the next-best models for investigating the structure and function of the ancient bacterial systems believed to be responsible for the construction of stromatolites, thrombolites, and microbialites throughout the geologic past (Reid et al., 2000).

#### 8.4 Mechanisms of calcification within biofilms

Biofilms are highly diverse bacterial communities that can precipitate CaCO<sub>3</sub> extracellularly within their m-to-cm thick matrices. Calcification within these biofilms results from the complex interplay of metabolic and geochemical reactions occurring within and adjacent to the biofilm matrix, often in association with exopolymeric substances (Dupraz and Visscher, 2005; Altermann et al., 2006).

The C, O, S, N, and Fe-based reduction-oxidation reactions that form the basis of microbial metabolisms greatly affect the biofilm system's pH, alkalinity, and dissolved inorganic carbon, and thus [CO<sub>3</sub><sup>2-</sup>] and  $\Omega_{\text{CaCO}_3}$  of the biofilm's intercellular space, which determines whether calcification will occur (Bosak and Newman, 2005; Dupraz and Visscher, 2005; Visscher and Stolz, 2005; Baumgartner et al., 2006). Simplified examples (Visscher and Stolz, 2005) of such microbial reactions that effectively *increase*

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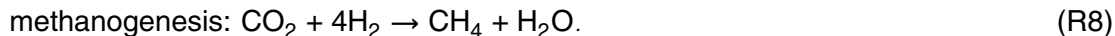
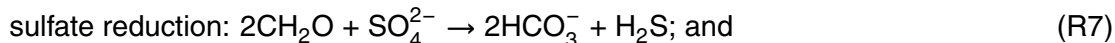
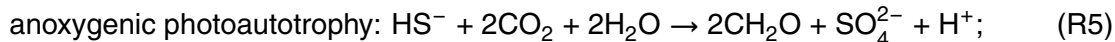
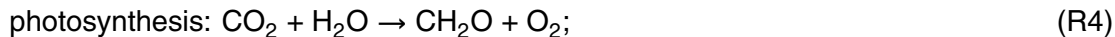
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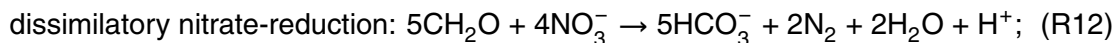
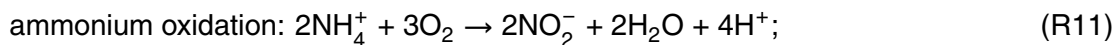
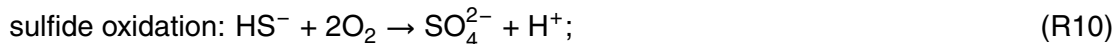
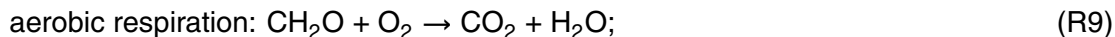
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$[\text{CO}_3^{2-}]$  and  $\Omega_{\text{CaCO}_3}$  are:



Examples (Visscher and Stolz, 2005) of microbial reactions that effectively *decrease*  $[\text{CO}_3^{2-}]$  and  $\Omega_{\text{CaCO}_3}$  are:



and



Such primary microbial metabolic reactions within the biofilm are moderated by secondary reactions associated with exopolymeric substance (EPS; Reid et al., 2000; Arp et al., 2001; Bosak and Newman, 2005; Dupraz and Visscher, 2005). EPS is an extension of the microbial cell that maintains biofilm structure, establishes chemical microgradients by reducing rates of diffusion, may regulate intercellular processes, and functions to bind cations, elevate  $\text{HCO}_3^-$ , and nucleate  $\text{CaCO}_3$  crystals (Arp et al., 2001; Dupraz and Visscher, 2005).

The observation made in this study that biofilm calcification proceeds nearly abiotically with respect to polymorph distribution and Mg fractionation is consistent with the assertion that calcification in biofilms occurs primarily through the elevation of  $[\text{CO}_3^{2-}]$  in the biofilm's intercellular space via fundamental microbial reduction-oxidation reactions

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that remove  $\text{CO}_2$  and/or  $\text{H}^+$  (McConnaughey and Whelan, 1997; Bosak and Newman, 2005; Dupraz and Visscher, 2005), rather than by elevating  $[\text{Ca}^{2+}]$  via  $\text{CaCO}_3$  dissolution and EPS decomposition (Dupraz and Visscher, 2005). The latter scenario of elevated  $\text{Ca}^{2+}$ , evidence of which was not observed in the presently reviewed study, would decrease the Mg/Ca ratio within the calcifying fluid of the biofilm and cause its patterns of  $\text{CaCO}_3$  polymorphism and Mg fractionation (Fig. 28), with respect to ambient  $\text{Mg}/\text{Ca}_{\text{sw}}$ , to deviate from those of abiotically precipitated  $\text{CaCO}_3$ .

## 8.5 Precambrian ocean chemistry reconstructions

The timing of aragonite and calcite sea intervals is fairly well-constrained for the Phanerozoic Eon (Sandberg, 1983; Hardie, 1996; Stanley and Hardie, 1999; Lowenstein et al., 2001; Horita et al., 2002; Dickson, 2004). However, the distribution of calcite and aragonite seas in Precambrian time is poorly known, primarily because of the scarcity of proxies for seawater chemistry identified in the Precambrian geologic record, such as primary fluid inclusions and calcareous fossils whose skeletons can be chemically calibrated with modern representatives. Our current understanding of Precambrian  $\text{Mg}/\text{Ca}_{\text{sw}}$  is derived primarily from Hardie's (2003) hydrothermal brine-river water mixing model driven by ocean crust-productions rates inferred from secular oscillations in granite-pluton production in North America (Engel and Engel, 1970) and from limited observations of aragonite seafloor precipitates (crystal fans, early marine cements, ooids) throughout Late Archean to Early Cambrian time, which were compiled by Hardie (2003, see references therein).

The observation that  $\text{CaCO}_3$  polymorph ratios (aragonite:calcite) and calcite Mg/Ca ratios within the biofilms varied with experimental  $\text{Mg}/\text{Ca}_{\text{sw}}$  suggests that well-preserved microbial carbonates may be a reliable monitor of aragonite-calcite sea intervals and  $\text{Mg}/\text{Ca}_{\text{sw}}$  throughout Precambrian time. However, an important assumption implicit in the use of the original mineralogy of microbial carbonates as a proxy for seawater Mg/Ca is that the physicochemical properties of Precambrian seawater were

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such that  $\text{Mg}/\text{Ca}_{\text{sw}}$  was the predominant variable influencing the polymorph mineralogy of  $\text{CaCO}_3$  precipitated from seawater, as it is believed to have been throughout Phanerozoic time (Hardie, 1996; Stanley and Hardie, 1998, 1999; Lowenstein et al., 2001).

5 Using modern soda lakes associated with volcanic regions as analogs, Kempe and Degens (1985) infer that the Earth's ocean prior to 1 Ga was a soda ocean ( $\text{HCO}_3^- > \text{Ca}^{2+}$ ) of high alkalinity, high pH, and low  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations. They further argue that by 1 Ga, the gradual leaching of chlorine from the oceanic crust and the removal of dissolved carbonates via biotic and abiotic  $\text{CaCO}_3$  precipitation had  
10 transformed the soda ocean into a halite ocean.

Morse and Mackenzie (1998), however, argue that if early seawater was buffered by reactions involving carbonates and silicates, then the composition of post-Hadean seawater may have been comparable to that of today. In contrast to earlier hypotheses that the Precambrian ocean was a soda ocean prior to 1 Ga (Kempe and Degens, 1985) or  
15 even 2 Ga (Grotzinger and Kasting, 1993), Morse and Mackenzie's calculations suggest that the Precambrian ocean had been a halite ocean since Late Hadean-Early Archean time, with somewhat higher DIC and alkalinity concentrations, higher  $\text{CaCO}_3$  saturation states, and possibly lower  $\text{Ca}^{2+}$  concentrations.

Grotzinger and Kasting (1993) argue that the occurrence of pseudomorphs after  
20  $\text{CaSO}_4$  minerals in the geologic record back to 2 Ga suggests that the ocean was not alkaline and maintained  $\text{Ca}^{2+} > \text{HCO}_3^-$  over this interval. They further propose that prior to 2 Ga, the absence of evidence for gypsum indicates either (1) such low  $\text{SO}_4^{2-}$  concentrations that  $\text{CaSO}_4$  minerals were unable to precipitate or (2)  $\text{HCO}_3^- > \text{Ca}^{2+}$ , such that all  $\text{Ca}^{2+}$  was depleted during progressive evaporation of seawater via  $\text{CaCO}_3$  precipita-  
25 tion before the gypsum field could be reached. If the latter scenario ( $\text{HCO}_3^- > \text{Ca}^{2+}$ ) occurred, then their assertions would push the soda-to-halite ocean transformation back to 2 Ga. If the former scenario (very low  $\text{SO}_4^{2-}$ ) occurred, as suggested by the Archean record of stable isotopes of sulphur (Canfield et al., 2000; Habicht et al., 2002), then

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the transition to a halite ocean could have occurred much earlier, and would not argue for a Precambrian ocean composition that was significantly different from that of today's, at least with respect to the role of  $Mg/Ca_{sw}$  in determining  $CaCO_3$  polymorph mineralogy.

5 Hardie (2003) argues, like Morse and Mackenzie (1998), that the post-Hadean Precambrian ocean was never a soda ocean, but instead was a near-neutral halite ocean with  $Ca^{2+} > HCO_3^-$ , comparable to modern seawater. Hardie contends that the extreme acidity caused by the high concentrations of dissolved HCl and  $CO_2$  in the Earth's primordial ocean (Garrels and Mackenzie, 1971) would have fostered a global scale  
10 acid-base titration that would have converted primordial igneous crust into aluminosilicate sediments and yielded a saline ocean with  $Na^{2+} \sim Ca^{2+} > Mg^{2+} > K^+$  and near neutral pH (Garrels and Mackenzie, 1971; Lafon and Mackenzie, 1974). Hardie (2003) proposes that the elevated production of  $CaCl_{2(aq)}$  relative to  $CaHCO_3^+_{(aq)}$ , due to the predominance of HCl over  $CO_2$  dissolved in the primordial acid rain, would have yielded  
15  $Ca^{2+} > HCO_3^-$  in this primordial ocean. Hardie cites reports of pseudomorphs after gypsum at 2.6 Ga (Simonson et al., 1993) and 3.45 Ga (Lowe, 1983) in support of this line of reasoning.

Temperature,  $pCO_2$ , and  $[SO_4^{2-}]$  have also been shown to influence the polymorph mineralogy of  $CaCO_3$  precipitated from seawater-based solutions (Morse et al., 1997; Burton and Walter, 1991; Bischoff and Fyfe, 1968; Walter, 1986). In modern seawater  
20 ( $S=35$  ppm, 1 atm, normal alkalinity) with  $mMg/Ca=5.2$ , the kinetically favored  $CaCO_3$  polymorph will switch from aragonite to calcite when temperature falls below  $6 \pm 3^\circ C$  and when  $pCO_2$  (assuming  $T=25^\circ C$ ) falls between  $\sim 2600$  and 3500 ppm (Morse et al., 1997), which represents the range over which modern seawater will be undersaturated with respect to aragonite yet supersaturated with respect to calcite. Because  
25 the stoichiometric solubility coefficients ( $K_{sp}$ ) of aragonite ( $10^{-6.19}$ ) and calcite ( $10^{-6.37}$ ) are relatively close, the range of calcite supersaturation states that yields simultaneous aragonite undersaturation is narrow ( $1 < \Omega_{calcite} < 1.5$ ), and generally requires that seawater be near undersaturation with respect to calcite.

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Given the ubiquity and abundance (Riding, 2000) of nearly abiotically precipitated microbial carbonates from Archean through Neoproterozoic time, it seems improbable that the  $\text{CaCO}_3$  saturation state of post-Hadean seawater was regularly constrained to such a narrow range that teetered on the edge of total  $\text{CaCO}_3$  undersaturation ( $1 < \Omega_{\text{calcite}} < 1.5$ ), a condition required by the hypothesis that elevated  $p\text{CO}_2$  was the primary driver of calcite sea intervals (Morse et al., 1997). To the contrary, it is asserted that Archean and Proterozoic seawater actually maintained  $\text{CaCO}_3$  saturation states that were much greater than modern seawater (modern seawater  $\Omega_{\text{calcite}} \sim 5.7$ ; Kempe and Degens, 1985; Grotzinger, 1989; Grotzinger and Kasting, 1993; Morse and Mackenzie, 1998; Grotzinger and Knoll, 1999; Grotzinger and James, 2000), and thus well above the range ( $1 < \Omega_{\text{calcite}} < 1.5$ ) that permits simultaneous aragonite undersaturation and calcite supersaturation. Such assertions cast doubt over the role of  $p\text{CO}_2$  as a primary driver of  $\text{CaCO}_3$  polymorph mineralogy throughout post-Hadean time.

Sulfate has also been shown experimentally to inhibit the precipitation of both calcite and, to a lesser extent, aragonite (Bischoff and Fyfe, 1968; Walter, 1986) in seawater based solutions. However, the effect of  $m\text{Mg}/\text{Ca}$  on  $\text{CaCO}_3$  polymorph specification (Stanley and Hardie, 1999; Morse et al., 1997; Leitmeier, 1910, 1915; Lippman, 1960; Müller et al., 1972; Berner, 1975) supersedes that of  $[\text{SO}_4^{2-}]$  (Bischoff and Fyfe, 1968) when considered over the geologically realistic ranges that stable isotopes of sulfur (Canfield et al., 2000; Habicht et al., 2002), fluid inclusions in halite (Horita et al., 2003; Lowenstein et al., 2003), and various ocean chemistry models (Hardie, 2003; Berner, 2004; Demicco et al., 2005) suggest for Precambrian seawater ( $0 < [\text{SO}_4^{2-}] < 20\text{--}25\text{ mM}$ ;  $1 < m\text{Mg}/\text{Ca} < 5.2$ ).

It is more conceivable, however, that temperature (Morse et al., 1997) played a significant role in determining the primary polymorph mineralogy of microbial carbonates throughout Precambrian time. It is therefore important that such reconstructions of seawater  $\text{Mg}/\text{Ca}$  preferentially employ microbial carbonates believed to have been deposited in tropical ( $25^\circ\text{C}$ ) seawater. Fortuitously, since  $\text{CaCO}_3$  saturation state increases with temperature, warm-water carbonates are inherently more abundant than

cool-water carbonates in the geological record.

It should be noted that workers have observed a transition in the mode of accretion of Precambrian microbial carbonates from one that occurs primarily via in situ precipitation in Archean through Mesoproterozoic time, to one involving a combination of in situ calcification and the trapping and binding of loose  $\text{CaCO}_3$  sediments in Neoproterozoic time and thereafter (Grotzinger and Knoll, 1999; Grotzinger and James, 2000; Sumner and Grotzinger, 2004). However, this transition in mode of accretion should have little bearing on the viability of microbial carbonates as a proxy of seawater  $\text{Mg}/\text{Ca}_{\text{sw}}$  throughout Precambrian time, as the polymorph mineralogy of abiotically precipitated  $\text{CaCO}_3$  sediments that are trapped and bound in the biofilms and microbial mats and the polymorph mineralogy of  $\text{CaCO}_3$  precipitated in situ should be comparably governed by, and thus equally indicative of, ambient seawater  $\text{Mg}/\text{Ca}$ .

The far greater challenge to using the original mineralogy of Precambrian microbial carbonates as a proxy for understanding secular variation in the major cation composition of Precambrian seawater relates to diagenesis. The aragonite polymorph is less stable than the calcite polymorph at Earth surface conditions and will thus convert to calcite over relatively short geologic timescales. However, various indicators, such as trace element composition ( $\text{Mg}^{2+}$ ,  $\text{Sr}^{2+}$ ), quality of textural preservation, and presence of relic aragonite needles (Grotzinger and Reed, 1983; Brand, 1989; Lasemi and Sandberg, 1984, 1993), have been successfully employed to deduce the precursor mineralogy of micritic carbonates altered in this way.

Diagenesis can also cause the loss of  $\text{Mg}^{2+}$  from magnesian calcite. Yet despite the effects of diagenesis, the  $\text{Mg}/\text{Ca}$  and dolomite content of well-preserved fossil echinoderms have been shown to generally track seawater  $\text{Mg}/\text{Ca}$  throughout Phanerozoic time (Dickson, 2002, 2004). Thus, the  $\text{Mg}/\text{Ca}$  ratio and dolomite content of well-preserved microbial calcite may similarly track Precambrian  $\text{Mg}/\text{Ca}_{\text{sw}}$ .

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## 8.6 Implications for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ isotope stratigraphy

Isotopes of carbon and oxygen are fractionated differently in calcite and aragonite due to differences in the internal vibrational frequencies of the polymorphs' carbonate ions (Rubinson and Clayton, 1969; Tarutani et al., 1969). For  $\text{CaCO}_3$  precipitated at  $25^\circ\text{C}$  from experimental seawater,  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  are enriched in the aragonite polymorph by 0.6‰ and 1.8‰, respectively, relative to the calcite polymorph.  $\delta^{18}\text{O}$  is also enriched in high Mg calcite (13 mole-%  $\text{MgCO}_3$ ) by 1.1‰ relative to pure calcite, indicating a 0.09‰ enrichment in  $\delta^{18}\text{O}$  per mole-% Mg. Thus,  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  isotope records derived from Precambrian microbial carbonates (e.g., Jacobsen and Kaufman, 1999; Halverson et al., 2005) may contain global, threshold excursions of up to 2‰ caused by secular variations in the primary mineralogy of the host carbonates that are independent of the biological and geological processes typically considered in the interpretation of these isotope records.

## 8.7 Conclusions – bacterial biofilms

1. Reductions in seawater Mg/Ca caused commensurate reductions in the aragonite:calcite ratios of  $\text{CaCO}_3$  precipitated within biofilms. Biofilms cultured in experimental aragonite seawater ( $m\text{Mg}/\text{Ca}_{\text{sw}}=5.2$ ) precipitated primarily aragonite, with lesser amounts of high Mg calcite, while biofilms cultured in experimental calcite seawater ( $m\text{Mg}/\text{Ca}_{\text{sw}}=1.5$ ) precipitated exclusively calcite.
2. The Mg/Ca ratios of the calcite precipitated within the biofilms varied proportionally with the Mg/Ca ratios of the experimental seawater. The observation that biofilm calcification mimics abiotic calcification with respect to  $\text{CaCO}_3$  polymorph specification and Mg fractionation suggests that the elevation in  $\text{CaCO}_3$  saturation state leading to calcification within the biofilm occurs mainly through the elevation of  $[\text{CO}_3^{2-}]$ , and not through the elevation of  $[\text{Ca}^{2+}]$ , which would inherently change the Mg/Ca ratio of the biofilm's calcifying fluid and cause its  $\text{CaCO}_3$  polymorph

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mineralogy to differ from that of abiotically precipitated  $\text{CaCO}_3$ .

3. The results of the present study suggest that the primary mineralogy and  $\text{Mg}/\text{Ca}_C$  of well-preserved microbial carbonates may be a viable proxy for calcite-  
5 aragonite seas throughout Precambrian time, assuming (as has been previously asserted) that the influence of seawater  $\text{Mg}/\text{Ca}$  on  $\text{CaCO}_3$  polymorph mineralogy in Precambrian seawater was comparable to that in Phanerozoic seawater (i.e.,  $m\text{Mg}/\text{Ca} \sim 2$  divided calcite and aragonite/high Mg calcite seas). These results invite a systematic study of the primary mineralogy and Mg content of well-preserved Precambrian microbial carbonates aimed at empirically constraining  
10 the history of Precambrian seawater  $\text{Mg}/\text{Ca}$ .

## 9 Implications for ocean acidification research

### 9.1 Insight into the composition of organisms' calcifying fluids

The anthropogenic elevation of atmospheric  $p\text{CO}_2$  is predicted to cause portions of the world's surface oceans to become undersaturated with respect to aragonite and  
15 high Mg calcite before the year 2150 (Brewer, 1997). Many experiments have shown that these predicted reductions in carbonate ion impair the ability of calcifying marine organisms to produce their protective shells and skeletons (cf. Hoegh-Guldberg et al., 2007; Kleympas et al., 2006; Langdon and Atkinson, 2005; Langdon et al., 2000; Gattuso et al., 1998). However, multiple studies (Iglesias-Rodriguez et al., 2008; Ries et al., 2009; Wood et al., 2008) have also demonstrated that calcification in some  
20 taxa is enhanced by elevated  $p\text{CO}_2$ , most likely due to the organism's ability to utilize  $\text{HCO}_3^-$  in calcification, which increases with  $p\text{CO}_2$ . Although the experiments reviewed here were designed to evaluate organisms' response to secular variation in seawater  $\text{Mg}/\text{Ca}$ , the results have important implications for our interpretation of the disparate  
25 responses exhibited by calcifying organisms investigated in recent ocean acidification experiments.

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Calcification within most organisms is catalyzed, in part, by elevating the saturation state of their calcifying fluid with respect to  $\text{CaCO}_3$ , which can be achieved by elevating either the  $[\text{Ca}^{2+}]$  or  $[\text{CO}_3^{2-}]$  of this fluid. Organisms whose skeletal mineralogy and calcite Mg-content varied with experimental  $\text{Mg}/\text{Ca}_{\text{sw}}$  in a manner that mimics abiotic calcification (i.e., produced high Mg calcite and/or aragonite when  $m\text{Mg}/\text{Ca}_{\text{sw}} > 2$  and low Mg calcite when  $m\text{Mg}/\text{Ca}_{\text{sw}} < 2$ ) probably induce calcification primarily by elevating  $[\text{CO}_3^{2-}]$ , since elevating  $[\text{Ca}^{2+}]$  would reduce the Mg/Ca ratio of the organisms calcifying fluid, causing their skeletal mineral polymorph and calcite Mg-content to deviate from that observed for abiotic calcification. Although we have limited data about the composition of organisms' calcifying fluids, the elevation of  $[\text{CO}_3^{2-}]$  within this fluid is believed to result from the elevation of calcifying fluid pH via direct proton pumping,  $\text{Ca}^{2+}$ - $\text{H}^+$  exchange, secretion of hydroxyl ions, dehydration of  $\text{H}_2\text{CO}_3$ , or the removal of  $\text{CO}_2$  via photosynthesis (Borowitzka and Larkum, 1976; McConnaughey and Falk, 1991; McConnaughey and Whelan, 1997; De Beer and Larkum, 2001; Cohen and McConnaughey, 2003).

Organisms that calcify at high pH relative to ambient seawater ( $\text{pH}=9.0$ – $11.0$ ) will convert a substantial portion of the elevated  $\text{HCO}_3^-$ , resulting from the  $\text{CO}_2$ -induced ocean acidification, back into the  $\text{CO}_3^{2-}$  ion that is used directly in calcification. Thus, it can be reasonably argued that organisms that mimic abiotic calcification with respect to  $\text{CaCO}_3$  polymorph specification and Mg-incorporation in calcite, an indicator that they induce calcification via the elevation of pH (and, thus,  $[\text{CO}_3^{2-}]$ ), will likely be the least negatively impacted by  $\text{CO}_2$ -induced ocean acidification (Ries et al., 2009).

Conversely, organisms that produce low Mg calcite in seawater that favors nucleation of aragonite and high Mg calcite probably force the precipitation of low Mg calcite by elevating  $[\text{Ca}^{2+}]$  within their calcifying fluid, which reduces the Mg/Ca ratio of this fluid. If this control over calcifying fluid Mg/Ca ratio comes at the expense of pH control, then these organisms may be less able to convert the elevated  $\text{HCO}_3^-$  that accompanies  $\text{CO}_2$ -induced ocean acidification back into  $\text{CO}_3^{2-}$ , which is required to maintain conditions favorable for biocalcification under such acidified conditions. Thus, modern low

Mg calcite organisms may be more negatively impacted by CO<sub>2</sub>-induced ocean acidification than aragonite and high Mg calcite organisms that maintain a high degree of control over the pH and, thus, CaCO<sub>3</sub> saturation state of their calcifying fluid.

However, low Mg calcite organisms should be more resistant to dissolution in CO<sub>2</sub>-acidified seawater than either aragonite or high Mg calcite organisms because their low Mg calcite skeletal mineral is less soluble. Additionally, the elevated concentration of Ca<sup>2+</sup> within their calcifying fluid (which forces precipitation of low-Mg calcite in modern, high Mg/Ca seawater) may mitigate the impact of reduced [CO<sub>3</sub><sup>2-</sup>] on calcification rate. So even though aragonite and high Mg calcite organisms may be more adept at converting the elevated HCO<sub>3</sub><sup>-</sup> that accompanies CO<sub>2</sub>-induced ocean acidification back into CO<sub>3</sub><sup>2-</sup> within their calcifying fluids, the greater solubility of their skeleton may ultimately render them more vulnerable to dissolution in CO<sub>2</sub>-enriched aragonite seas, such as those existing today. Of course, this lack of control over calcifying fluid Mg/Ca would have been less of a detriment during calcite sea intervals of the geologic past, when modern high Mg calcite-secreting organisms would have apparently secreted the less soluble low Mg calcite form of CaCO<sub>3</sub>. Thus, it may be reasonable to expect that during calcite seas intervals, organisms that induce calcification primarily by elevating [CO<sub>3</sub><sup>2-</sup>] would be the most resistant to CO<sub>2</sub>-induced ocean acidification. During aragonite sea intervals – such as the modern one – it is likely the balance of these two mechanisms of calcification (pH vs. Mg/Ca control) within an organism's calcifying fluid that determines its unique response to CO<sub>2</sub>-induced ocean acidification.

## 9.2 Calcite-aragonite seas and past ocean acidification events

Over geologic timescales, seawater [Ca<sup>2+</sup>] is thought to have generally varied inversely with seawater [CO<sub>3</sub><sup>2-</sup>] (Fig. 29; Royer et al., 2004; Hardie et al., 1996; Demicco et al., 2005). This is because the primary mechanisms responsible for fluctuations in these parameters – hydrothermal brine-basalt reactions ([Ca<sup>2+</sup>]) and volcanic CO<sub>2</sub> emission ([CO<sub>3</sub><sup>2-</sup>]) – are both thought to have been largely driven by the global rate of ocean crust

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production. Thus, tectonically induced reductions in  $[\text{CO}_3^{2-}]$  (via volcanic degassing of  $p\text{CO}_2$ ) would have been partially offset, in terms of  $\text{CaCO}_3$  saturation state, by commensurate increases in seawater  $[\text{Ca}^{2+}]$  driven by enhanced  $\text{Mg}^{2+}$ - $\text{Ca}^{2+}$  exchange along zones of ocean crust production. Additionally, the inverse relationship between seawater  $[\text{Ca}^{2+}]$  and  $[\text{CO}_3^{2-}]$  fortuitously causes low Mg calcite – the least soluble form of  $\text{CaCO}_3$  – to be the dominant form of  $\text{CaCO}_3$  (because elevated  $[\text{Ca}^{2+}]$  causes low seawater Mg/Ca) when the oceans are least saturated with respect to  $\text{CaCO}_3$  (because of low  $[\text{CO}_3^{2-}]$ ). Therefore, the impact of tectonically-induced ocean acidification (via  $\text{CO}_2$  outgassing) on hypercalcifying taxa may have been mitigated throughout the geologic past by coeval tectonically-induced calcite sea conditions, which would have favored nucleation of the less soluble low-Mg calcite polymorph of  $\text{CaCO}_3$  and maintained seawater  $[\text{Ca}^{2+}]$  at an elevated level (Fig. 29).

However, the modern  $p\text{CO}_2$ -induced ocean acidification event, driven by the combustion of fossil fuels, differs from the tectonically forced acidification events of the geologic past in four critical ways: (1) the modern acidification event will not be accompanied by a coincident, tectonically forced elevation in  $[\text{Ca}^{2+}]$  that mitigates the  $p\text{CO}_2$ -induced reduction in  $[\text{CO}_3^{2-}]$  and, thus,  $\text{CaCO}_3$  saturation state; (2) the modern acidification event will not be mitigated by a coincident, tectonically forced reduction in seawater Mg/Ca that favors the nucleation of the less soluble low Mg calcite polymorph of  $\text{CaCO}_3$ ; (3) the rapidity of the modern acidification event will initially outpace the build-up of alkalinity that accompanies weathering of continents by the more acidic rainwater; and (4) the rapidity of the modern acidification event may preclude evolutionary responses by hypercalcifying taxa. It is for these reasons that the modern ocean acidification event poses an unusually grave threat for hypercalcifying taxa, even when compared with the more protracted and extreme elevations in atmospheric  $p\text{CO}_2$  that have occurred throughout Phanerozoic time.

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## 10 General conclusions

### 10.1 Tectonic controls on seawater chemistry

Sandberg (1983) observed that the primary mineralogy of ooids and early marine cements has alternated between three aragonite and two calcite intervals over the Phanerozoic Eon. Stanley and Hardie (1998, 1999) observed that major reef-building and sediment-producing organisms have shifted mineralogy in phase with these non-skeletal carbonates. Hardie (1996) interprets these shifts in carbonate mineralogy as responses to secular variations in the Mg/Ca ratio of seawater caused by fluctuations in the mixing rate of mid-ocean-ridge (MOR)/large-igneous-province (LIP) hydrothermal brines and average river water, which is primarily driven by changes in the global rate of ocean crust production. As upwelling MOR/LIP basalt interacts with marine brine, the basalt is converted to greenstone, thereby removing  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  from seawater and releasing  $\text{Ca}^{2+}$  and  $\text{K}^+$  to it. The rate of MOR/LIP ocean-crust production controls the rates of this ion exchange and, therefore, the respective concentrations of these ions in seawater (Spencer and Hardie, 1990).

Hardie (1996) used this model to calculate Mg/Ca ratios for the entire Phanerozoic Eon from historical rates of ocean crust production (inferred from eustatic sea level change). Füchtbauer and Hardie (1976, 1980) showed experimentally that for earth surface temperatures and pressures, seawater with *m*Mg/Ca ratios greater than 2 precipitate aragonite+high Mg calcite (*m*Mg/Ca in calcite >0.04), while *m*Mg/Ca ratios less than 2 precipitate only low Mg calcite (*m*Mg/Ca in calcite <0.04). The combination of these carbonate nucleation fields with Hardie's (1996) Phanerozoic Mg/Ca curve accurately predicts Sandberg's (1983) and Stanley and Hardie's (1998, 1999) variation in non-skeletal and skeletal carbonates. Hardie's oceanic Mg/Ca model is further supported by synchronized transitions between  $\text{MgSO}_4$  and KCl evaporites (Hardie, 1996; Lowenstein et al., 2003), fluid inclusion data (Lowenstein et al., 2001, 2003, 2005; Brennan and Lowenstein, 2002; Brennan, 2002; Horita et al., 2002; Brennan et al.,

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2004; Timofeeff et al., 2006), secular variation in the skeletal Mg/Ca ratio of fossil molluscs (Steuber and Rauch, 2005) and echinoderms (Dickson, 2002, 2004), and secular variation in the Br concentration of marine halite (Siemann, 2003).

## 10.2 Fossil evidence for the influence of seawater Mg/Ca on calcareous biomineralization

Stanley and Hardie (1998, 1999) found that the carbonate mineralogy of simple, hypercalcifying organisms has varied in concert with Sandberg's aragonite and calcite seas throughout Phanerozoic time. During Calcite I seas (middle Paleozoic), calcitic corals (tabulate, heliolitid and rugose), and stromatoporoids (possibly calcitic) were the dominant reef builders, while receptaculitids (possibly calcitic) were the dominant sediment producers. During Aragonite II seas (late Paleozoic – early Mesozoic), the reefs were dominated by aragonitic groups of sponges, scleractinian corals and phylloid algae and high Mg calcitic red algae, while aragonitic dasycladaceans were the dominant algal sediment producers. During Calcite II seas (Mid-Jurassic-late Paleogene), the largely calcitic rudist bivalves replaced the aragonitic scleractinian corals as the major reef builders, while calcitic nannoplankton (coccolithophores) became major chalk producers. Finally, during Aragonite III seas, which include the modern ocean, aragonitic scleractinian corals and high Mg calcitic red algae again dominate reef construction while the aragonitic bryopsidalean algae are the major sediment producers.

Stanley and Hardie (1998, 1999) assert that the synchronicity between skeletal and non-skeletal carbonates is most evident for hypercalcifying organisms, including the reef-building corals and sponges and the sediment-producing algae. Kiessling et al. (2008) confirmed that this trend is most evident for reef-building taxa. This is probably because these organisms' characteristically rapid rate of calcification allows them to exercise only limited control over the chemical milieu of their calcifying fluid. However, Porter (2007) showed that even non-hypercalcifying taxa follow suit at the time of skeletal origination – but not necessarily thereafter (Kiessling et al., 2008).

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### 10.3 Experimental evidence for the effect of seawater Mg/Ca on growth and calcification rates

The aragonite-secreting bryopsidalean algae (*Penicillus capitatus*, *Udotea flabellum*, and *Halimeda incrassata*) and the scleractinian corals (*Porites cylindrica*, *Montipora digitata*, and *Acropora cervicornis*) exhibited higher rates of calcification and growth in seawater of Mg/Ca ratios that favored their aragonitic mineralogy. Conversely, the coccolithophores (*Pleurochrysis carterae*, *Ochrosphaera neopolitana*, and *Coccolithus neohelis*) exhibited higher rates of growth and calcification in seawater of Mg/Ca ratios that favored their calcitic mineralogy. It is reasonable, if not expected, that the algae's and corals' precipitation of aragonite in the low Mg calcite nucleation field, and the coccolithophores precipitation of calcite in the aragonite nucleation field, proceeds at a slower rate than it does in seawater that favors the organisms' inherent skeletal mineralogy. It appears that such reduced rates of calcification liberate less CO<sub>2</sub> for photosynthesis (Paasche, 1968; Borowitzka and Larkum, 1976b; Borowitzka, 1977; Sikes et al., 1980; Reiskind et al., 1988, 1989; Ries, 2005a, 2005b, 2006a; Stanley et al., 2005, 2009), thereby resulting in the concomitant reductions in linear growth and primary productivity for these autotrophic organisms when grown in mineralogically unfavorable seawater.

### 10.4 Experimental evidence for the effect of seawater Mg/Ca on CaCO<sub>3</sub> polymorph mineralogy and Mg incorporation

The bryopsidalean algae (*Halimeda incrassata*, *Udotea flabellum*, and *Penicillus capitatus*) and the scleractinian corals produced approximately one-quarter and one-third, respectively, of their CaCO<sub>3</sub> as the calcite polymorph, as opposed to their normal aragonite polymorph, when grown in the experimental calcite seawater (*m*Mg/Ca < 2). Bacterial biofilms, which produce a mixture of aragonite and high Mg calcite in modern aragonite seawater, produced exclusively calcite in the experimental calcite seawater. The Mg/Ca of the biofilm calcite varied proportionally with the Mg/Ca of the experi-

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mental seawater. The two species of coccolithophores investigated that secrete high Mg calcite in modern aragonite seawater (*Pleurochrysis carterae* and *Ochrosphaera neopolitana*), exhibited reductions in calcite Mg/Ca when grown in experimental seawaters of reduced Mg/Ca. The Mg/Ca ratio of calcite secreted by the third species of coccolithophore (*Coccolithus neohelis*), which secretes low Mg calcite even in modern aragonite seawater, was not affected by the experimental reductions in seawater Mg/Ca. The skeletal Mg/Ca of the calcite-secreting coralline algae (*Neogoniolithon* sp., *Amphiroa fragilissima*, *Amphiroa* sp. A, and *Amphiroa* sp. B) and reef-dwelling animals (the echinoid *Eucidaris tribuloides*, the crab *Perchon gibbesi*, the shrimp *Palaemonetes pugio*, the calcareous serpulid worm *Hydroides crucigera*) varied proportionally with Mg/Ca of the experimental seawater in which these organisms were reared.

## 10.5 Implications for biomineralogical control

The bryopsidalean algae's and scleractinian corals' precipitation of a mostly aragonitic skeleton, even in seawater that favors the abiotic precipitation of calcite, suggests that these organisms exert significant control over their biomineralization. However, the precipitation of one-quarter to one-half of the algae's CaCO<sub>3</sub> and one-third of the corals' CaCO<sub>3</sub> as the calcite polymorph, as opposed to the normal aragonite polymorph, suggests that the algae's and corals' biomineralogical control is somewhat limited and can be partially overridden by ambient seawater chemistry (Ries, 2005b).

Likewise, the observed influence of seawater Mg/Ca on the skeletal Mg/Ca of two of the three species of coccolithophores, the coralline red algae, and the calcite-secreting animals suggests that although these organisms are capable of specifying precipitation of the calcite polymorph, even in seawater that favors the abiotic precipitation of aragonite, their biomineralogical control is limited in its ability to prevent Mg incorporation in that calcite. However, the deviation of many of these organisms' Mg fractionation patterns from that of abiotic calcite, combined with variations in Mg fractionation observed amongst closely related genera and species, and even between anatomical components within single organisms, suggests that these organisms are exerting substantial

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biological control over their calcification process (Ries, 2005b). Although Chave (1954) correlated taxonomic complexity with temperature-driven Mg fractionation in calcifying organisms, a similar correlation could not be unequivocally established here for seawater Mg/Ca-driven Mg fractionation. However, as a general rule, Mg fractionation within the photosynthetic organisms (coccolithophores, corals, coralline algae, bryopsidalean algae) appears to be more strongly influenced by ambient Mg/Ca than Mg fractionation within the non-photosynthetic ones (echinoids, crabs, shrimp and calcareous serpulid worms; Fig. 30). This increased susceptibility of photosynthetic organisms to seawater Mg/Ca suggests that autotrophic calcifiers *induce* precipitation of  $\text{CaCO}_3$  through the removal of  $\text{CO}_2$ , thereby resembling abiotic calcification to a greater extent than the more regulated heterotrophic calcifiers, which apparently *control* calcification via ionic pumping and/or organic mineral templates (Ries, 2005b).

## 10.6 Implications for biocalcification throughout Phanerozoic time

The elevated rates of calcification and growth observed for the bryopsidalean algae and scleractinian corals grown in the experimental aragonite seawaters ( $m\text{Mg}/\text{Ca} > 2$ ), and for the coccolithophores grown in the experimental calcitic seawaters ( $m\text{Mg}/\text{Ca} < 2$ ), supports the paleontological evidence (Stanley and Hardie, 1998, 1999; Kiessling et al., 2008; Porter, 2007) that oceanic Mg/Ca was an important factor in determining the role of these organisms as dominant sediment producers and reef builders during aragonite and calcite seas. The elevated productivity and calcification of the coccolithophores in the experimental calcite seawater is particularly significant given its occurrence in the experimental treatment ( $m\text{Mg}/\text{Ca} = 1.0$ ) that deviated most from what modern coccolithophores are accustomed ( $m\text{Mg}/\text{Ca} = 5.2$ ). The link between calcification and growth in the photosynthetic organisms – via  $\text{CO}_2$  liberation – suggests that autotrophic calcifiers would have been most influenced by secular variations in the Mg/Ca ratio of seawater throughout Phanerozoic time (Ries, 2005b).

The correlation observed between skeletal Mg/Ca and seawater Mg/Ca for the coccolithophores, the coralline red algae, and the calcite-secreting animals supports the

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assertion that the skeletal Mg/Ca of organisms that secrete high Mg calcite in modern seas has varied in synchronicity with oceanic Mg/Ca throughout Phanerozoic time (Stanley and Hardie 1998, 1999). The secretion of low Mg calcite by each of these organisms in the experimental calcite seawater ( $m\text{Mg}/\text{Ca} < 2$ ) suggests that they would have secreted low Mg calcite in ancient calcite seas, such as those reported for middle Paleozoic and mid-Late Cretaceous time. The wide range of organisms that exhibit this proportionality between skeletal and seawater Mg/Ca suggests that this is a universal trend for organisms that secrete high Mg calcite in modern seas.

## 10.7 Paleocceanographic reconstructions

The observed relationship between seawater Mg/Ca and skeletal Mg incorporation in the coccolithophores, the coralline algae, the calcite-secreting animals, and the calcitic portions of the scleractinian corals, the bryopsidalean algae, and the bacterial biofilms suggests that well-preserved fossils of these organisms may be an archive of oceanic Mg/Ca throughout Phanerozoic and Precambrian time. Likewise, the reconstruction of ancient seawater temperatures from skeletal Mg/Ca ratios must correct for the effect of secular variation in the Mg/Ca ratio of seawater. Mg fractionation algorithms that define skeletal Mg/Ca as a function of seawater Mg/Ca and temperature were derived for the organisms evaluated in these experiments. Oceanic Mg/Ca ratios calculated from the Mg content of fossil echinoderms, established paleotemperature data, and the echinoid Mg fractionation algorithm are in general agreement with other independent estimates of oceanic Mg/Ca throughout Phanerozoic time.

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**Table 1.** Summary of mineralogy, linear growth, calcification, and primary productivity for *Halimeda incrassata*, *Penicillus capitatus*, and *Udotea flabellum* algae grown in artificial seawater treatments formulated at differing Mg/Ca ratios.

Alga	SW mMg/Ca <sup>a</sup>	Mineralogy (%cal:%arag)	Linear growth± SE (mm/day)	Calcification± SE (mg/day)	Primary production ±SE (mg/day)	Study
<i>Halimeda incrassata</i>	5.2	8:92±2	0.41±0.04	0.83±0.07	0.73±0.02	This study
<i>Halimeda incrassata</i>	2.5	16:84±2	0.28±0.03	0.52±0.03	0.43±0.05	This study
<i>Halimeda incrassata</i>	1.5	46:54±8	0.21±0.03	0.40±0.04	0.33±0.04	This study
<i>Penicillus capitatus</i>	5.2	0:100±3	1.00±0.11	0.70±0.06	0.87±0.10	Ries (2006)
<i>Penicillus capitatus</i>	2.5	0:100±3	0.75±0.07	0.42±0.07	0.36±0.04	Ries (2006)
<i>Penicillus capitatus</i>	1.0	22:78±3	0.14±0.02	0.06±0.03	0.15±0.04	Ries (2006)
<i>Udotea flabellum</i>	5.2	0:100±3	0.29±0.05	0.55±0.04	0.38±0.05	Ries (2005)
<i>Udotea flabellum</i>	2.5	0:100±3	0.20±0.02	0.30±0.03	0.14±0.03	Ries (2005)
<i>Udotea flabellum</i>	1.0	25:75±3	0.10±0.02	0.12±0.03	0.09±0.03	Ries (2005)

<sup>a</sup> mMg/Ca=1.0, [Ca<sup>2+</sup>]=31.6 mM; mMg/Ca=1.5, [Ca<sup>2+</sup>]=25.3 mM; mMg/Ca=2.5, [Ca<sup>2+</sup>]=18.1 mM; mMg/Ca=5.2, [Ca<sup>2+</sup>]=10.2 mM

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Table 2. Algorithms relating  $Mg/Ca_{SW}$ ,  $Mg/Ca_C$ , and temperature.

CaCO <sub>3</sub> source	$Mg/Ca_C = f(Mg/Ca_{SW})$ (species-normalized, $T = 25^\circ C$ )	$Mg/Ca_C = f(T)$ ( $Mg/Ca = 5.2$ )	$Mg/Ca_C = f(Mg/Ca_{SW}, T)$
Echinoid plate	$Mg/Ca_C = 0.0471 Mg/Ca_{SW}^{0.668}$	$Mg/Ca_C = 0.00216 T + 0.0876^a$	$Mg/Ca_C = S(0.000719 T + 0.0292) Mg/Ca_{SW}^{0.668}$
Echinoid spine	$Mg/Ca_C = 0.0364 Mg/Ca_{SW}^{0.538}$	$Mg/Ca_C = 0.00203 T + 0.0375^b$	$Mg/Ca_C = S(0.000837 T + 0.0155) Mg/Ca_{SW}^{0.538}$
Crab carapace	$Mg/Ca_C = 0.0275 Mg/Ca_{SW}^{0.956}$	$Mg/Ca_C = 0.00299 T + 0.0582^c$	$Mg/Ca_C = S(0.000619 T + 0.0120) Mg/Ca_{SW}^{0.956}$
Serpulid worm	$Mg/Ca_C = 0.101 \ln Mg/Ca_{SW} + 0.0259$	$Mg/Ca_C = 0.00463 T + 0.0761^d$	$Mg/Ca_C = S(0.00243 T + 0.0399)(\ln Mg/Ca_{SW} + 0.257)$
Coralline algae	$Mg/Ca_C = 0.0582 Mg/Ca_{SW}^{0.904e}$	$Mg/Ca_C = 0.0825e^{0.0457T}$	$Mg/Ca_C = S(0.0186e^{0.0457T} Mg/Ca_{SW}^{0.904})$
Non-skeleta	$Mg/Ca_C = 0.0482 Mg/Ca_{SW}^{0.898g}$	$Mg/Ca_C = 0.00672 T + 0.0392^g$	$Mg/Ca_C = (0.00158 T + 0.00924) Mg/Ca_{SW}^{0.898}$

Note: SW is seawater; C is calcite.

<sup>a</sup> Algorithm based on Chave's (1954) echinoid and crinoid data ( $R^2 = 0.417$ ).

<sup>b</sup> Algorithm based on Chave's (1954) echinoid data ( $R^2 = 0.490$ ).

<sup>c</sup> Algorithm based on Chave's (1954) decapod crustacean data ( $R^2 = 0.734$ ).

<sup>d</sup> Algorithm based on Chave's (1954) annelid worm data ( $R^2 = 0.777$ ).

<sup>e</sup> Algorithm based on Stanley et al.'s (2002) coralline algae data ( $R^2 = 0.891$ ).

<sup>f</sup> Algorithm based on Chave's (1954) calcareous algae data ( $R^2 = 0.762$ ).

<sup>g</sup> Algorithms based on Fichtbauer and Hardie's (1976) non-skeletal precipitates data ( $R^2 = 0.930$  for  $Mg/Ca_C = f[Mg/Ca_{SW}]$ ;  $R^2 = 0.861$  for  $Mg/Ca_C = f[T]$  @  $Mg/Ca_{SW} = 5.0$ )

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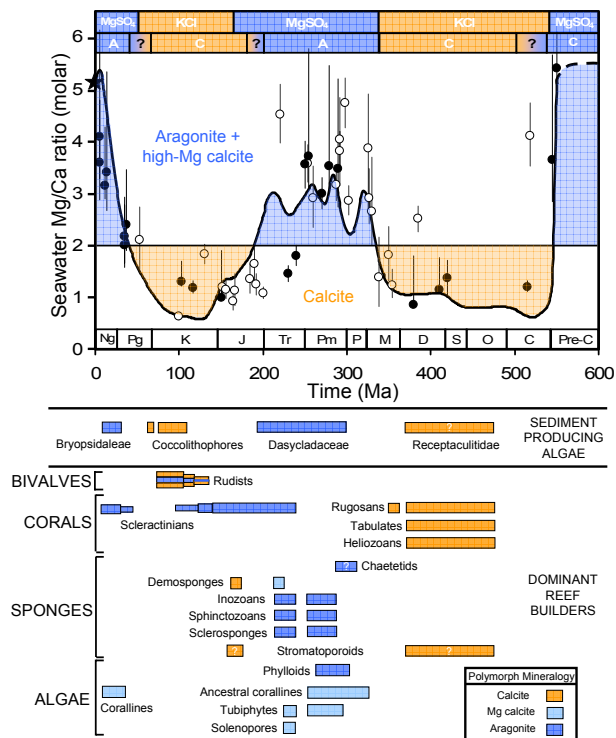
**Table 3.** Diversity of bacteria in biofilm communities determined by 16S rRNA gene sequence analysis.

Phylogenetic group	Control <sup>a</sup> (mMg/Ca=5.2)	Aragonite SW (mMg/Ca=5.2)	Calcite SW (mMg/Ca=1.5)
Cyanobacteria	32%	26%	25%
$\alpha$ -Proteobacteria	25%	25%	23%
Bacteroidetes	15%	16%	8%
$\gamma$ -Proteobacteria	10%	19%	17%
Planctomycetes	8%	6%	2%
Chloroflexi	–	6%	8%
Actinomycetes	5%	–	6%
Verrucomicrobia	–	–	4%
Legionella	–	–	4%
Acidobacteria	–	–	2%
Chlamydiales	2%	–	–
$\delta$ -Proteobacteria	2%	–	–
Gemmatimonadetes	–	1%	–
No. of clones analyzed	59	68	48

<sup>a</sup> biofilm processed shortly after removal from lagoon and not grown in experimental seawater

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**Fig. 1.** Synchronized transitions in the mineralogy of dominant reef-building and sediment-producing marine calcifiers (Stanley and Hardie, 1998, 1999), marine evaporites (Hardie, 1996), nonskeletal carbonates (Sandberg, 1983), and seawater Mg/Ca ratio (Hardie, 1996; Demicco et al., 2005; Lowenstein et al., 2001, 2003, 2005; Brennan and Lowenstein, 2002; Brennan, 2002; Horita et al., 2002; Brennan et al., 2004; Timofeeff et al., 2006) throughout Phanerozoic time. Curve is  $m\text{Mg}/\text{Ca}$  ratio of seawater (Hardie, 1996; Demicco et al., 2005) estimated using a mid-ocean ridge hydrothermal flux/river water mixing model driven by global rates of ocean crust production. Closed circles correspond to seawater  $m\text{Mg}/\text{Ca}$  ratios estimated from fluid inclusions in primary marine halite (Lowenstein et al., 2001, 2003, 2005; Brennan, 2002; Horita et al., 2002; Brennan and Lowenstein, 2002; Brennan et al., 2004; Timofeeff et al., 2006). Open circles are seawater  $m\text{Mg}/\text{Ca}$  ranges estimated from the Mg content of fossil echinoids (Dickson, 2002, 2004; Ries, 2004). Star represents modern seawater ( $m\text{Mg}/\text{Ca}=5.2$ ). Horizontal line divides the calcite ( $m\text{Mg}/\text{Ca}<2$ ) and aragonite+high Mg calcite ( $m\text{Mg}/\text{Ca}>2$ ) nucleation fields in seawater at 25°C. Intervals of primarily aragonitic (“A”) and calcitic (“C”) abiotic precipitates (ooids, marine cements, seafloor precipitates; Sandberg, 1983; Lasemi and Sandberg, 2000) and KCl and  $\text{MgSO}_4$  marine evaporites (Hardie, 1996) are plotted along top of figure. These data suggest that secular variation in seawater Mg/Ca ratios throughout Phanerozoic time supported three intervals of predominantly aragonite+high Mg calcite precipitation (seawater  $m\text{Mg}/\text{Ca}>2$ ) alternating with two intervals of predominantly calcite precipitation (seawater  $m\text{Mg}/\text{Ca}<2$ ). Adapted from Stanley and Hardie (1999).

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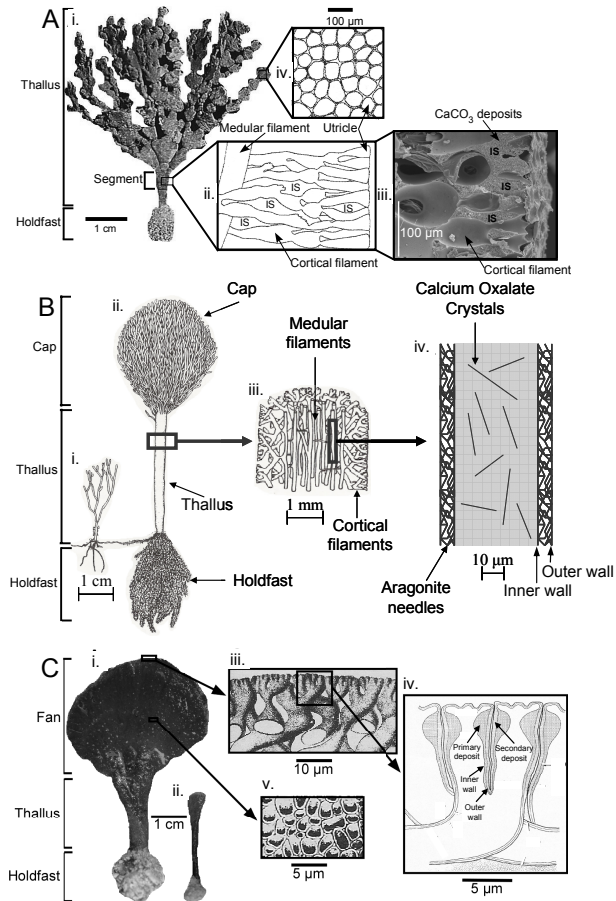
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**Fig. 2.**

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**Fig. 2.** Anatomy of the predominant aragonite-producing bryopsidalean algae in modern carbonate platform environments. **(A)** *Halimeda incrassata* alga showing **(i)** the thallus, the calcified segments, and the uncalcified holdfast; **(ii)** a diagram of a vertical section through the cortical layer of the thallus, “IS”=interutricular space; **(iii)** a backscatter electron image of a vertical section through the alga’s cortical layer, showing extracellular calcification in the IS (external to the outer algal wall); and **(iv)** cortication of a calcified segment caused by utricle coalescence. **(B)** *Penicillus capitatus* alga showing **(i)** an offspring alga sprouting from rhizoids; **(ii)** a full grown plant revealing uncalcified holdfast, calcified thallus and calcified cap; **(iii)** magnified diagram of thallus revealing the constituent calcified medullar and cortical filaments; **(iv)** magnified longitudinal cross-section of a medullar filament showing intracellular deposition of aragonite needles between the inner and outer algal walls (extracellular deposition also occurs, but is not shown here), as well as distribution of calcium oxalate crystals within the cytoplasm (after Van den Hoek, 1981). **(C)** *Udotea flabellum* alga showing **(i)** full grown alga revealing uncalcified holdfast, calcified thallus, and calcified fan; **(ii)** young alga; **(iii)** vertical section of surface of fan showing cortex and individual utricles; **(iv)** vertical section through cortical layer – primary deposit is precipitated intracellularly between inner and outer algal wall, secondary deposit is precipitated extracellularly within the interutricular space (external to the outer algal wall); and **(v)** corticated surface of the fan (after Fritsch, 1948; Böhm et al., 1978).

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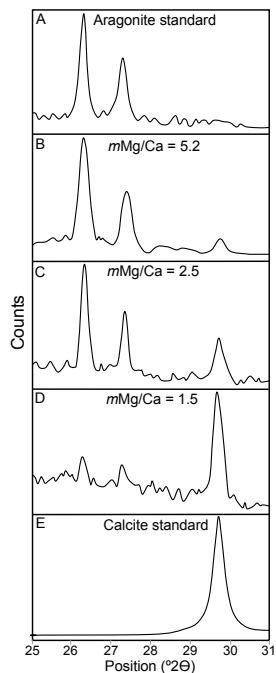
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**Fig. 3.** (A) X-ray diffraction pattern for pure aragonite, revealing primary aragonite peak [ $d(111)$ ] at  $2\theta = 26.2^\circ$  ( $3.40 \text{ \AA}$ ). (B) X-ray diffraction pattern for a *Halimeda incrassata* alga that produced 92% aragonite and 8% calcite when reared in experimental seawater that favors the nucleation of the aragonite polymorph ( $mMg/Ca = 5.2$ ;  $[Ca^{2+}] = 10.2 \text{ mM}$ ). (C) X-ray diffraction pattern for a *H. incrassata* alga that produced 84% aragonite and 16% calcite when reared in the boundary aragonite-calcite experimental seawater ( $mMg/Ca = 2.5$ ;  $[Ca^{2+}] = 18.1 \text{ mM}$ ). (D) X-ray diffraction pattern for a *H. incrassata* alga that produced 54% aragonite and 46% calcite when reared in the experimental calcite seawater ( $mMg/Ca = 1.5$ ;  $[Ca^{2+}] = 25.3 \text{ mM}$ ). (E) X-ray diffraction pattern for pure calcite, revealing primary calcite peak [ $d(104)$ ];  $3.03\text{--}3.04 \text{ \AA}$ ;  $2\theta = 29.4\text{--}29.5^\circ$ ] (from Stanley et al., 2009).

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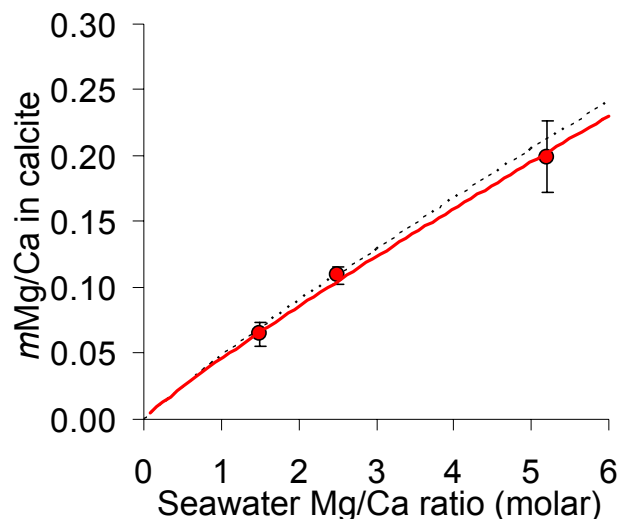
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**Fig. 4.** Molar Mg/Ca of calcite precipitated by *Halimeda incrustata* algae in the experimental seawaters ( $m\text{Mg}/\text{Ca}=1.5$ ,  $[\text{Ca}^{2+}]=25.3$  mM;  $m\text{Mg}/\text{Ca}=2.5$ ,  $[\text{Ca}^{2+}]=18.1$  mM;  $m\text{Mg}/\text{Ca}=5.2$ ,  $[\text{Ca}^{2+}]=10.2$  mM), as determined by powder X-ray diffraction and energy dispersive spectrometry. Mg fractionation algorithm (solid red curve) is calculated using a least squares regression and is defined as  $\text{Mg}/\text{Ca}_C=0.0460\text{Mg}/\text{Ca}_{\text{sw}}^{0.899}$  ( $R^2=0.996$ ) at  $25^\circ\text{C}$ . Dashed black curve is Mg fractionation curve for calcite precipitated abiotically from seawater at  $25^\circ\text{C}$  ( $\text{Mg}/\text{Ca}_C=0.0482\text{Mg}/\text{Ca}_{\text{sw}}^{0.898}$ ,  $R^2=0.930$ ; Füchtbauer and Hardie, 1976). Error bars represent instrument error and variation within and amongst specimens (from Stanley et al., 2009).

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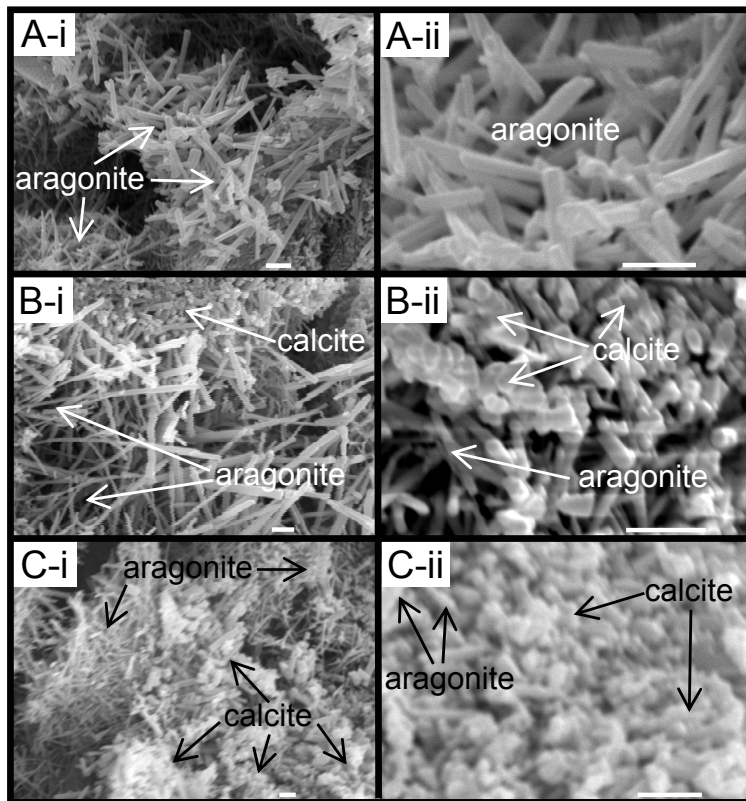
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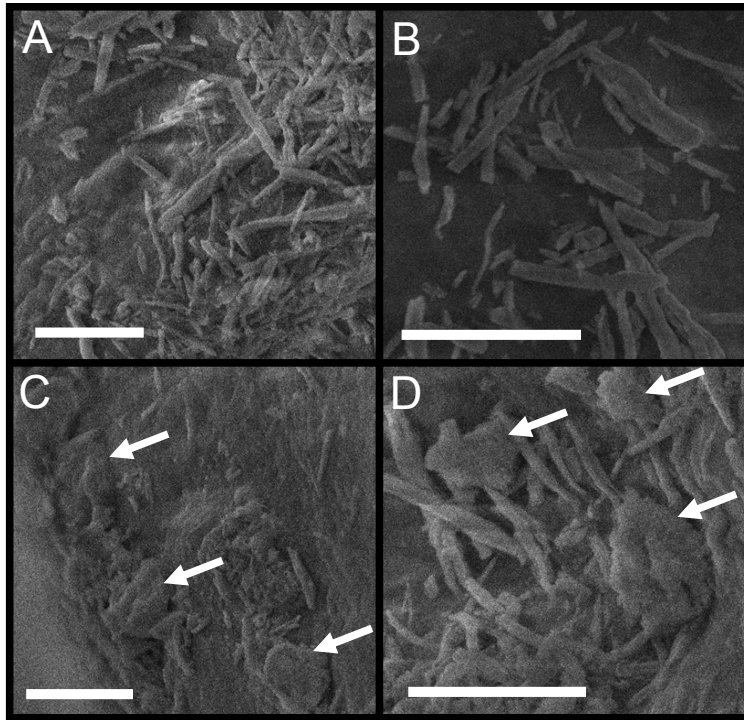
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**Fig. 5.** Back-scatter electron images showing the distribution of the aragonite and calcite precipitated within the interutricular space of segments comprising the thalli of *Halimeda incrasata* algae reared in experimental seawaters with  $m\text{Mg}/\text{Ca}=5.2$  and  $[\text{Ca}^{2+}]=10.2$  mM (aragonite seawater **(A-i, A-ii)**),  $m\text{Mg}/\text{Ca}=2.5$  and  $[\text{Ca}^{2+}]=18.1$  mM (aragonite-calcite boundary seawater **(B-i, B-ii)**), and  $m\text{Mg}/\text{Ca}=1.5$  and  $[\text{Ca}^{2+}]=25.3$  mM (calcite seawater **(C-i, C-ii)**). Scale bars are 1  $\mu\text{m}$  (from Stanley et al., 2009).

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**Fig. 6.** Back-scatter electron images showing the distribution of the aragonite needles and calcite rhombs (indicated by arrows) precipitated within the interutricular space of segments comprising the thalli of *Udokea flabellum* algae reared in experimental seawaters with  $m\text{Mg}/\text{Ca}=5.2$  and  $[\text{Ca}^{2+}]=10.2$  mM (aragonite seawater **(A, B)**) and  $m\text{Mg}/\text{Ca}=1.5$  and  $[\text{Ca}^{2+}]=25.3$  mM (calcite seawater **(C, D)**). Note that calcite is only evident in algae grown in the experimental calcite seawater. Scale bars are  $1\ \mu\text{m}$  (from Ries, 2006a).

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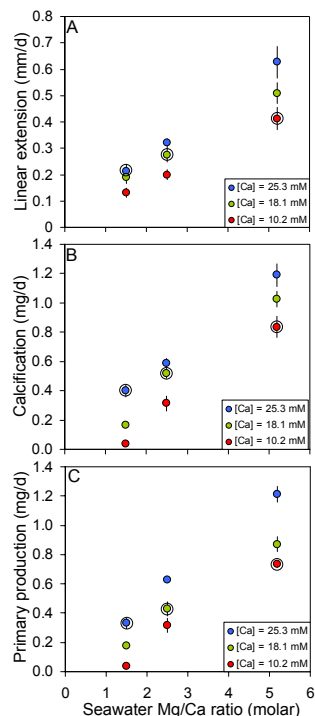
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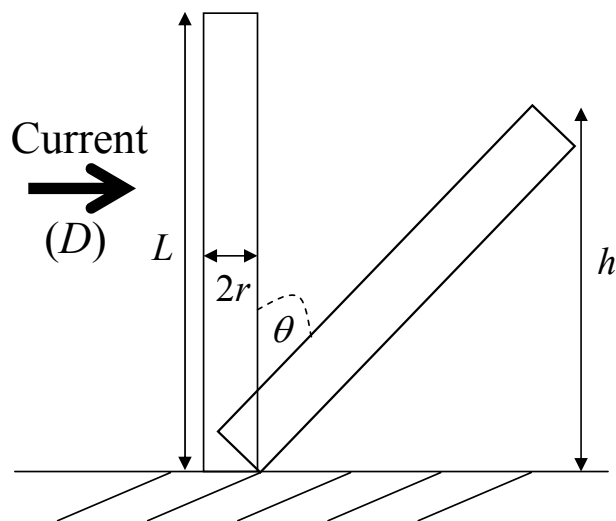
**Fig. 7.** Rates of linear extension (**A**), calcification (**B**), and primary production (**C**) for *Halimeda* algae reared in the nine experimental seawaters formulated to isolate the effects of seawater Mg/Ca and [Ca<sup>2+</sup>]. Rates of linear extension, calcification, and primary production increase significantly ( $p < 0.05$ ) with both increasing seawater Mg/Ca ([Ca<sup>2+</sup>] fixed) and increasing seawater [Ca<sup>2+</sup>] (Mg/Ca fixed). Rates of linear extension, calcification, and primary production also increase significantly ( $p < 0.05$ ) with elevations in seawater Mg/Ca that are formulated with geologically realistic (Hardie, 1996; Demicco et al., 2005) reductions in [Ca<sup>2+</sup>] (circumscribed data). Error bars represent standard error (from Stanley et al., 2009).

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**Fig. 8.** Free body diagram of a decapitated *Penicillus capitatus* alga modeled as a cantilever beam stressed by a unidirectional current. Stress ( $\sigma$ ) is calculated as  $4Dh/(\pi r^3)$ , where  $D$  is the current velocity,  $h$  is the height of the stalk and  $r$  is the radius of the stalk. Note that height ( $h$ ) decreases as a function of  $L \cos \theta$ , where  $L$  is the length of the stalk and  $\theta$  is the angle of stalk deflection. From Ries (2005a).

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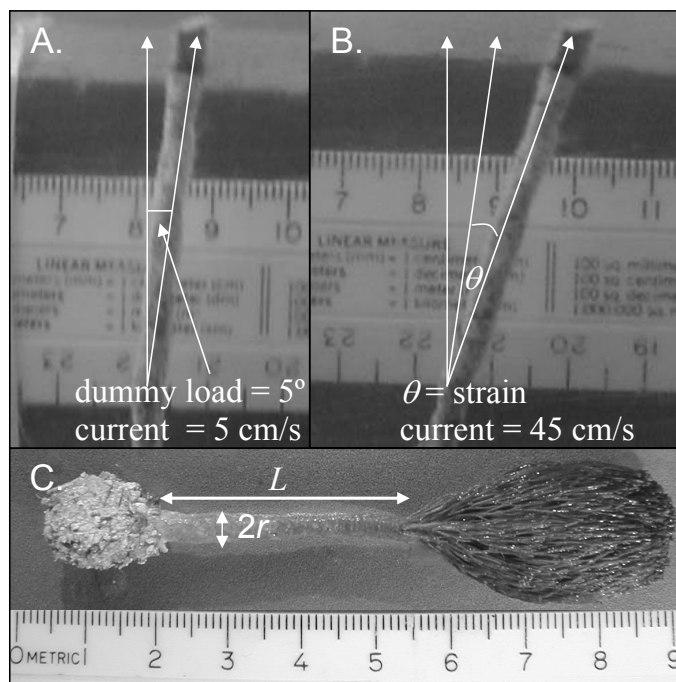
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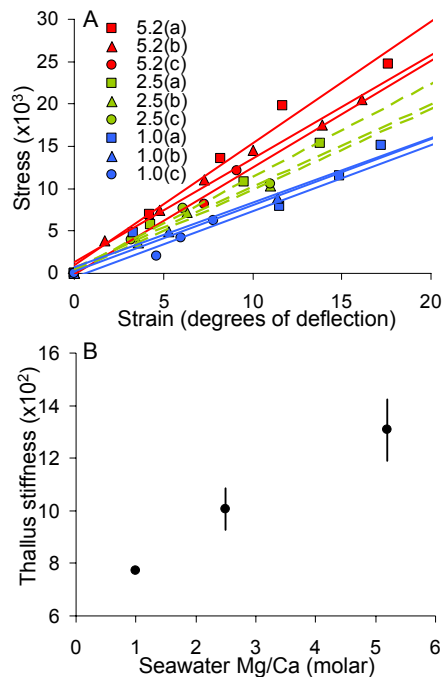


**Fig. 9.** (A) Decapitated *Penicillus capitatus* alga pre-strained to 5° deflection with the dummy load (current velocity=5 cm/s). (B) Decapitated *P. capitatus* alga strained beyond the 5° pre-strain dummy load (current velocity=45 cm/s). Angles of deflection ( $\theta$ ) beyond the 5° pre-strain were employed in the stress-strain analyses. (C) Photograph of a *P. capitatus* alga depicting the length ( $L$ ) and radius ( $r$ ) dimensions employed in modeling its thallus as a cantilever beam. From Ries (2005a).

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**Fig. 10. (A)** Stress-strain data generated for the thalli of nine *Penicillus capitatus* algae reared in the three seawater treatments (from Ries, 2005a). Stress-strain curves were generated by fitting linear regressions to the data using the least squares method. The solid red, dashed green, and solid blue curves correspond to *P. capitatus* algae reared in experimental seawaters formulated with  $m\text{Mg}/\text{Ca}$  of 5.2, 2.5 and 1.0, respectively. Average stiffnesses were calculated from the slopes of these stress-strain curves and plotted against seawater Mg/Ca in panel **(B)**. Thallus stiffness decreased significantly ( $p < 0.001$ ) with reductions in seawater Mg/Ca, such that algae were most stiff when reared in seawater that supports precipitation of their inherent aragonite skeletal mineral ( $m\text{Mg}/\text{Ca}=5.2$ ) and least stiff in seawater that supports the nucleation of calcite ( $m\text{Mg}/\text{Ca}=1.0$ ). Error bars represent standard deviation.

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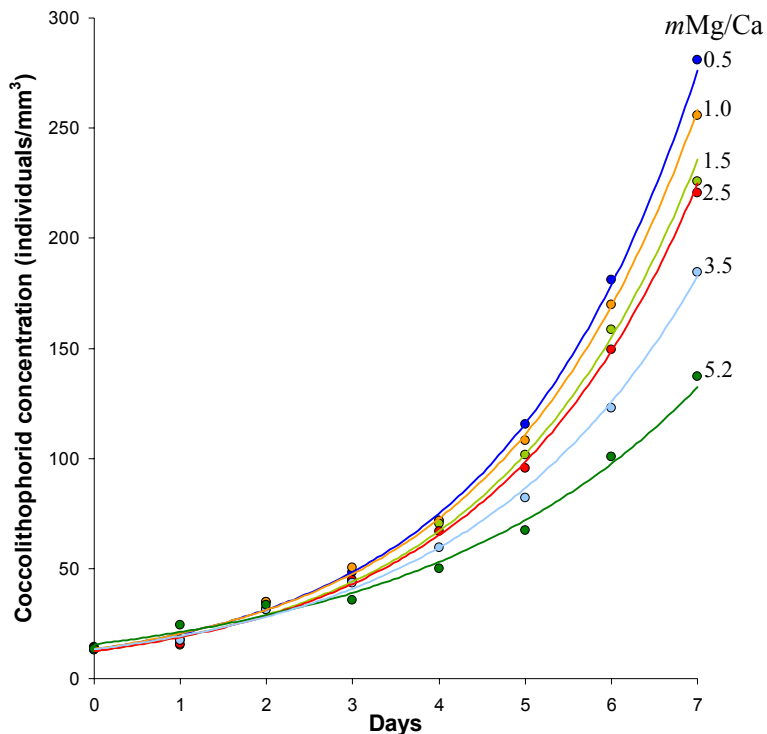
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**Fig. 11.** Exponential population growth for the coccolithophore *Pleurochrysis carterae* as a function of seawater Mg/Ca. Rates of population growth increased significantly ( $p < 0.05$ ) as seawater Mg/Ca declined into the calcite stability field, which favors precipitation of the coccolithophores' calcite skeletal mineral. For modern seawater,  $m\text{Mg}/\text{Ca}$  is 5.2 and the absolute concentration of  $\text{Ca}^{2+}$  is 10 mM; for the imputed Late Cretaceous seawater, the  $m\text{Mg}/\text{Ca}$  ratio is between 0.5 and 1.5 and the absolute concentration of  $\text{Ca}^{2+}$  is between 42 and 25 mM.  $R^2$  is between 0.98 and 0.99 for exponential fitted curves. Spearman rank correlation ( $r_s$ ) = 0.99 for growth rates. From Stanley et al. (2005).

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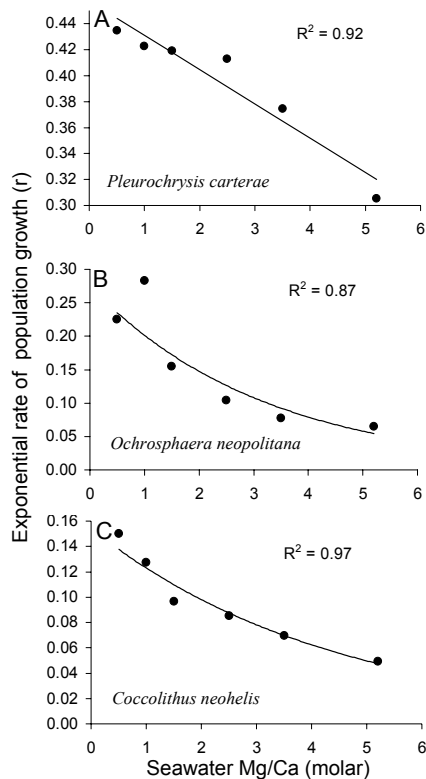
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**Fig. 12.** Exponential rates of population growth ( $r$ ) as a function of seawater Mg/Ca ratio for the coccolithophore species *Pleurochrysis carterae* (A), *Ochrosphaera neopolitana* (B), and *Coccolithus neohelis* (C). Rates of population growth increased significantly ( $p < 0.05$ ) for each of the three species as seawater Mg/Ca declined into the calcite stability field, which favors precipitation of the coccolithophores' calcite skeletal mineral. Fitted curve in (A) is linear, while fitted curves in (B) and (C) are exponential. Spearman rank correlation ( $r_s$ ) = 0.99 for all three species. From Stanley et al. (2005).

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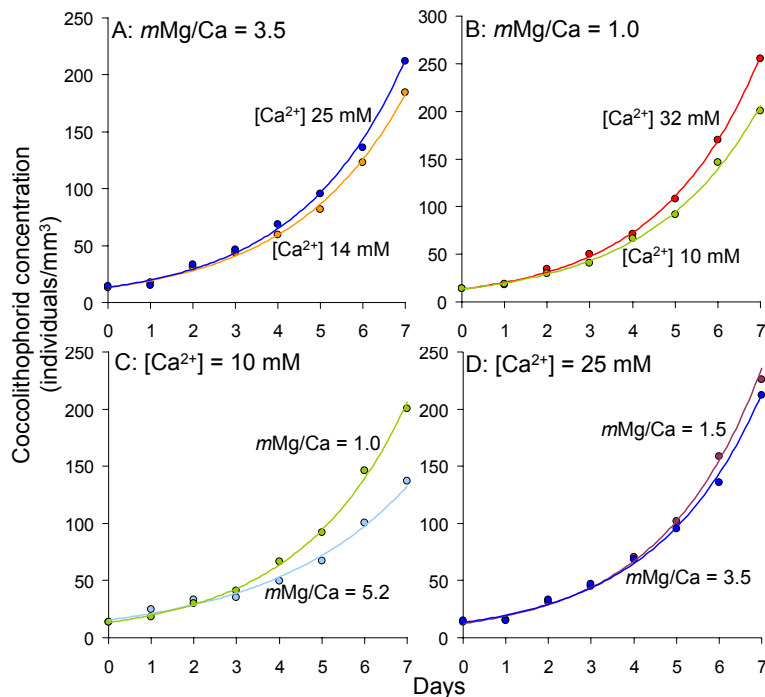
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**Fig. 13.** Effect of seawater Mg/Ca ratio and absolute  $\text{Ca}^{2+}$  concentration on population growth rate of *Pleurochrysis carterae*. **(A)** With  $m\text{Mg}/\text{Ca}$  ratio fixed at 3.5, elevation of  $\text{Ca}^{2+}$  concentration from 14.1 mM (orange curve) to 25.3 mM (dark blue curve) produced faster population growth. **(B)** With  $m\text{Mg}/\text{Ca}$  ratio fixed at 1.0, reduction of  $\text{Ca}^{2+}$  concentration from 31.6 mM (red curve) to 10.2 mM (green curve) produced slower population growth. **(C)** With  $\text{Ca}^{2+}$  fixed at 10.2 mM, reduction of  $m\text{Mg}/\text{Ca}$  from 5.2 (light blue curve) to 1.0 (green curve) produced faster population growth. **(D)** With  $\text{Ca}^{2+}$  fixed at 25.3 mM, elevation of the  $m\text{Mg}/\text{Ca}$  ratio from 1.5 (purple curve) to 3.5 (dark blue curve) yielded slower population growth. Experiments with *Coccolithus neohelis* yielded similar results. From Stanley et al. (2005).

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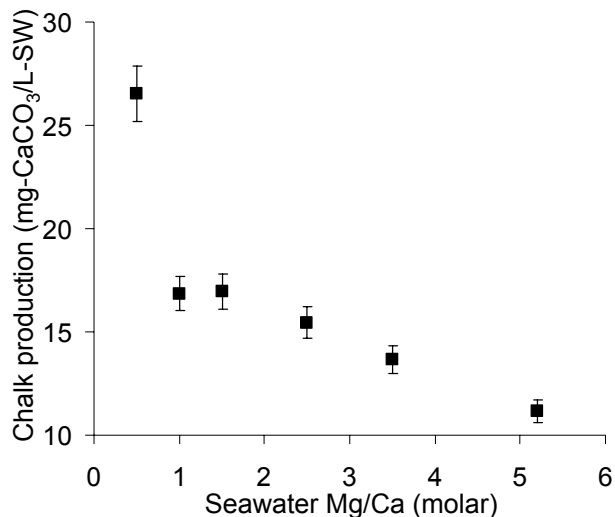
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**Fig. 14.** Chalk production by *Pleurochrysis carterae* after seven days of growth in the six experimental seawater treatments. Chalk production increases as seawater Mg/Ca declines into the calcite stability field. Low seawater Mg/Ca favors precipitation of the coccolithophores' calcite skeletal mineral and is believed to have characterized seawater in Cretaceous time (Fig. 1) – when chalk production by coccolithophores was at its apex. Vertical bars represent measurement error. From Stanley et al. (2005).

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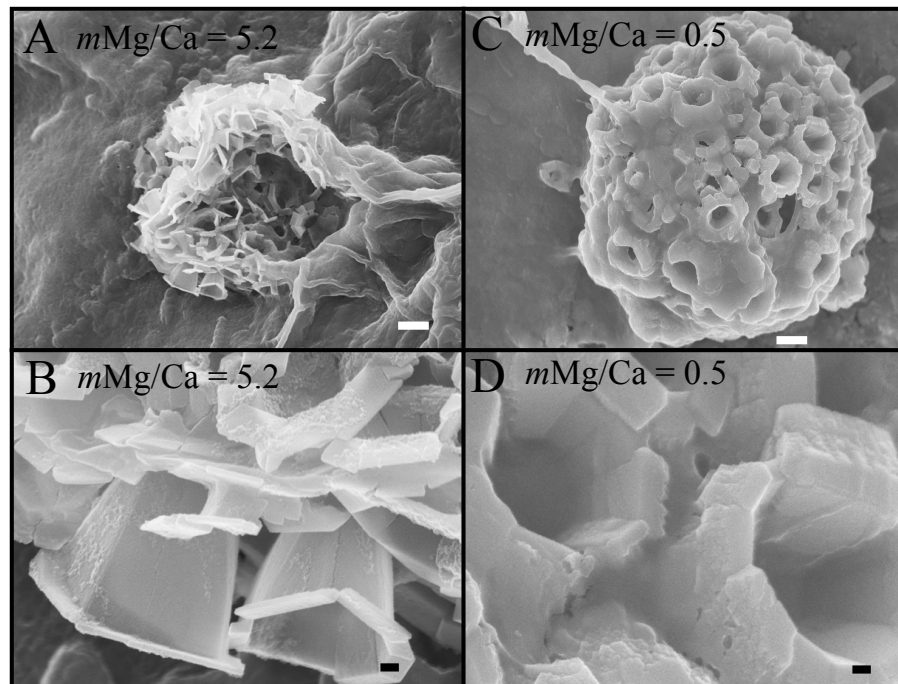
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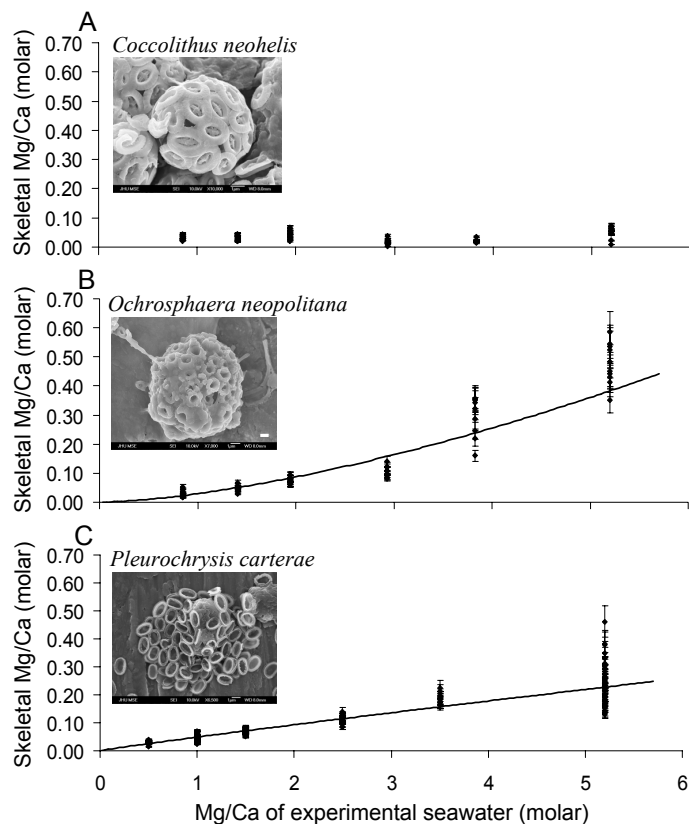
**Fig. 15.** Backscatter electron images of the coccolithophore *Ochrosphaera neopolitana* after growth in experimental modern ( $m\text{Mg}/\text{Ca}=5.2$  (**A**, **B**)) and Cretaceous ( $m\text{Mg}/\text{Ca}=0.5$  (**C**, **D**)) seawaters. Coccoliths precipitated in experimental Cretaceous seawater appear to be larger and more heavily calcified than those precipitated in the modern seawater. White bars are 1  $\mu\text{m}$ ; black bars are 100 nm. From Stanley et al. (2005).

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**Fig. 16.** Molar Mg/Ca ratio of calcite secreted by coccolithophore species *Coccolithus neohelis* (A), *Ochrosphaera neopolitana* (B), and *Pleurochrysis carterae* (C) as a function of the Mg/Ca ratio of the experimental seawater in which they were reared. Error bars represent standard error associated with microprobe precision. Fitted curves are power functions fit to the data using least squares regression. From Stanley et al. (2005).

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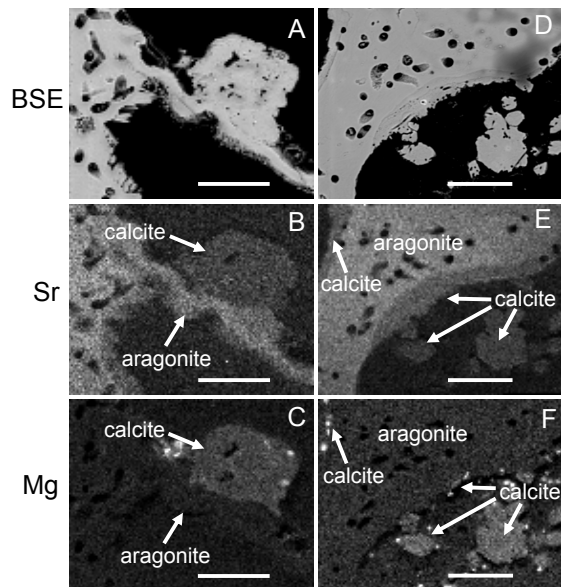
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**Fig. 17.** Backscatter electron images (**A, D**), Sr/Ca maps (**B, E**) and Mg/Ca maps (**C, F**) showing, respectively, skeletal microstructure, aragonite and calcite in two specimens of *Porites cylindrica* (**A–C, D–F**) reared for 60 d in experimental seawater that favors the abiotic precipitation of calcite over aragonite ( $mMg/Ca=1.0$ ). Light areas ( $mSr/Ca=0.011–0.016$ ) of the Sr/Ca maps (**B, E**) correspond to aragonite in the coral skeleton, while dark areas ( $mSr/Ca=0.001–0.005$ ) correspond to calcite. Light areas ( $mMg/Ca=0.03–0.04$ ) of the Mg/Ca maps (**C, F**) correspond to calcite in the coral skeleton, while dark areas ( $mMg/Ca=0.004–0.008$ ) correspond to aragonite. Aragonite typically incorporates about an order of magnitude more  $Sr^{2+}$  in its crystal lattice than does calcite, while calcite incorporates about one order of magnitude more  $Mg^{2+}$  in its crystal lattice than does aragonite. These characteristics make Sr/Ca and Mg/Ca reliable proxies for mapping the distribution of aragonite and calcite, respectively, within the coral skeletons. Scale bars are 100  $\mu m$ . From Ries et al. (2006).

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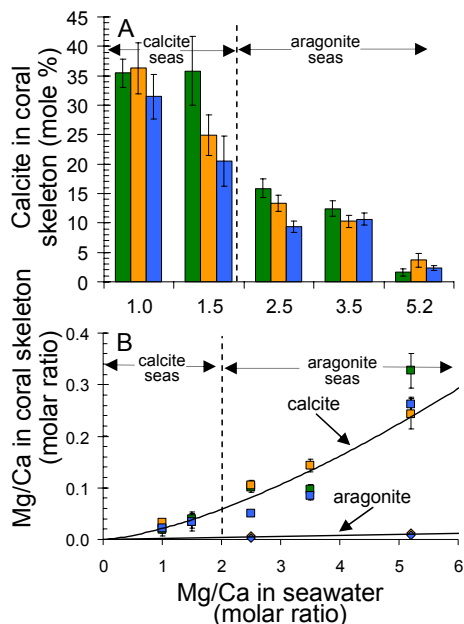
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**Fig. 18.** Mineralogy and geochemistry of *Acropora cervicornis*, *Montipora digitata*, and *Porites cylindrica* reared in experimental seawaters with  $m\text{Mg}/\text{Ca}$  ratios ranging from 1.0 to 5.2 (from Ries et al., 2006). **(A)** Molar percentage of calcite in coral skeletons versus  $m\text{Mg}/\text{Ca}$  ratio of experimental seawater. Green bars=*A. cervicornis*, orange bars=*M. digitata*, and blue bars=*P. cylindrica*. **(B)** Molar  $\text{Mg}/\text{Ca}$  ratio of calcitic (green squares=*A. cervicornis*, orange squares=*M. digitata*, and blue squares=*P. cylindrica*) and aragonitic (orange diamonds=*M. digitata*, blue diamonds=*P. cylindrica*) portions of coral skeleton. Solid black lines represent Mg fractionation curves for coral calcite ( $\text{Mg}/\text{Ca}_C = 0.02129 \text{Mg}/\text{Ca}_{\text{SW}}^{1.4628}$ ,  $R^2 = 0.9458$ ,  $n = 43$ ) and coral aragonite ( $\text{Mg}/\text{Ca}_C = 0.002007 \text{Mg}/\text{Ca}_{\text{SW}}$ ,  $R^2 = 0.7537$ ,  $n = 43$ ), calculated using least squares regression. Error bars correspond to instrument error plus specimen variation. Molar  $\text{Mg}/\text{Ca} < 2 =$  calcite seas;  $m\text{Mg}/\text{Ca} > 2 =$  aragonite+high Mg calcite seas.

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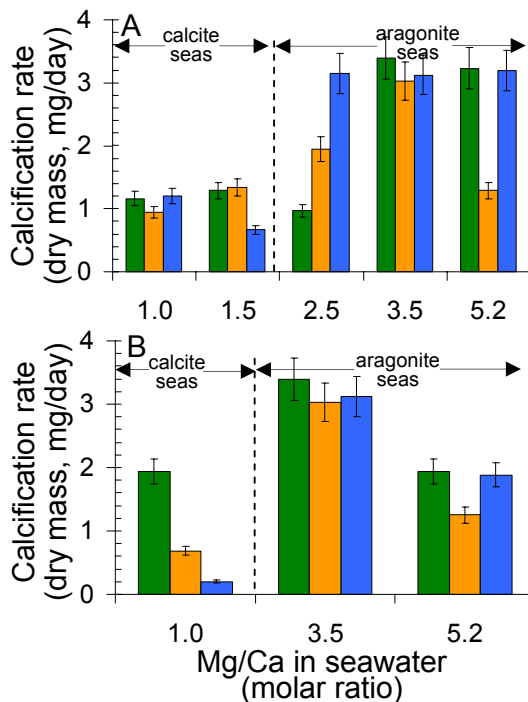
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**Fig. 19.** Calcification rates of *Acropora cervicornis* (green bars, n=60), *Montipora digitata* (orange bars, n=60), and *Porites cylindrica* (blue bars, n=60) reared in eight chemically unique experimental seawater treatments (from Ries et al., 2006). **(A)** Growth rates versus mMg/Ca ratio of experimental seawater. Ca<sup>2+</sup> concentration of seawater decreases as Mg/Ca increases. **(B)** Calcification rates versus mMg/Ca ratio of seawater treatments. Ca<sup>2+</sup> concentration held constant at 14.1 mM in all three treatments, to isolate the effect of Mg/Ca ratio on coral growth rates. Error bars correspond to instrument error plus specimen variation. Molar Mg/Ca < 2 = calcite seas; mMg/Ca > 2 = aragonite + high Mg calcite seas.

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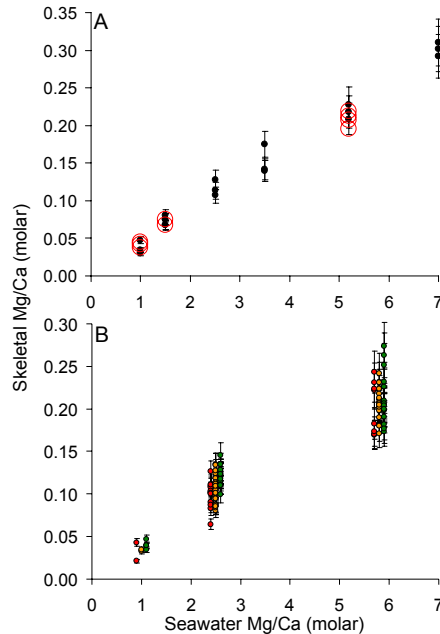
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**Fig. 20.** Mg fractionation data for **(A)** the encrusting coralline alga *Neogoniolithon* sp. and for **(B)** the three species of branching coralline algae *Amphiroa* A (closed red circles), *Amphiroa* B (closed orange circles), and *Amphiroa rigida* (closed green circles) reared in experimental seawater treatments formulated at *m*Mg/Ca ratios ranging from 1.0 to 7.0 (from Ries, 2006b; Stanley et al., 2002). Skeletal Mg/Ca ratios increase in lock-step with seawater Mg/Ca ratios. Large open red circles in **(A)** correspond to skeletal Mg/Ca ratios for specimens of *Neogoniolithon* sp. reared in a second set of experimental seawaters with *m*Mg/Ca ratios of 1.0, 1.5, and 5.2, that have reduced (1.0, 1.5) and elevated (5.2) absolute concentrations of Mg<sup>2+</sup> and Ca<sup>2+</sup>. Changes in the absolute Mg<sup>2+</sup> concentration of seawater had no significant ( $p < 0.05$ ) effect on algal skeletal Mg fractionation at fixed ambient Mg/Ca ratios.

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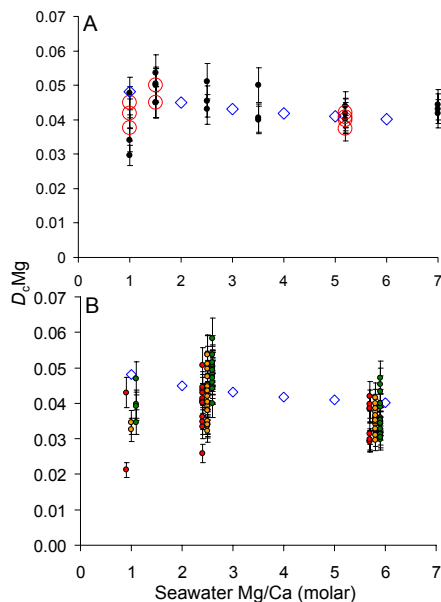
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**Fig. 21.** Mg fractionation coefficients ( $D_c\text{Mg}$ ) for **(A)** the encrusting coralline alga *Neogoniolithon* sp. and for **(B)** the three species of branching coralline algae *Amphiroa* A (closed red circles), *Amphiroa* B (closed orange circles), and *Amphiroa rigida* (closed green circles) reared in the experimental seawater treatments formulated at  $m\text{Mg}/\text{Ca}$  ratios ranging from 1.0 to 7.0 (from Ries, 2006b; Stanley et al., 2002).  $D_c\text{Mg}$  is calculated as  $\text{Mg}/\text{Ca}_c$  divided by  $\text{Mg}/\text{Ca}_{\text{sw}}$ . Large open red circles in (A) correspond to  $D_c\text{Mg}$  for the second set of experimental seawaters with  $m\text{Mg}/\text{Ca}$  ratios of 1.0, 1.5, and 5.2 that have reduced (1.0, 1.5) and elevated (5.2) absolute concentrations of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ , respectively. These results indicate that  $D_c\text{Mg}$  varies with  $\text{Mg}/\text{Ca}_{\text{sw}}$ . However, changes in the absolute  $\text{Mg}^{2+}$  concentration of seawater had no significant ( $p < 0.05$ ) effect on  $D_c\text{Mg}$  when  $\text{Mg}/\text{Ca}_{\text{sw}}$  was fixed with proportional elevations in  $[\text{Ca}^{2+}]$ . Large open blue diamonds correspond to the  $D_c\text{Mg}$  of abiotic calcite (Füchtbauer and Hardie, 1976).

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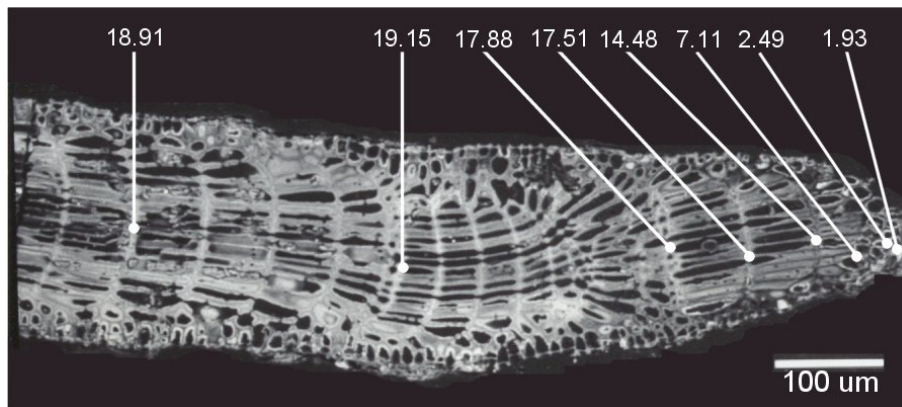
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**Fig. 22.** Backscatter electron image of a longitudinal section through the tip of the branching coralline alga *Amphiroa* sp. reared in seawater with the estimated Late Cretaceous  $m\text{Mg}/\text{Ca}$  ratio of 1.0. Numbers are mole percentages of magnesium in substitution for calcium in cell wall calcite. Measurements are at junctures of four cells along cell rows, one of which is added daily. Percentages in the 17.51 to 19.15 range are for calcification in modern seawater. During 4 d of growth in the Late Cretaceous experimental seawater, the percentage of Mg progressively declined, ultimately reaching 1.93 (low Mg calcite; from Stanley et al., 2002).

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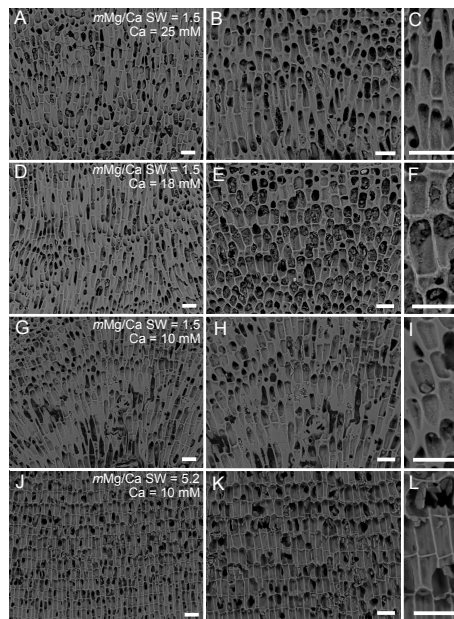
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**Fig. 23.** Backscatter electron images of specimens of the encrusting coralline alga *Neogoniolithon* sp. reared in experimental seawaters with  $mMg/Ca$  ratios and absolute  $Ca^{2+}$  concentrations (mM), respectively, of 1.5 and 25 (**A–C**), 1.5 and 18 (**D–F**), 1.5 and 10 (**G–I**), and 5.2 and 10 (equivalent to modern seawater, **J–L**). Specimens reared in the low  $mMg/Ca$  seawaters (1.5, **A–I**), which favor the algae’s inherently calcitic skeletal mineral, produced an apparently more heavily calcified and less organized skeleton than did specimens reared in the modern, high  $Mg/Ca$  seawater, which naturally favors the precipitation of aragonite. Changes in the absolute concentration of  $Ca^{2+}$ , for specimens reared in experimental seawaters with  $mMg/Ca$  ratios fixed at 1.5 (**A–I**), appear to have little effect on skeletal thickness and organization, suggesting that, for the range of values evaluated in this study, the ambient  $Mg/Ca$  ratio is more important than the  $CaCO_3$  saturation state of seawater in influencing rates of algal calcification. Scale bar is 20  $\mu m$ . From Ries (2006b).

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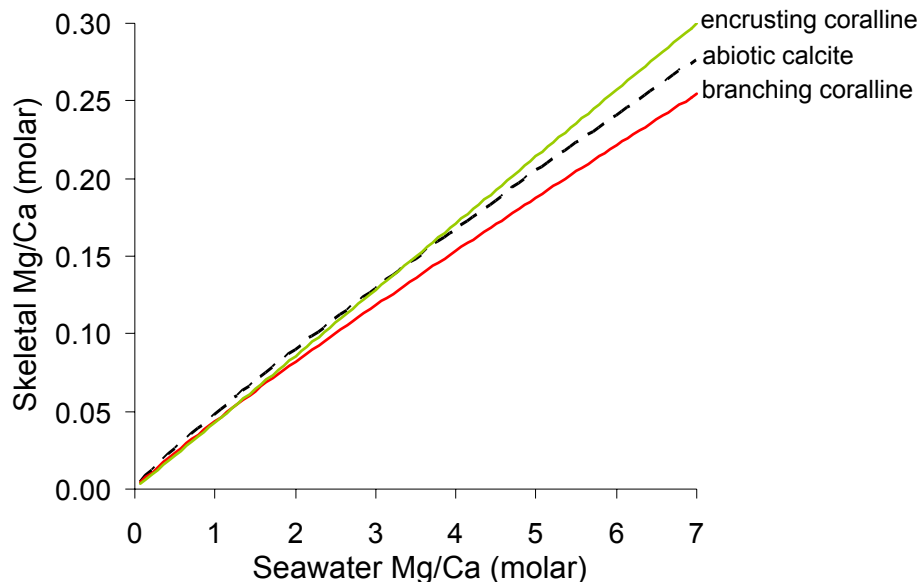
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**Fig. 24.** Experimentally derived Mg fractionation curves for the encrusting coralline alga *Neogoniolithon* sp. (solid green curve;  $\text{Mg}/\text{Ca}_C = 0.0421 \text{Mg}/\text{Ca}_{\text{SW}}^{1.01}$ ), for the three species of branching coralline algae *Amphiroa* A, *Amphiroa* B, and *Amphiroa rigida* (averaged; solid red curve;  $\text{Mg}/\text{Ca}_C = 0.0582 \text{Mg}/\text{Ca}_{\text{SW}}^{0.904}$ ), and for abiotically precipitated calcite (dashed black curve;  $\text{Mg}/\text{Ca}_C = 0.0482 \text{Mg}/\text{Ca}_{\text{SW}}^{0.898}$ ; Füchtbauer and Hardie, 1976). This reveals that Mg fractionation within coralline algae generally mimics that of abiotic calcification. Mg fractionation curves were calculated using least squares regressions. From Ries (2006b).

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Effects of secular variation in seawater Mg/Ca on marine biocalcification

J. B. Ries

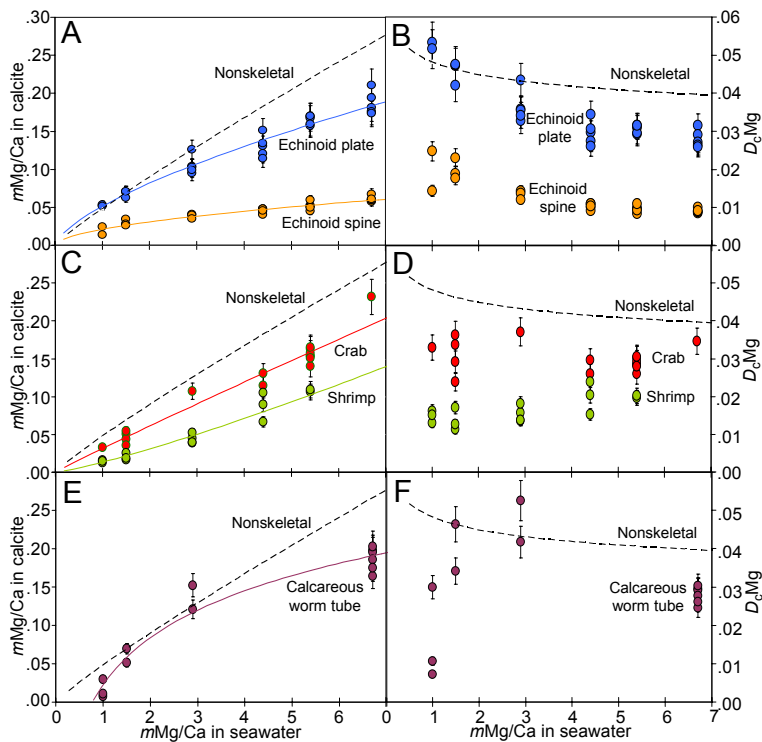


Fig. 25.

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**Fig. 25.** Mg fractionation data for four calcite-secreting marine animals. **(A)** Mg fractionation curves for echinoid spines (*Eucidaris tribuloides*, closed orange circles,  $\text{Mg}/\text{Ca}_C = 0.0213 \text{Mg}/\text{Ca}_{\text{SW}}^{0.538}$ ;  $R^2 = 0.873$ ,  $n = 23$ ) and coronal plates (*Eucidaris tribuloides*, closed blue circles,  $\text{Mg}/\text{Ca}_C = 0.0516 \text{Mg}/\text{Ca}_{\text{SW}}^{0.668}$ ;  $R^2 = 0.959$ ,  $n = 23$ ). **(B)** Mg fractionation coefficients for echinoid spines (closed orange circles) and coronal plates (closed blue circles). **(C)** Mg fractionation curves for crabs (*Perchon gibbesi*, closed red circles,  $\text{Mg}/\text{Ca}_C = 0.0317 \text{Mg}/\text{Ca}_{\text{SW}}^{0.956}$ ,  $R^2 = 0.964$ ,  $n = 16$ ) and shrimps (*Palaemonetes pugio*, closed green circles,  $\text{Mg}/\text{Ca}_C = 0.0134 \text{Mg}/\text{Ca}_{\text{SW}}^{1.21}$ ,  $R^2 = 0.955$ ,  $n = 15$ ). **(D)** Mg fractionation coefficients for crabs (closed red circles) and shrimps (closed green circles). **(E)** Mg fractionation curve for calcareous serpulid worm tubes (*Hydroides crucigera*, closed purple circles,  $\text{Mg}/\text{Ca}_C = 0.0883 \ln(\text{Mg}/\text{Ca}_{\text{SW}}) + 0.0227$ ,  $R^2 = 0.956$ ,  $n = 13$ ). **(F)** Mg fractionation coefficients for calcareous serpulid worm tubes (closed purple circles). For each of the animals investigated, skeletal  $\text{Mg}/\text{Ca}_C$  increased with  $\text{Mg}/\text{Ca}_{\text{SW}}$ . However,  $D_C \text{Mg}$  was not fixed, as it also varied (non-linearly) with  $\text{Mg}/\text{Ca}_{\text{SW}}$ . Dashed black lines are Mg fractionation curves and coefficients for nonskeletal calcite (Füchtbauer and Hardie, 1976).  $D_C \text{Mg}$  is Mg fractionation coefficient equal to  $\text{Mg}/\text{Ca}_C$  divided by its corresponding  $\text{Mg}/\text{Ca}_{\text{SW}}$ . Mg fractionation curves are fit to data using least squares regression. Vertical bars represent uncertainty due to analytical error and specimen variation.

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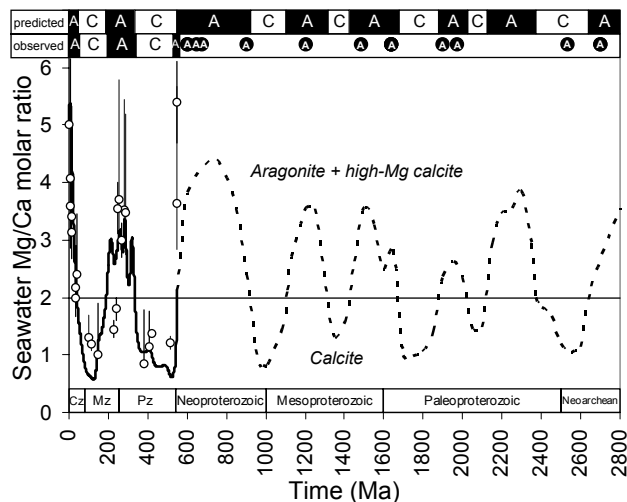
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**Fig. 26.** Secular variation in  $\text{Mg}/\text{Ca}_{\text{sw}}$  and the original polymorph mineralogy of nonskeletal  $\text{CaCO}_3$  precipitates, including ooids, seafloor precipitates, and marine cements, since Late Archean time (from Ries et al., 2008). Phanerozoic (solid curve; Hardie, 1996; Demicco et al., 2005) and Precambrian (dashed curve; Hardie, 2003) seawater  $\text{Mg}/\text{Ca}$  is calculated from hydrothermal brine-river water mixing models driven by rates of ocean crust production (Gaffin, 1987) and granite pluton data (Engel and Engel, 1970), respectively. Open circles correspond to  $m\text{Mg}/\text{Ca}_{\text{sw}}$  estimated from fluid inclusions in primary marine halites (Lowenstein et al., 2001, 2003, 2005; Brennan and Lowenstein, 2002; Brennan, 2002; Horita et al., 2002; Brennan et al., 2004; Timofeeff et al., 2006). Horizontal line divides the calcite ( $m\text{Mg}/\text{Ca}_{\text{sw}} < 2$ ) and aragonite-high Mg calcite ( $m\text{Mg}/\text{Ca}_{\text{sw}} > 2$ ) nucleation fields in seawater at  $25^\circ\text{C}$  (Leitmeier, 1910, 1915; Lippman, 1960; Müller et al., 1972; Berner, 1975; Given and Wilkinson, 1985; Stanley and Hardie, 1999). Temporal distribution of predicted (Hardie, 1996, 2003) and observed (Sandberg, 1983; Hardie, 2003) nonskeletal calcite (“C”) and aragonite (“A”) precipitates are plotted along top of figure. Closed black circles circumscribing “A” correspond to inferred aragonitic seafloor precipitates observed in Precambrian deposits (cf. Hardie, 2003).

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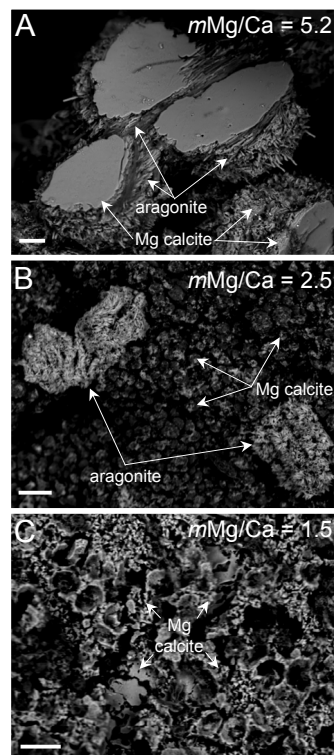
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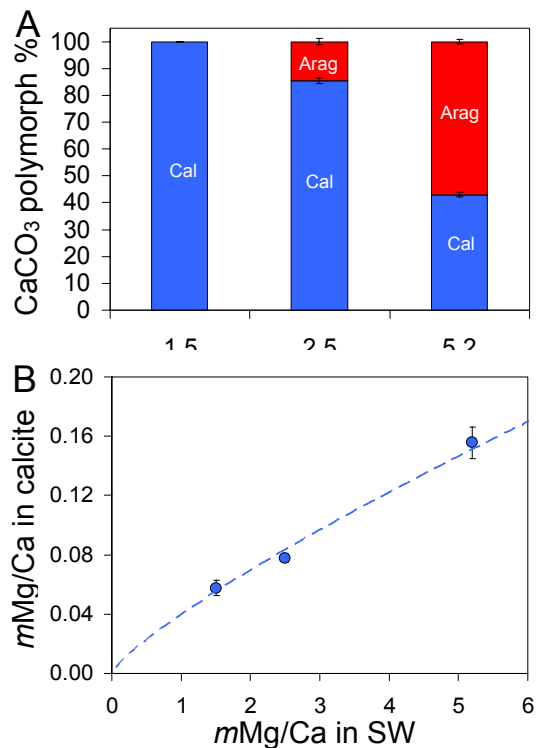
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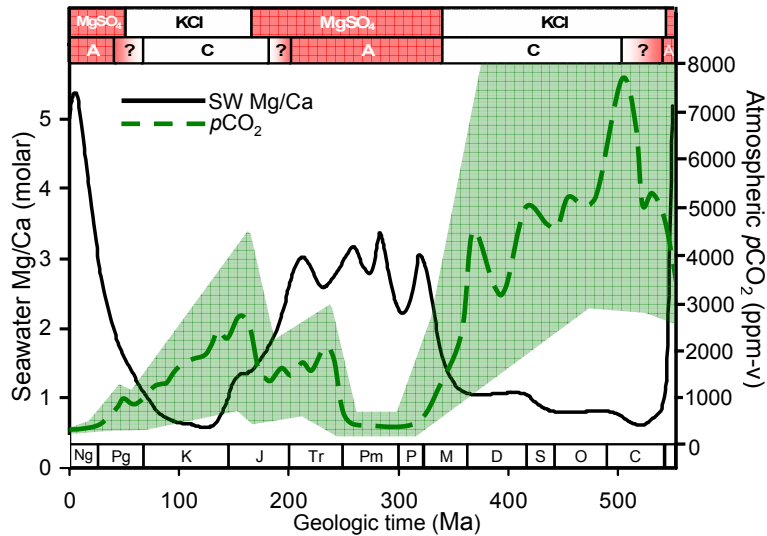


**Fig. 27.** Backscattered electron images showing distribution of aragonite (large, acicular crystals) and Mg calcite (small, micritic crystals) precipitates within biofilms grown in the three experimental seawaters. **(A)**  $m\text{Mg}/\text{Ca}_{\text{sw}}=5.2$ ; 43 mole-% calcite ( $m\text{Mg}/\text{Ca}_{\text{c}}=0.156$ ); 57 mole-% aragonite. **(B)**  $m\text{Mg}/\text{Ca}_{\text{sw}}=2.5$ ; 86 mole-% calcite ( $m\text{Mg}/\text{Ca}_{\text{c}}=0.078$ ); 14 mole-% aragonite. **(C)**  $m\text{Mg}/\text{Ca}_{\text{sw}}=1.5$ ; 100 mole-% calcite ( $m\text{Mg}/\text{Ca}_{\text{c}}=0.058$ ). Scale bars are 20  $\mu\text{m}$ . Relative abundance of  $\text{CaCO}_3$  polymorphs was determined by powder X-ray diffraction. From Ries et al. (2008).

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**Fig. 28.** Mineralogy and geochemistry of CaCO<sub>3</sub> precipitated within biofilms grown in the three experimental seawaters (Ries et al., 2008). **(A)** Relative abundance (mole-%) of calcite (blue) and aragonite (red) within biofilm CaCO<sub>3</sub>, determined by powder X-ray diffraction. **(B)** mMg/Ca of calcite precipitated within biofilms, determined by powder X-ray diffraction and energy dispersive spectrometry. Mg fractionation algorithm (dashed curve) calculated using least squares regression is defined as  $\text{Mg}/\text{Ca}_C = 0.0397 \text{Mg}/\text{Ca}_{\text{SW}}^{0.811}$  ( $R^2 = 0.99$ ). Error bars represent uncertainty due to instrument error and specimen variation. From Ries et al. (2008).



**Fig. 29.** Models of seawater Mg/Ca (solid black curve; Hardie, 1996; DeMicco et al., 2005) and atmospheric  $p\text{CO}_2$  (dashed green curve—green shading represents model uncertainty; Berner and Kothavala, 2001) throughout Phanerozoic time. These two models generally vary inversely with one another because they are both thought to be largely driven by the global rate of ocean crust production. Thus, the effect of tectonically-induced ocean acidification (via volcanic outgassing of  $\text{CO}_2$ ) on biocalcification throughout the geologic past may have been mitigated by corresponding elevations in  $[\text{Ca}^{2+}]$ , which would have (1) favored the precipitation of the less soluble low Mg calcite polymorph (because of low seawater Mg/Ca) when seawater  $\text{CaCO}_3$  saturation state was low and (2) partially offset the reduction in  $\text{CaCO}_3$  saturation state that was associated with the  $\text{CO}_2$ -induced reduction in  $[\text{CO}_3^{2-}]$ . Because the modern anthropogenic ocean acidification event is not tectonically driven, there should be no commensurate elevation in seawater  $[\text{Ca}^{2+}]$  to mitigate the effect of the  $\text{CO}_2$ -induced reduction in  $[\text{CO}_3^{2-}]$  on the calcium carbonate saturation state of seawater.

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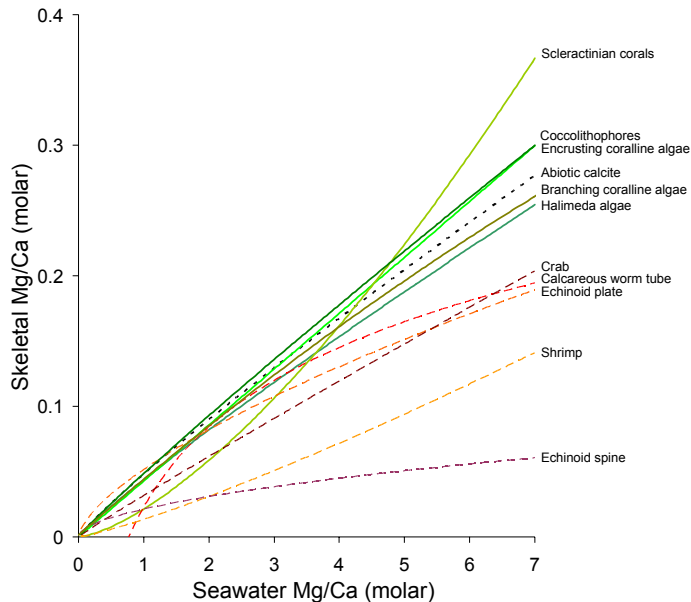
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**Fig. 30.** The relationship between skeletal Mg/Ca and seawater Mg/Ca for organisms that secrete at least part of their skeleton as calcite. Solid lines are Mg fractionation curves for photosynthetic organisms: the two coccolithophores *Pleurochrysis carterae* and *Ochrosphaera neopolitana* (Stanley et al., 2005); the encrusting coralline red algae *Neogoniolithon* sp. (Ries, 2006b); the scleractinian corals *Porites cylindrica*, *Montipora digitata*, and *Acropora cervicornis* (Ries et al., 2006); three species of branching coralline algae of the genus *Amphiroa* (Stanley et al., 2002); and the bryopsidalean alga *Halimeda incrassata*. Dotted line is Mg fractionation curve for abiotic calcite (Füchtbauer and Hardie, 1976). Dashed lines are Mg fractionation curves for non-photosynthetic organisms: the echinoid *Eucidaris tribuloides*; the crab *Perchonia gibbesi*; the shrimp *Palaemonetes pugio*; and the calcareous serpulid worm *Hydroides crucigera* (Ries, 2004). Photosynthetic organisms appear to be more influenced by ambient Mg/Ca than non-photosynthetic ones. From Ries (2006b).

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