

Mg fractionation in crustose coralline algae: Geochemical, biological, and sedimentological implications of secular variation in the Mg/Ca ratio of seawater

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Abstract

The Mg/Ca ratio of seawater has varied significantly throughout the Phanerozoic Eon, primarily as a function of the rate of ocean crust production. Specimens of the crustose coralline alga *Neogoniolithon* sp. were grown in artificial seawaters encompassing the range of Mg/Ca ratios shown to have existed throughout the Phanerozoic. Significantly, the coralline algae's skeletal Mg/Ca ratio varied in lockstep with the Mg/Ca ratio of the artificial seawater. Specimens grown in seawater treatments formulated with identical Mg/Ca ratios but differing absolute concentrations of Mg and Ca exhibited no significant differences in skeletal Mg/Ca ratios, thereby emphasizing the importance of the ambient Mg/Ca ratio, and not the absolute concentration of Mg, in determining the Mg/Ca ratio of coralline algal calcite. Specimens grown in seawater of the lowest molar Mg/Ca ratio ($m\text{Mg}/\text{Ca} = 1.0$) actually changed their skeletal mineralogy from high-Mg (skeletal $m\text{Mg}/\text{Ca} > 0.04$) to low-Mg calcite (skeletal $m\text{Mg}/\text{Ca} < 0.04$), suggesting that ancient calcitic red algae, which exhibit morphologies and modes of calcification comparable to *Neogoniolithon* sp., would have produced low-Mg calcite from the middle Cambrian to middle Mississippian and during the middle to Late Cretaceous, when oceanic $m\text{Mg}/\text{Ca}$ approached unity. By influencing the original Mg content of carbonate facies in which these algae have been ubiquitous, this condition has significant implications for the geochemistry and diagenesis of algal limestones throughout most of the Phanerozoic. The crustose coralline algae's precipitation of high-Mg calcite from seawater that favors the abiotic precipitation of aragonite indicates that these algae dictate the precipitation of the calcitic polymorph of CaCO_3 . However, the algae's nearly abiotic pattern of Mg fractionation in their skeletal calcite suggests that their biomineralogical control is limited to polymorph specification and is generally ineffectual in the regulation of skeletal Mg incorporation. Therefore, the Mg/Ca ratio of well-preserved fossils of crustose coralline algae, when corrected for the effect of seawater temperature, may be an archive of oceanic Mg/Ca throughout the Phanerozoic. Magnesium fractionation algorithms that model algal skeletal Mg/Ca as a function of seawater Mg/Ca and temperature are presented herein. The results of this study support the empirical fossil evidence that secular variation of oceanic Mg/Ca has caused the mineralogy and skeletal chemistry of many calcifying marine organisms to change significantly over geologic time.

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1. Introduction

Secular variation in the Mg/Ca ratio of seawater (Fig. 1) is believed to be responsible for pandemic changes in the polymorph mineralogy of biotic and abiotic carbonates throughout the Phanerozoic (Wilkinson, 1979; Sandberg,

1983; Holland, 1984; Wilkinson and Given, 1986; Railsback, 1993; Hardie, 1996; Stanley and Hardie, 1998, 1999; Montañez, 2002). This variation in seawater chemistry would have subjected the geologically important crustose coralline algae to ambient molar Mg/Ca ($m\text{Mg}/\text{Ca}$) ratios oscillating between 1.0 and 5.2 (the modern value). Stanley and Hardie (1998, 1999) assert that modern coralline red algae secrete a high-Mg calcite skeleton ($m\text{Mg}/\text{Ca} = 0.18$) because of the elevated Mg/Ca ratio of modern

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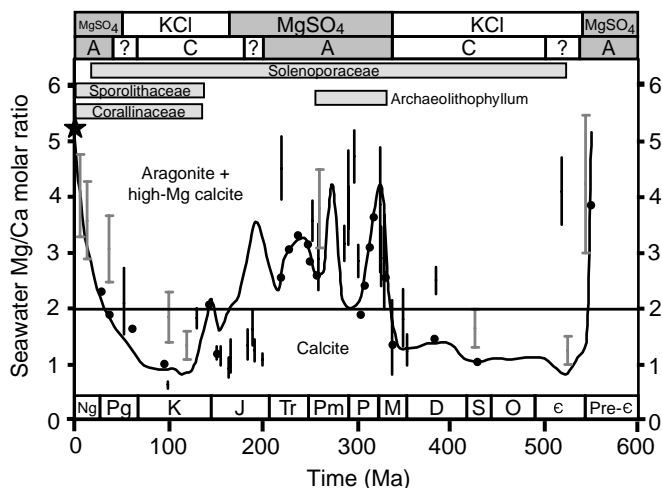


Fig. 1. Secular variation in the Mg/Ca ratio of seawater and distribution of the calcifying Rhodophyta (Wray, 1977; Aguirre et al., 2000) throughout the Phanerozoic. Curve is the $m\text{Mg}/\text{Ca}$ ratio of seawater calculated from a brine-magma-river water flux model (Hardie, 1996). Black vertical bars are Mg/Ca ranges calculated from fossil echinoderm Mg/Ca and paleotemperature data (Dickson, 2002, 2004; Ries, 2004a). Bars include error associated with the echinoderm Mg fractionation algorithm used in the calculation. Gray I-bars are Mg/Ca ranges estimated from fluid inclusions in marine halite (Lowenstein et al., 2001, 2003). Solid black circles are Mg/Ca ratios estimated from Br in basal marine halite (Siemann, 2003). Star represents modern seawater chemistry ($m\text{Mg}/\text{Ca} = 5.2$). The distribution of the calcifying Rhodophyta is represented by horizontal bars (Wray, 1977; Stanley and Hardie, 1998, 1999; Aguirre et al., 2000). Horizontal line is the division between 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. Temporal distributions of non-skeletal aragonite and calcite (Sandberg, 1983) and KCl and MgSO_4 marine evaporites (Hardie, 1996) are plotted along top of figure. A—marine aragonite deposition; C—marine calcite deposition.

seawater. If their assertion is correct, the Mg content of these important reef-cementing, sediment-producing algae should have varied concomitantly with oceanic Mg/Ca throughout the Phanerozoic.

Laboratory experiments have shown that the Mg/Ca ratio of abiotic calcite precipitated from artificial seawater 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). Experiments on organisms have also shown that the amount of Mg incorporated in the calcitic skeletons of articulate (non-encrusting) coralline algae of the genus *Amphiroa* (Stanley et al., 2002), the sea urchin *Eucidaris tribuloides*, the crab *Perchon gibbesi*, the shrimp *Palaeomonetes pugio*, the calcareous serpulid worm *Hydroides crucigera* (Ries, 2004a), the coccolithophores *Ochrosphaera neopolitana*, and *Pleurochrysis carterae* (Stanley et al., 2005), the calcitic portions of the scleractinian corals *Porites cylindrica*, *Montipora digitata*, and *Acropora cervicornis* (Ries, 2004b), the blue mussel *Mytilus edulis* (Lorens and Bender, 1980), and the euryhaline ostracode *Cyprideis australiensis* (Deckker et al., 1999), varies as a function of the Mg/Ca ratio of the seawater in which these organisms are grown.

The purpose of this study was to grow modern crustose coralline algae of the genus *Neogoniolithon* in artificial seawaters formulated at Mg/Ca ratios that have existed since their origin in the Early Cretaceous (Wray, 1977; Aguirre et al., 2000), to determine whether these geologically important reef cementers and sediment producers are also mineralogically influenced by the Mg/Ca ratio of their ambient seawater. The results have far-reaching implications in the fields of carbonate and marine geochemistry, biomineralization, paleobiology, paleoceanography, and carbonate sedimentology.

2. Background

2.1. Secular variation in the Mg/Ca ratio of seawater

Abiotic calcium carbonate precipitates in the Earth's oceans (Fig. 1) are believed to have alternated between the low-Mg calcite and the aragonite + high-Mg calcite polymorphs throughout the Phanerozoic (Sandberg, 1983). These so-called calcite and aragonite seas have occurred in general synchronicity with intervals of KCl and MgSO_4 marine evaporites, respectively. Laboratory experiments have shown that such synchronicity can be caused by variations in the molality of Ca versus Mg and SO_4 in the precipitating seawater solution. Molar Mg/Ca ratios < 2 and concomitantly elevated Ca concentrations (versus SO_4 at the point of gypsum saturation) yield, respectively, low-Mg calcite precipitates and KCl evaporites, while $m\text{Mg}/\text{Ca}$ ratios > 2 and concomitantly reduced Ca concentrations yield, respectively, aragonite + high-Mg calcite precipitates and MgSO_4 evaporites (Leitmeier, 1910, 1915; Lippman, 1960; Müller et al., 1972; Folk, 1974; Füchtbauer and Hardie, 1976, 1980). These experiments suggest that secular variation in the Mg/Ca ratio of seawater has resulted in the observed distribution of calcite and aragonite seas throughout the Phanerozoic. Furthermore, ancient Mg/Ca ratios derived from fluid inclusions (Lowenstein et al., 2001, 2003) and Br (Siemann, 2003) in marine halite, and the Mg/Ca ratios of fossil echinoderms (Dickson, 2002, 2004), reveal a history of oceanic Mg/Ca that is consistent with the observed distribution of calcite and aragonite seas (Fig. 1).

Secular variation in the Mg/Ca ratio of seawater is likely driven primarily by the global rate of ocean crust production (Wilkinson and Given, 1986; Hardie, 1996). As mid-ocean ridge and large igneous province basalts interact with marine brines, they are converted to greenstone, thereby releasing Ca^{2+} and K^+ to the seawater and removing Mg^{2+} and SO_4^{2-} from it. High rates of ocean crust production accelerate this ion exchange and result in relatively low Mg/Ca ratios throughout the Earth's oceans, as occurred during the tectonically active mid-Late Cretaceous period. Oceanic Mg/Ca ratios and SO_4^{2-} concentrations calculated from this model using established rates of ocean crust production, predict a pattern of aragonite and calcite seas and

KCl and MgSO₄ evaporites consistent with that observed in the geological record (Hardie, 1996).

2.2. Geological history and importance of crustose coralline algae

Calcifying red algae of the phylum Rhodophyta have been important contributors to limestones throughout the Phanerozoic (Wray, 1977; Aguirre et al., 2000). The calcifying families of this phylum are the Solenoporaceae (Cambrian–Neogene), Sporolithaceae (Early Cretaceous–modern), and Corallinaceae (Early Cretaceous–modern; Fig. 1). The Corallinaceae family can be further divided into the geniculate (articulate) forms, which comprise the Amphiroideae, Corallinoideae, and Metagoniolithoideae subfamilies, and the non-geniculate (non-articulate or crustose) forms, which comprise the Austrolithoideae, Melobesioideae, Choreonematoideae, Lithophylloideae, and Mastophoroideae subfamilies (Aguirre et al., 2000). The latter subfamily contains the *Neogoniolithon* (the subject of the present study) and *Porolithon* genera, which are important reef builders and sediment producers in modern tropical and subtropical seas throughout the world (Wray, 1977; Aguirre et al., 2000).

The Corallinaceae are globally distributed in modern seas, ranging from the tropics to the poles and occurring from the intertidal zone to depths of up to 250 m (Adey and Macintyre, 1973). *Neogoniolithon* sp., however, is restricted to subtropical-tropical waters of normal salinity and depths of less than 10 m. The encrusting Corallinaceae vary from producing thin crusts of only a single cell in thickness to building massive nodules up to 10 cm in diameter.

The heavily calcified tissue of the Corallinaceae lends them to extensive representation in the geological record (Aguirre et al., 2000). These algae are some of the most common and widespread skeletal constituents in Cretaceous and Cenozoic marine carbonate facies (Wray, 1977; Aguirre et al., 2000). Their contribution to reef limestones since the Early Cretaceous, while probably not comparable (Macintyre, 1997) to their abundance on the surfaces of modern, wave-exposed reefs [where they have been documented to cover up to 40% of the reef's surface (Littler, 1973; Macintyre, 1997) and produce up to 1.5–10.3 kg CaCO₃ m⁻² y⁻¹ (Chisholm, 2003)], is still believed to have been significant (Alexandersson, 1977; James et al., 1988; Berner, 1990; Aguirre et al., 2000). The abundance of fossil Corallinaceae in post-Jurassic reef and sediment limestones suggests significant geological implications for the results of this experimental study.

This study may also be applicable to the ancient Solenoporaceae and *Archaeolithophyllum* algae that have been invoked, somewhat controversially (Aguirre et al., 2000), as potential ancestors of the Corallinaceae because of their similar morphologies, environmental distributions, and calcitic mineralogies (Wray, 1977). The Solenoporaceae were major contributors to shelf, reefal, and bioherm car-

bonates throughout the Paleozoic and Mesozoic, albeit probably not to the extent of modern Corallinaceae (Johnson, 1961). The *Archaeolithophyllum*, an encrusting alga of disputed affinity, is one of the dominant skeletal constituents of the thick, widespread carbonate buildups of the Late Mississippian to Late Permian (Wray, 1964). Regardless of the phylogenetic relationship between the modern crustose coralline algae and the geologically important Solenoporaceae and *Archaeolithophyllum*, their similar morphologies, modes of calcification, and mineralogies suggest that the findings of this study (concerning Mg incorporation in crustose coralline algae) can possibly be extrapolated back for most calcitic encrusting algae, and the limestones they helped form, throughout the Phanerozoic.

3. Methods

3.1. Seawater preparation

Specimens of *Neogoniolithon* sp. algae were grown in artificial seawaters which were identical (Bidwell and Spotte, 1985) except for their *m*Mg/Ca ratios, which were formulated at 1.0, 1.5, 2.5, 3.5, 5.2, and 7.0, thereby encompassing the range of values shown to have existed since the algae's origin (1.0–5.2; Fig. 1; Hardie, 1996). Mg and Ca concentrations remained within 5% of their initial values throughout the duration of the experiment. To differentiate between the effects of Mg/Ca ratio and absolute Mg concentration on skeletal Mg-fractionation, three additional artificial seawaters were formulated at *m*Mg/Ca ratios of 1.0 and 1.5, with reduced absolute concentrations of Mg and Ca, and 5.2, with elevated absolute concentrations of Mg and Ca. For *m*Mg/Ca = 1.0, [Mg] was reduced from 32 to 18 mM; for *m*Mg/Ca = 1.5, [Mg] was reduced from 38 to 27 mM; for *m*Mg/Ca = 5.2, [Mg] was elevated from 53 to 94 mM. The sums of the molar concentrations of Mg and Ca were held constant in the first set of artificial seawaters, thereby fixing the salinity at modern values of 35 ppt. In the second set of artificial seawaters, for which the sum of the molar Mg and Ca concentrations could not be fixed, the salinity was maintained at 35 ppt by adjusting the concentration of Na.

3.2. Algal culture

Five specimens of *Neogoniolithon* sp. were grown for 100 days in each of the nine aquaria. Water was maintained at 25 ± 1 °C with a single 50 watt heater and continuously filtered with Millennium 2000 Wet-Dry Multi-filters (rate of filtration = 600 L/h). Ten hours per day of identical irradiation was provided by twin *Power Compact* lights which emit wavelengths commensurate with the mid-day and dawn/twilight spectra. The seawater was fertilized with 20.0 mg/L NaNO₃, 1.3 mg/L NaH₂PO₄·H₂O, and 0.025 mL/L EDTA, all within the normal range for near-shore tropical marine waters (Spotte, 1979). The algae were

acclimated to the artificial seawater treatments in stages, over a 30-day period, to minimize any shock they may experience when exposed to the unfamiliar Mg/Ca ratios.

3.3. Sample preparation, chemical analysis, and micro-imaging

Comparison of the algae after 100 days of growth with photographs taken of them at the beginning of the experiment identified growth that occurred exclusively in the experimental seawaters. Samples from the perimeter of these new growth sections were obtained from three specimens in each of the seawater treatments, briefly rinsed in distilled water, and allowed to dry overnight. The material was then moistened with several drops of ethyl alcohol and ground to a fine paste with a mortar and pestle. Enough alcohol was then added to the paste to suspend the algal material. Ten drops of the algae–alcohol suspension was eye-dropped onto a glass slide and allowed to dry. A powder X-ray diffraction (XRD) pattern was generated from the algal mineral residue on the slide. The Mg/Ca ratio of the algal calcite was calculated from the 2θ -value (d-spacing) of the primary calcite peak (Milliman, 1974).

Additional specimen material was embedded in *Epotek* epoxy resin, sectioned parallel to the growth axis, and photomicrographed with back-scatter electron imaging in a JEOL 8600 Superprobe electron microprobe. Electron dispersive spectrometry (EDS, beam current = 0.02 μ A, accelerating potential = 15 kV, counting time = 30 s, beam diameter = 1–2 μ m) was employed to perform spot analyses of the coralline algae's skeletal Mg/Ca ratio, to ensure the accuracy of the powder XRD technique. Average skeletal Mg/Ca ratios obtained using EDS spot analysis were within 4% of average Mg/Ca ratios obtained using powder XRD.

3.4. Quantification of Mg fractionation

The algae's skeletal Mg/Ca ratios, Mg/Ca_C , were plotted against the seawater Mg/Ca ratios, Mg/Ca_{SW} (Fig. 2). A Mg-fractionation curve was fitted to the data using a least squares regression.

Mg fractionation coefficients, D_cMg , were calculated for the algae by dividing Mg/Ca_C by Mg/Ca_{SW} (Morse and Bender, 1990):

$$D_cMg = \frac{Mg/Ca_C}{Mg/Ca_{SW}}$$

D_cMg values were plotted against ambient Mg/Ca_{SW} ratios (Fig. 3).

4. Results

The *Neogoniolithon* sp. specimens precipitated exclusively the calcite polymorph of $CaCO_3$, in each of the artificial seawater treatments. However, the algae incorporated less Mg into their skeletal calcite as the Mg/Ca ratio of the artificial

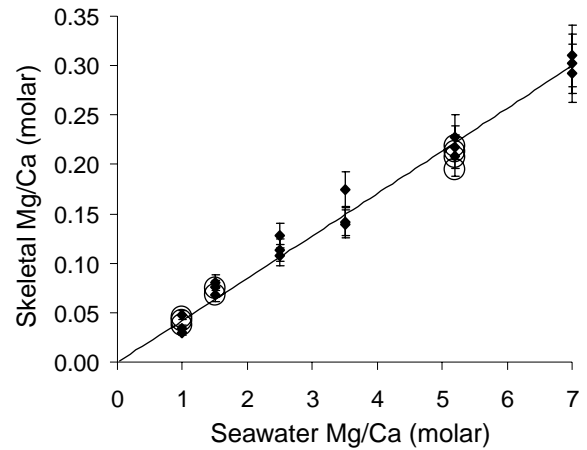


Fig. 2. Mg-fractionation curve for specimens of the crustose coralline alga *Neogoniolithon* sp. grown in artificial seawater treatments formulated at mMg/Ca ratios ranging from 1.0 to 7.0. Skeletal Mg/Ca ratios increase in lockstep with seawater Mg/Ca ratios. The Mg fractionation curve is the least squares regression through the data ($y = 0.0421x^{1.01}$, $R^2 = 0.97$). Large open circles correspond to skeletal Mg/Ca ratios for the second set of artificial seawaters with mMg/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 and Ca. Changes in the absolute Mg concentration of seawater had no significant ($p < 0.05$) effect on algal skeletal Mg fractionation at fixed ambient Mg/Ca ratios.

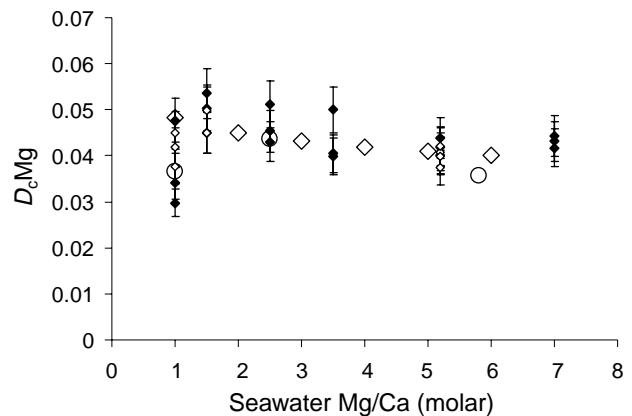


Fig. 3. Mg fractionation coefficients (D_cMg) for specimens of the crustose coralline alga *Neogoniolithon* sp. grown in the artificial seawater treatments formulated at mMg/Ca ratios ranging from 1.0 to 7.0 (small solid diamonds). D_cMg is calculated as Mg/Ca_C divided by Mg/Ca_{SW} . Small open diamonds correspond to D_cMg for the second set of artificial seawaters with mMg/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 and Ca. These results reveal that changes in the absolute Mg concentration of seawater had no significant ($p < 0.05$) effect on algal skeletal Mg fractionation at fixed ambient Mg/Ca ratios. Large open circles correspond to the D_cMg of articulate coralline algae (Stanley et al., 2002). Large open diamonds correspond to the D_cMg of abiotic calcite (Füchtbauer and Hardie, 1976).

seawater decreased (Fig. 2). Specimens grown in the lowest seawater mMg/Ca ratio of 1.0 actually changed their mineralogy from high-Mg ($mMg/Ca > 0.04$) to low-Mg calcite ($mMg/Ca < 0.04$). Specimens grown in the higher seawater mMg/Ca ratios of 1.5, 2.5, 3.5, 5.2, and 7.0 produced high-Mg calcite with, respectively, increasing average skeletal

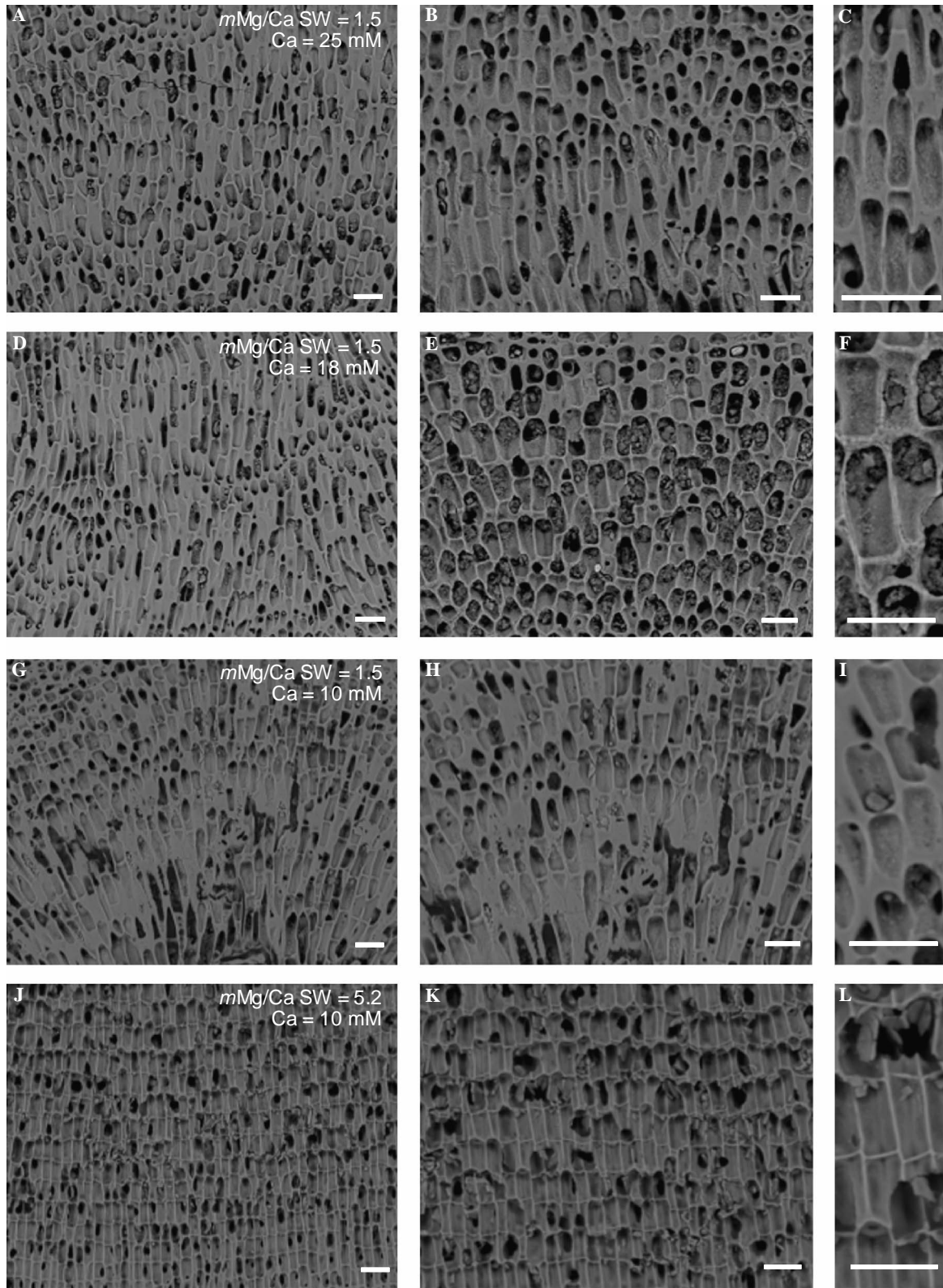


Fig. 4. Back-scatter electron images of *Neogoniolithon* sp. specimens grown in artificial seawaters with $m\text{Mg}/\text{Ca}$ ratios and absolute Ca concentrations (mM), respectively, of 1.5 and 25 (A–C), 1.5 and 18 (D–F), 1.5 and 10 (G–I), and 5.2 and 10 (equivalent to modern seawater, J–L). Specimens grown in the low Mg/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 grown in the modern, high Mg/Ca seawater, which naturally favors the precipitation of aragonite. Changes in the absolute concentration of Ca, for specimens grown in artificial seawaters with $m\text{Mg}/\text{Ca}$ 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 μm .

$m\text{Mg}/\text{Ca}$ ratios (\pm standard error) of 0.075 ± 0.004 , 0.116 ± 0.006 , 0.152 ± 0.011 , 0.213 ± 0.004 , and 0.301 ± 0.005 . The skeletal Mg/Ca ratios of the specimens grown in the artificial “modern” seawater ($m\text{Mg}/\text{Ca} = 5.2$) remained within 3% of their natural, pre-experimental values.

Algae grown in the second set of artificial seawaters with $m\text{Mg}/\text{Ca}$ ratios of 1.0, 1.5, and 5.2 and with reduced (1.0, 1.5) and elevated (5.2) absolute concentrations of Mg and Ca exhibited skeletal Mg/Ca ratios that were not significantly ($p < 0.05$) different than those for algae grown in seawater with equivalent Mg/Ca ratios and the normal sum of absolute Mg and Ca molar concentrations (Fig. 2).

$D_c\text{Mg}$ values calculated for algae grown in the various artificial seawaters revealed that the fractionation coefficient is not fixed for different ambient Mg/Ca ratios. Excluding the lowest ambient Mg/Ca condition ($m\text{Mg}/\text{Ca} = 1$), $D_c\text{Mg}$ significantly ($p < 0.05$) decreases as $\text{Mg}/\text{Ca}_{\text{SW}}$ increases (Fig. 3).

Back-scatter electron images of the *Neogoniolithon* sp. algae reveal that specimens grown in the low Mg/Ca artificial seawater ($m\text{Mg}/\text{Ca} = 1.5$; Fig. 4A–I) produced a more heavily calcified and less organized skeleton than algae grown in the high Mg/Ca artificial seawater ($m\text{Mg}/\text{Ca} = 5.2$; Fig. 4J–L), which produced well-defined cell layers so weakly calcified that they frequently appear to be shattered. Algae grown in artificial seawaters formulated at a fixed $m\text{Mg}/\text{Ca}$ ratio (1.5) and varying absolute concentrations of Ca exhibit no observable differences in skeletal organization or thickness (Fig. 4A–I).

5. Discussion

The correlation between the Mg/Ca ratios of the algal calcite and the artificial seawaters indicates that the skeletal chemistry of crustose coralline algae is variable, and that this variability can be driven by ambient seawater chemistry. The similarity between the Mg/Ca ratios of algae grown in the three sets of artificial seawaters of equivalent $m\text{Mg}/\text{Ca}$ ratios (1.0, 1.5, and 5.2) and differing absolute concentrations of Mg and Ca suggests that the incorporation of Mg in algal calcite is determined primarily by the relative proportions of Mg and Ca in seawater, rather than the absolute concentration of Mg.

5.1. Mg fractionation patterns in coralline algae and other calcareous organisms

Stanley et al. (2002) have shown that the skeletal Mg/Ca ratios of three species of articulate (non-encrusting) coralline algae, of the genus *Amphiroa*, also vary with the Mg/Ca ratio of ambient seawater (Fig. 4). The Mg-fractionation curve for these articulate coralline algae is slightly lower than the Mg-fractionation curve generated in this study for the encrusting coralline alga *Neogoniolithon* sp. (Fig. 5).

This correlation between seawater Mg/Ca and algal skeletal Mg/Ca is generally consistent with the results of similar experiments on the coccolithophores *P. carterae*

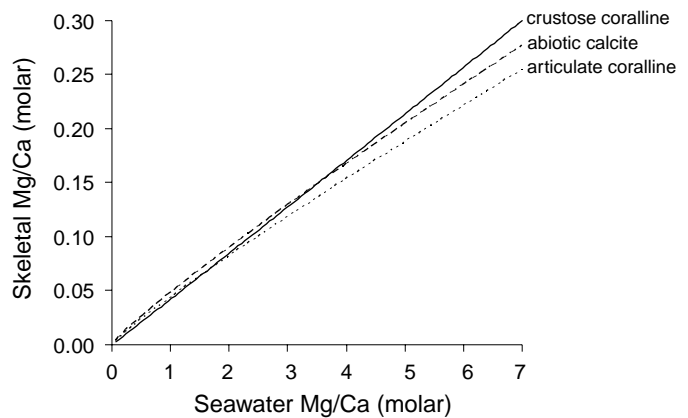


Fig. 5. Mg-fractionation curves for the crustose coralline alga *Neogoniolithon* sp., abiotic calcite (Füchtbauer and Hardie, 1976), and three species of articulate coralline algae of the genus *Amphiroa* (Stanley et al., 2002). The coralline algae appear to mimic abiotic calcite with respect to Mg fractionation.

and *O. neopolitana* (Stanley et al., 2005), the calcitic portions of the scleractinian corals *P. cylindrica*, *M. digitata*, and *A. cervicornis* (Ries, 2004b), the echinoid *E. tribuloides*, the crab *P. gibbesi*, the shrimp *P. pugio*, and the calcareous serpulid worm *H. crucigera* (Ries, 2004a).

While Chave (1954) correlated the degree of temperature-driven Mg fractionation in calcifying organisms with their taxonomic complexity, a similar correlation cannot be unequivocally established here for seawater Mg/Ca -driven Mg fractionation. However, the photosynthetic organisms (coccolithophores, corals, and coralline algae) generally appear to be more influenced by the ambient Mg/Ca ratio than the non-photosynthetic organisms (echinoids, crabs, shrimp, and calcareous serpulid worms; Fig. 6).

The similarity between the Mg-fractionation curves for autotrophic and abiotic calcification (Fig. 5) suggests that calcification is mostly induced, rather than controlled, by autotrophs, which increase the CaCO_3 saturation state of their precipitating medium through the removal of CO_2 via photosynthesis. Likewise, heterotrophs, which apparently control calcification via ionic pumping and organic mineral templates, produce Mg-fractionation curves that differ substantially from the Mg-fractionation curves associated with autotrophic and abiotic calcification (Fig. 6).

5.2. Mg fractionation coefficients ($D_c\text{Mg}$) for *Neogoniolithon* sp

The inverse relationship observed between $D_c\text{Mg}$ and $\text{Mg}/\text{Ca}_{\text{SW}}$ (Fig. 3), excluding the $D_c\text{Mg}$ value at $\text{Mg}/\text{Ca}_{\text{SW}} = 1.0$, is consistent with other studies on Mg fractionation in biotic and abiotic calcite (Füchtbauer and Hardie, 1976; Mucci and Morse, 1983; Stanley et al., 2002; Ries, 2004a). The relationship suggests that the algae are more efficient at excluding Mg from their skeletal

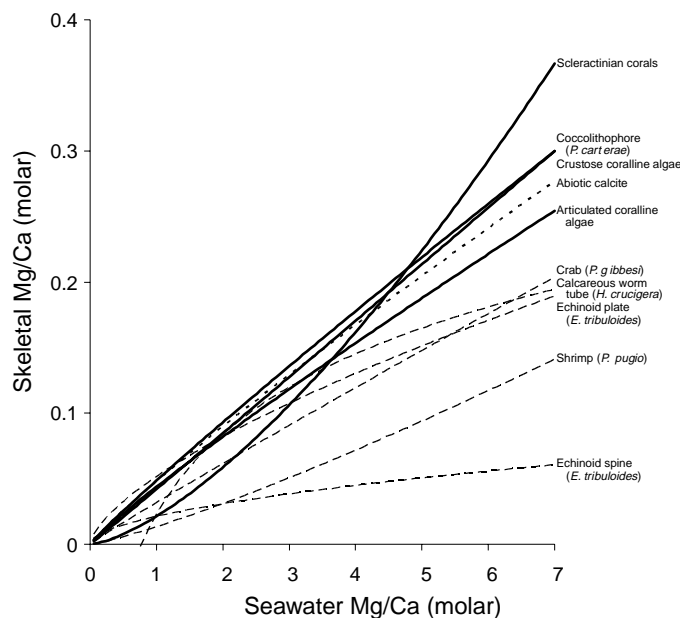


Fig. 6. The relationship between skeletal Mg/Ca and seawater Mg/Ca for various marine organisms which secrete at least part of their skeleton as calcite. Solid lines are Mg-fractionation curves for photosynthetic organisms [the coccolithophore *P. carterae* (Stanley et al., 2005); the crustose coralline red algae *Neogoniolithon* sp.; the calcitic portions of the scleractinian corals *P. cylindrica*, *M. digitata*, and *A. cervicornis* (Ries, 2004b); and three species of articulate coralline algae of the genus *Amphiroa* (Stanley et al., 2002)]; dotted line is Mg fractionation curve for abiotic calcite (Füchtbauer and Hardie, 1976); and dashed lines are Mg-fractionation curves for non-photosynthetic organisms (the echinoid *E. tribuloides*, the crab *P. gibbesi*, the shrimp *P. pugio*; and the calcareous serpulid worm *H. crucigera*; Ries, 2004a). Photosynthetic organisms appear to be more influenced by ambient Mg/Ca than non-photosynthetic organisms.

calcite when the ambient concentration of Mg is high relative to Ca. As the relative Mg concentration decreases, the organisms become less efficient at excluding it, thereby resulting in the elevated $D_c\text{Mg}$ values. However, the occurrence of this inverse proportionality between $D_c\text{Mg}$ and $\text{Mg}/\text{Ca}_{\text{SW}}$ in abiotic Mg-calcite (Fig. 3; 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.

5.3. Biomineralogical control and consequences of Mg incorporation in calcite

The algae's precipitation of high-Mg calcite from the artificial seawater formulated at a $m\text{Mg}/\text{Ca}$ ratio of 7.0, which naturally favors the abiotic precipitation of the aragonitic polymorph (Füchtbauer and Hardie, 1976), suggests that the algae are actively specifying the nucleation of the calcitic polymorph. However, the similarity of the algae's Mg-fractionation curve to that for abiotic calcite (Fig. 5; Füchtbauer and Hardie, 1976; Mucci and Morse, 1983) suggests that the algae's biomineralogical control is limited to polymorph specification, as they are apparently

unable to regulate Mg incorporation in their calcite crystal lattice.

The biological consequences of Mg incorporation in the skeletal calcite of crustose coralline algae are not well understood (Milliman et al., 1971). The size differences between the Mg and Ca cations in the Mg-calcite crystal lattice may reduce crack propagation, relative to the homogeneous crystal lattice of pure calcite (Magdanas and Gies, 2004). However, Mg has also 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), which would presumably reduce the algae's rate of skeletal accretion.

The *Neogoniolithon* sp. specimens' production of a skeleton that is more heavily calcified in the low Mg/Ca seawater (1.5) than in the high Mg/Ca seawater (5.2) suggests that the low ambient Mg/Ca ratio favored the production of the algae's inherently calcitic skeletal mineral (Fig. 4). This is consistent with the experimental evidence that seawater with a $m\text{Mg}/\text{Ca}$ ratio < 2 favors the abiotic precipitation of the calcite polymorph of CaCO_3 (i.e., calcite seas), while seawater with a $m\text{Mg}/\text{Ca}$ ratio > 2 favors the abiotic precipitation of the aragonite polymorph (i.e., aragonite seas; Leitmeier, 1910, 1915; Lippman, 1960; Müller et al., 1972; Folk, 1974; Füchtbauer and Hardie, 1976, 1980). The reduced calcification observed for algae grown in the higher Mg/Ca artificial seawater is probably caused by reductions in the growth rate (Davis et al., 2000) and unit-cell volume (Bischoff et al., 1983) of their calcite crystal lattice, which is caused by the substitution of Mg for Ca in calcite. Furthermore, the elevated rates of calcification for algae grown in the artificial calcite seawater may disrupt their normally well-ordered, daily growth layers which are evident in the less-calcified algae grown in the artificial aragonite seawater (Figs. 4J–L), resulting in the poorly organized skeletal structure observed in the former algae (Figs. 4A–I).

The *Neogoniolithon* sp. specimens' production of comparably thick skeletons (Fig. 4) in three artificial seawaters with identical Mg/Ca ratios (1.5) and differing Ca concentrations (10, 18, and 25 mM) suggests that, for the range of values evaluated in this study, the calcium carbonate saturation state of seawater ($[\text{Ca}^{2+}] \times [\text{CO}_3^{2-}]$) is not as important a factor in determining algal skeletal calcite thickness as is the ambient Mg/Ca ratio.

5.4. Paleoenvironmental reconstructions

The crustose coralline algae are identified as potential paleoenvironmental indicators because of their well-defined growth bands, widespread distribution, relatively long life spans, and ubiquity in carbonate rocks throughout the Phanerozoic (Wray, 1977). The relationship observed in this study between the Mg/Ca ratios of algal calcite and ambient seawater suggests that fossil crustose coralline algae may be an archive of past oceanic Mg/Ca ratios.

5.4.1. Derivation of the Mg fractionation algorithm

The relationship between seawater $m\text{Mg}/\text{Ca}$ ($\text{Mg}/\text{Ca}_{\text{SW}}$) and algal skeletal $m\text{Mg}/\text{Ca}$ ($\text{Mg}/\text{Ca}_{\text{C}}$) can be defined by the following algorithm (Fig. 2):

$$\text{Mg}/\text{Ca}_{\text{C}} = 0.0421\text{Mg}/\text{Ca}_{\text{SW}}^{1.01}$$

However, the Mg/Ca of coralline algal calcite is also known to increase proportionally with ambient seawater temperature (Chave, 1954). For temperatures ranging from 5.2 to 28.0 °C, skeletal $m\text{Mg}/\text{Ca}$ ratios increase from 0.083 to 0.404. A least-squares regression ($R^2 = 0.76$) through Chave's (1954) data, when calibrated for *Neogoniolithon* sp., is defined as:

$$\text{Mg}/\text{Ca}_{\text{C}} = 0.0709e^{0.0457T}$$

These two Mg fractionation algorithms can be solved simultaneously at $\text{Mg}/\text{Ca}_{\text{SW}} = 5.2$ to yield a single Mg fractionation algorithm that varies as a function of both temperature and the seawater Mg/Ca ratio:

$$\text{Mg}/\text{Ca}_{\text{C}} = 0.0134e^{0.0457T}\text{Mg}/\text{Ca}_{\text{SW}}^{1.01}$$

5.4.2. Ocean temperature reconstructions

The correlation between temperature and skeletal Mg incorporation (Chave, 1954) also permits the reconstruction of ancient seawater temperatures from the Mg/Ca ratios of coralline algal calcite. However, such reconstructions must correct skeletal Mg/Ca for the effect of secular variation in the Mg/Ca ratio of seawater. Recent paleotemperature reconstructions from the Mg/Ca ratios of fossil foraminifera (Lear et al., 2000) and corals (Hart and Cohen, 1996; Mitsuguchi et al., 1996) could be improved by employing experimentally derived Mg fractionation algorithms for these organisms, such as those obtained for crustose coralline algae in the present study, that account for the effects of both temperature and seawater Mg/Ca on skeletal Mg.

5.4.3. Effects of diagenesis

High-Mg calcite can rapidly lose Mg during even the early stages of diagenesis (Müller et al., 1972; Mackenzie et al., 1983; Morse, 1983; Frank and Lohmann, 1996; Hover et al., 2001). Therefore, one of the greatest challenges in using fossil Mg/Ca to deduce oceanic Mg/Ca is the identification of carbonate material that has retained evidence of its original Mg content. Conditions do exist that stabilize high-Mg calcite, as demonstrated in recent studies which deduced ancient oceanic Mg/Ca ratios from the Mg content of well-preserved fossil echinoderms from throughout the Phanerozoic (Dickson, 2002, 2004). Furthermore, the 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; Lohmann and Meyers, 1977). Assuming that the Mg in these dolomite rhombs was derived primarily from original skeletal Mg, the algae's original Mg content can be estimated from the volume of that dolomite relative to the skeletal volume of the fossil. A suite of petrographic,

cathodoluminescent, geochemical, and isotopic techniques can also be employed to reconstruct the diagenetic history of calcitic fossils, which is required for their application as paleoenvironmental indicators (Dickson, 1995; Frank and Lohmann, 1996; Frank et al., 1996; Benito et al., 2001; Cicero and Lohmann, 2001; Hover et al., 2001).

5.4.4. Limitations of the model

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 such as severe diagenesis (in which Mg is lost or gained), uncorrected species-specific Mg fractionation, fluctuations of other cations in seawater, and unknown environmental factors that influence Mg partitioning in algal calcite. Furthermore, the growth rate of calcite crystals has been shown to be proportional to the degree of Mg incorporation in calcite (Mucci and Morse, 1983), thereby introducing the possibility that the low skeletal Mg/Ca ratios produced in the lower Mg/Ca seawaters were caused by reduced growth rates of the algae living under such unfamiliar conditions. However, this appears unlikely for two reasons: (1) specimens grown in the unfamiliar elevated Mg/Ca seawater ($m\text{Mg}/\text{Ca} = 7.0$) incorporated more skeletal Mg than specimens grown in the familiar modern seawater; and (2) specimens that incorporated the least skeletal Mg also had the thickest skeletons, which were presumably constructed from the fastest calcite growth.

6. Conclusion

The following conclusions can be drawn from the present study:

- (1) The Mg/Ca ratio of calcite produced by the crustose coralline alga *Neogoniolithon* sp. varies as a function of the Mg/Ca ratio of its 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. First-order reconstructions of oceanic Mg/Ca ratios or paleotemperatures can be made from the Mg content of well-preserved fossils of these encrusting coralline algae, given that one of these variables is known for the seawater in which the fossilized algae originally lived.
- (2) The Mg-fractionation curve for calcite produced by the *Neogoniolithon* sp. alga is nearly identical to the Mg-fractionation curve for abiotically precipitated calcite. This suggests that the *Neogoniolithon* sp. alga exercises little or no influence over the incorporation of Mg into its skeleton. Its biomineralogical control is apparently limited to the specification of the calcite polymorph over the aragonite polymorph, as evidenced by its exclusive production of calcite even in artificial seawater that favors the abiotic precipitation of aragonite ($m\text{Mg}/\text{Ca} = 7.0$).

- (3) The crustose coralline alga *Neogoniolithon* sp. changes its skeletal composition from high-Mg calcite to low-Mg calcite when moved from artificial seawater with a *mMg/Ca* ratio of 5.2 to artificial seawater with a *mMg/Ca* ratio of 1.0. This suggests that these encrusting coralline algae, which produce exclusively high-Mg calcite in modern seas (*mMg/Ca* = 5.2), probably produced low-Mg calcite during the middle to Late Cretaceous, when seawater *mMg/Ca* ratios were near unity (Lowenstein et al., 2001, 2003). This assertion may also be applicable to the 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.
- (4) These results support the empirical fossil evidence that secular variation in oceanic Mg/Ca has caused the mineralogy and skeletal chemistry of many calcifying marine organisms to change significantly over the Phanerozoic Eon (Stanley and Hardie, 1998, 1999).

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References

- Adey, W.H., Macintyre, I.G., 1973. Crustose coralline algae: a re-evaluation in the geological sciences. *Geological Society of America Bulletin* **84**, 883–904.
- Aguirre, J., Riding, R., Braga, J.C., 2000. Diversity of coralline red algae: origination and extinction patterns from the Early Cretaceous to the Pleistocene. *Paleobiology* **26**, 651–667.
- Alexandersson, T., 1977. Carbonate cementation in Recent coralline algal constructions. In: Flugel, E. (Ed.), *Fossil Algae: Recent Result and Developments*. Springer-Verlag, New York, pp. 261–269.
- Benito, M.I., Lohmann, K.C., Mas, R., 2001. Discrimination of multiple episodes of meteoric diagenesis in a Kimmeridgian reefal complex, North Iberian Range, Spain. *Journal of Sedimentary Research* **71**, 380–393.
- Berner, R.A., 1975. The role of magnesium in the crystal growth of calcite and aragonite from sea water. *Geochimica et Cosmochimica Acta* **39**, 489–504.
- Berner, T., 1990. Coral-reef algae. In: Dubinsky, Z. (Ed.), *Coral Reefs*. Elsevier, Amsterdam, pp. 253–264.
- Bidwell, J.P., Spotte, S., 1985. *Artificial Seawaters: Formulas and Methods*. Jones and Bartlett, Boston, MA.
- Bischoff, W.D., Bishop, F.C., Mackenzie, F.T., 1983. Biogenically produced magnesian calcite: inhomogeneities in chemical and physical properties: comparison with synthetic phases. *American Mineralogist* **68**, 1183–1188.
- Chave, K.E., 1954. Aspects of the Biogeochemistry of 1. Calcareous marine organisms. *Journal of Geology* **62**, 266–283.
- Chisholm, J.R.M., 2003. Primary productivity of reef-building crustose coralline algae. *Limnology and Oceanography* **48**, 1376–1387.
- Cicero, A.D., Lohmann, K.C., 2001. Sr/ Mg variation during rock-water interaction; implications for secular changes in the elemental chemistry of ancient seawater. *Geochimica et Cosmochimica Acta* **65**, 741–761.
- Davis, K.J., Dove, P.M., De Yoreo, J.J., 2000. The role of Mg²⁺ as an impurity in calcite growth. *Science* **290**, 1134–1137.
- Decker, P.D., Chivas, A.R., Shelley, J.M.G., 1999. Uptake of Mg and Sr in the euryhaline ostracod *Cyprideis* determined from in vitro experiments. *Palaeogeography, Palaeoclimatology, Palaeoecology* **148**, 105–116.
- Dickson, J.A.D., 1995. Paleozoic Mg calcite preserved: implications for the Carboniferous ocean. *Geology* **23**, 535–538.
- Dickson, J.A.D., 2002. Fossil echinoderms as monitor of the Mg/Ca ratio of Phanerozoic oceans. *Science* **298**, 1222–1224.
- Dickson, J.A.D., 2004. Echinoderm skeletal preservation: calcite-aragonite seas and the Mg/Ca ratio of Phanerozoic oceans. *Journal of Sedimentary Research* **74**, 355–365.
- Folk, R.L., 1974. The natural history of crystalline calcium carbonate: effect of magnesium content and salinity. *Journal of Sedimentary Petrology* **44**, 40–53.
- Frank, T.D., Lohmann, K.C., 1996. Diagenesis of fibrous magnesian calcite marine cement: implications for the interpretation of delta O-18 and delta C-13 values of ancient equivalents. *Geochimica et Cosmochimica Acta* **60**, 2427–2436.
- Frank, T.D., Lohmann, K.C., Meyers, W.J., 1996. Chronostratigraphic significance of cathodoluminescence zoning in syntaxial cement: Mississippian lake valley formation, New Mexico. *Sedimentary Geology* **105**, 29–50.
- Füchtbauer, H., Hardie, L.A., 1976. Experimentally determined homogeneous distribution coefficients for precipitated magnesian calcites: application to marine carbonate cements. *Geological Society of America Abstracts with Program* **8**, 877.
- Füchtbauer, H., Hardie, L.A., 1980. Comparison of experimental and natural magnesian calcites. *International Association of Sedimentologists, Bochum*, 167–169.
- Hardie, L.A., 1996. Secular variation in seawater chemistry: an explanation for the coupled secular variation in the mineralogies of marine limestones and potash evaporites over the past 600 m.y. *Geology* **24**, 279–283.
- Hart, S.R., Cohen, A.L., 1996. Sr/Ca in corals: an ion microprobe study of annual cycles and microscale coherence with other trace elements. *Geochimica et Cosmochimica Acta* **60**, 3075–3084.
- Holland, H.D., 1984. *The Chemical Evolution of the Atmosphere and Oceans*. Princeton University Press, Princeton, NJ.
- Hover, V.C., Walter, L.M., Peacor, D.R., 2001. Early marine diagenesis of biogenic aragonite and Mg-calcite: new constraints from high-resolution STEM and AEM analyses of modern platform carbonates. *Chemical Geology* **175**, 221–248.
- James, N.P., Wray, J.L., Ginsburg, R.N., 1988. Calcification of encrusting aragonitic algae (Peyssonneliaceae): implications for the origin of Late Paleozoic reefs and cements. *Journal of Sedimentary Petrology* **58**, 291–303.
- Johnson, J.H., 1961. *Limestone-building Algae and Algal Limestones*. Colorado School of Mines.
- Lear, C.H., Elderfield, H., Wilson, P.A., 2000. Cenozoic deep-sea temperatures and global ice volumes from Mg/Ca in benthic foraminiferal calcite. *Science* **287**, 269–272.
- Leitmeier, H., 1910. Zur kenntnis der carbonate, die dimorphie des Kohlensauren Kalkes I. Teil. *Neues Jahrbuch für Mineralogie, Heft 1*, 49–74.
- Leitmeier, H., 1915. Zur kenntnis der carbonate. II. Teil. *Neues Jahrbuch für Mineralogie, Beilageband* **40**, 655–700.
- Lippman, F., 1960. Versuche zur aufklarung der bildungsbedingungen von calcit und aragonit. *Fortschritte der Mineralogie* **38**, 156–161.

- Littler, M.M., 1973. The population and community structure of Hawaiian fringing reef crustose Corallinaceae. *Journal of Experimental Marine Biology and Ecology* **11**, 103–120.
- Lohmann, K.C., Meyers, W.J., 1977. Microdolomite inclusions in cloudy prismatic calcites—proposed criterion for former high-magnesium calcites. *Journal of Sedimentary Petrology* **47**, 1078–1088.
- Lorens, R.B., Bender, M.L., 1980. The impact of solution chemistry on *Mytilus edulis* calcite and aragonite. *Geochimica et Cosmochimica Acta* **44**, 1265–1278.
- Lowenstein, T.K., Hardie, L.A., Timofeeff, M.N., Demicco, R.V., 2003. Secular variation in seawater chemistry and the origin of calcium chloride basinal brines. *Geology* **31**, 857–860.
- Lowenstein, T.K., Timofeeff, M.N., Brennan, S.T., Hardie, L.A., Demicco, R.V., 2001. Oscillations in Phanerozoic seawater chemistry: evidence from fluid inclusions. *Science* **294**, 1086–1088.
- Macintyre, I.G., 1997. Reevaluating the role of crustose coralline algae in the construction of coral reefs. In: *Proceedings of the 8th International Coral Reef Symposium* **1**, 725–730.
- Mackenzie, F.T., Bischoff, W.D., Bishop, F.C., Loijens, M., Schoonmaker, J., Wollast, R., 1983. Magnesian calcites: low temperature occurrence, solubility and solid-solution behavior. In: Reeder, R. (Ed.), *Carbonates: Mineralogy and Chemistry*. Mineralogical Society of America, pp. 97–144.
- Magdani, U., Gies, H., 2004. Single crystal structure analysis of sea urchin spine calcites: systematic investigations of the Ca/Mg distribution as a function of habitat of the sea urchin and the sample location in the spine. *European Journal of Mineralogy* **16**, 261–268.
- Milliman, J.D., 1974. *Marine carbonates*. Springer-Verlag, New York.
- Milliman, J.D., Gastner, M., Muller, J., 1971. Utilization of magnesium in coralline algae. *Geological Society of America Bulletin* **82**, 573–580.
- Mitsuguchi, T., Matsumoto, E., Abe, O., Uchida, T., Isdale, P.J., 1996. Mg/Ca thermometry in coral skeletons. *Science* **274**, 961–963.
- Montañez, I.P., 2002. Biological skeletal carbonate records changes in major-ion chemistry of paleo-oceans. *Proceedings of the National Academy of Sciences* **99**, 15852–15854.
- Morse, J.W., 1983. The kinetics of calcium carbonate dissolution and precipitation. In: Reeder, R. (Ed.), *Carbonates: Mineralogy and Chemistry*. Mineralogical Society of America, pp. 227–264.
- Morse, J.W., Bender, M.L., 1990. Partition coefficients in calcite: examination of factors influencing the validity of experimental results and their application to natural systems. *Chemical Geology* **82**, 265–277.
- Morse, J.W., Wang, Q., Tsio, M.Y., 1997. Influences of temperature and Mg:Ca ratio on CaCO₃ precipitates from seawater. *Geology* **25**, 85–87.
- Mucci, A., Morse, J.W., 1983. The incorporation of Mg²⁺ and Sr²⁺ into calcite overgrowths: influence of growth rate and solution composition. *Geochimica et Cosmochimica Acta* **47**, 217–233.
- Müller, G., Irion, G., Förstner, U., 1972. Formation and diagenesis of inorganic Ca-Mg carbonates in the lacustrine environment. *Naturwissenschaften* **59**, 158–164.
- Railsback, L.B., 1993. Original mineralogy of carboniferous worm tubes—evidence for changing marine chemistry and biomineralization. *Geology* **21**, 703–706.
- Ries, J.B., 2004a. Effect of ambient Mg/Ca ratio on Mg fractionation in calcareous marine invertebrates: a record of the oceanic Mg/Ca ratio over the Phanerozoic. *Geology* **32**, 981–984.
- Ries, J.B., 2004b. Modern scleractinian corals produce calcite in experimental Mid-Paleozoic/Cretaceous seawater. *Geological Society of America Abstracts with Programs* **36**, 544.
- Sandberg, P.A., 1983. An oscillating trend in Phanerozoic nonskeletal carbonate mineralogy. *Nature* **305**, 19–22.
- Schlanger, S.O., 1957. Dolomite growth in coralline algae. *Journal of Sedimentary Petrology* **27**, 181–186.
- Siemann, M.G., 2003. Extensive and rapid changes in seawater chemistry during the Phanerozoic: evidence from Br contents in basal halite. *Terra Nova* **15**, 243–248.
- Spotte, S.H., 1979. *Seawater Aquariums: The Captive Environment*. Wiley and Sons, Hoboken, NJ.
- Stanley, S.M., Hardie, L.A., 1998. Secular oscillations in carbonate mineralogy of reef-building and sediment-producing organisms driven by tectonically forced shifts in seawater chemistry. *Paleogeography, Paleoclimatology, Paleoecology* **144**, 3–19.
- Stanley, S.M., Hardie, L.A., 1999. Hypercalcification: paleontology links plate tectonics and geochemistry to sedimentology. *GSA Today* **9**, 2–7.
- Stanley, S.M., Ries, J.B., Hardie, L.A., 2002. Low-magnesium calcite produced by coralline algae in seawater of Late Cretaceous composition. *Proceedings of the National Academy of Sciences* **99**, 15323–15326.
- Stanley, S.M., Ries, J.B., Hardie, L.A., 2005. Seawater chemistry, coccolithophore population growth, and the origin of Cretaceous chalk. *Geology* **33**, 593–596.
- Wilkinson, B.H., 1979. Biomineralization, paleoceanography, and the evolution of calcareous marine organisms. *Geology* **7**, 524–527.
- Wilkinson, B.H., Given, K.R., 1986. Secular variation in abiotic marine carbonates: constraints on Phanerozoic atmospheric carbon dioxide contents and oceanic Mg/Ca ratios. *Journal of Geology* **94**, 321–333.
- Wray, J.L., 1964. *Archaeolithophyllum*, an abundant calcareous alga in limestones of the Lansing Group (Pennsylvanian), southeastern Kansas. *Kansas Geological Survey Bulletin* **170**, 1–13.
- Wray, J.L., 1977. *Calcareous Algae*. Elsevier, Amsterdam.