

Aragonite production in calcite seas: effect of seawater Mg/Ca ratio on the calcification and growth of the calcareous alga *Penicillus capitatus*

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Abstract.—Previous studies have shown that secular variation in the Mg/Ca ratio of seawater throughout the Phanerozoic would have subjected the aragonite-producing codiacean algae to at least three transitions between the low-Mg calcite (molar Mg/Ca <2) and aragonite + high-Mg calcite (molar Mg/Ca >2) nucleation fields in the oceans, since their origin in the Ordovician. These studies have asserted that major sediment production by codiacean algae in Recent tropical seas is permitted by the Mg/Ca ratio of modern seawater (molar Mg/Ca ~5.2) remaining within the aragonitic/high-Mg calcite nucleation field (molar Mg/Ca >2). Here I present the results of experiments conducted to determine the effects of ambient Mg/Ca on the mineralogy, growth rate, primary productivity, calcification rate, and biomechanics of the codiacean alga *Penicillus capitatus*.

P. capitatus specimens were grown in three artificial seawater treatments that mimic ancient seawater of differing Mg/Ca ratios, corresponding to the low-Mg calcite nucleation field (molar Mg/Ca ~1.0), a “boundary field” (molar Mg/Ca ~2.5), and the aragonite + high-Mg calcite nucleation field (molar Mg/Ca ~5.2). Significantly, *P. capitatus* specimens maintained a mostly aragonitic mineralogy in all three seawater treatments. However, linear growth rates, primary productivity, calcification, and thallus stiffness decreased with reductions in ambient Mg/Ca. That *P. capitatus* precipitates approximately three-quarters of its CaCO₃ as aragonite in the seawater treatment that favors the inorganic precipitation of low-Mg calcite suggests that the alga dictates the precipitation of that polymorph, either by pumping cations to create an internal aragonite nucleation field (molar Mg/Ca >2) or by employing organic templates that specify the nucleation of the aragonite polymorph (Borowitzka 1984). However, the alga’s precipitation of one-quarter of its CaCO₃ as low-Mg calcite suggests that its mineralogical control is limited and can be partially overridden by the Mg/Ca ratio of ambient seawater. The reduced calcification of *P. capitatus* specimens grown in the low-Mg calcite and boundary nucleation fields is probably due to the inherent difficulty of precipitating aragonite from seawater which does not naturally support its nucleation. The decreased rates of linear growth and primary production are probably caused by reductions in CO₂ available for photosynthesis due to the reduction in calcification (Borowitzka and Larkum 1977). The observed decrease in thallus stiffness is probably due to the reductions in calcification and primary productivity observed in *P. capitatus* specimens grown in the low-Mg calcite and boundary nucleation fields.

The present study suggests that aragonitic algae would have been handicapped in oceans characterized by Mg/Ca ratios that did not support their inherent mineralogy. Producing aragonite in seawater outside of the aragonite + high-Mg calcite nucleation field would probably have reduced the competitiveness of these algae, made them more susceptible to predation, and reduced their contribution to carbonate sedimentation. These findings support earlier assertions that the dominant ecological and sedimentological roles of codiacean algae in Recent tropical seas is permitted by a Mg/Ca ratio of seawater that supports the algae’s aragonitic mineralogy during this time.

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Introduction

The topic of changing seawater chemistry throughout the Phanerozoic is a particularly exciting one because it links the typically disparate fields of plate tectonics, aqueous geochemistry, and paleontology (Stanley and Hardie 1998, 1999; Stanley et al. 2002; Montañez 2002; Ries 2004). The purpose of the research presented here is to explore a critical aspect of the geochemistry-paleontology link:

the relationship between seawater Mg/Ca and carbonate biomineralization.

Stanley and Hardie (1998, 1999) demonstrated that the mineralogies of the major reef-building and sediment-producing marine organisms have tracked transitions in the mineralogy of ooids and marine cements, the so-called calcite and aragonite seas (Sandberg 1983) (Fig. 1). They further asserted that the role of aragonitic algae as dominant sediment producers in Recent tropical seas is permitted

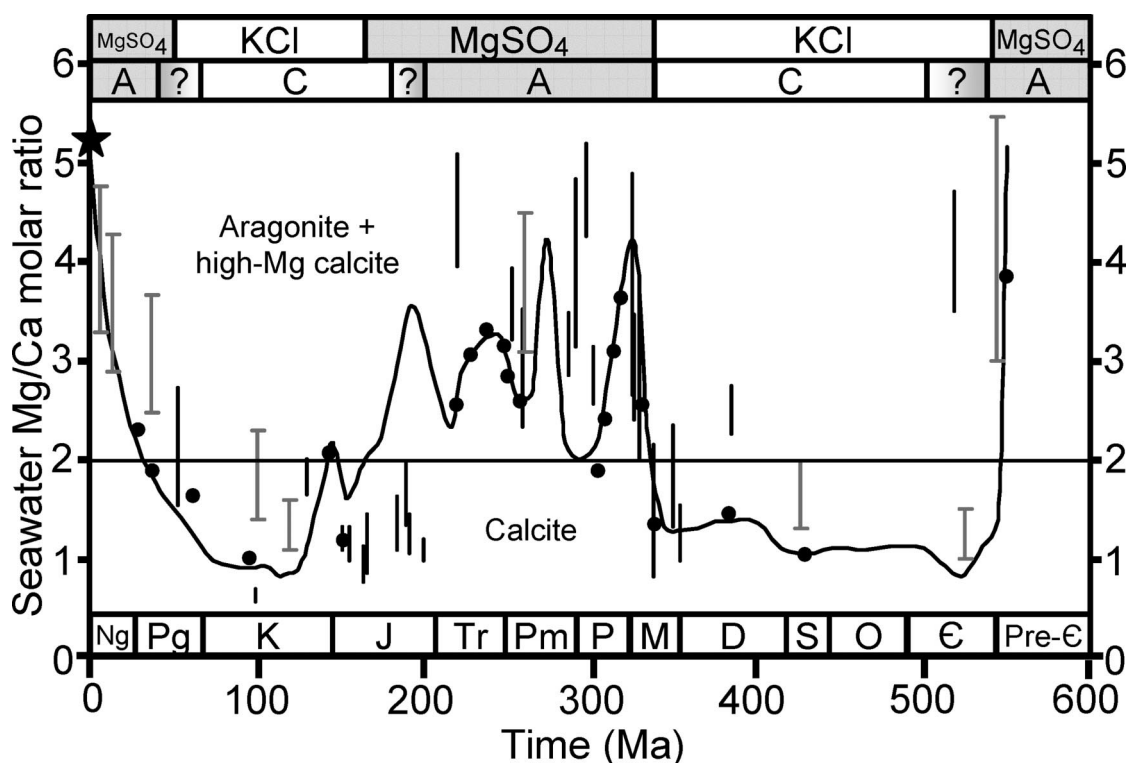


FIGURE 1. Evidence and predictions of secular variation in the molar Mg/Ca ratio of seawater during the Phanerozoic, which supported three periods of aragonite + high-Mg calcite nucleation and two periods of calcite nucleation. Curve is the molar Mg/Ca ratio of seawater predicted by Hardie (1996). Gray vertical bars with t-tops are molar Mg/Ca ranges estimated from fluid inclusions in marine halites (Lowenstein et al. 2001, 2003). Black vertical bars are molar Mg/Ca ranges calculated from the Mg content of fossil echinoderms (Dickson 2002, 2004; Ries 2004). Solid black circles are molar Mg/Ca values estimated from Br in basal marine halite (Siemann 2003). Star represents modern seawater chemistry (molar Mg/Ca \approx 5.2). Horizontal line is the divide between the calcite (molar Mg/Ca $<$ 2) and aragonite + high-Mg calcite (molar Mg/Ca $>$ 2) nucleation fields in seawater at 25°C. Temporal distributions of nonskeletal aragonite and calcite (Sandberg 1983) and KCl and MgSO₄ marine evaporites (Hardie 1996) are plotted along the top of the figure (modified from Lowenstein et al. 2001).

by the Mg/Ca ratio of seawater remaining in the aragonite nucleation field (molar Mg/Ca $>$ 2).

The present study evaluates this relationship identified by Stanley and Hardie experimentally, by growing a modern aragonite producing alga, *Penicillus capitatus*, in artificial seawaters that encompass the range of Mg/Ca ratios believed to have existed since the origin of the Codiaceae (Hardie 1996). This work complements other experiments by Stanley et al. (2002, in press) and Ries (2004), which demonstrated that calcareous organisms that produce high-Mg calcite in modern "aragonite seawater" (molar Mg/Ca \approx 5.2), such as coralline algae, echinoids, serpulid worms, crabs, shrimp, and coccolithophores, produced low-Mg calcite and, in the case of the

coccolithophores, grew faster in artificial "calcite seawater" (molar Mg/Ca \sim 1.0).

Background

Geologic History of Penicillus.—The codiacean algae have existed since at least the Ordovician (Chuvashov and Riding 1984; Flügel 1991; Mamet 1991; Riding and Guo 1991; Roux 1991), as evidenced by the Ordovician alga *Dimorphosiphon*, which demonstrates a level of organization like that of the modern *Halimeda* (Mu 1991). Unlike *Halimeda*, whose geologic history since the Cretaceous is revealed through its easily preserved plates, *Penicillus* rapidly disaggregates into inconspicuous needles, which are generally unidentifiable at the organismal level. As a result, the geologic history of *Penicillus* is relatively un-

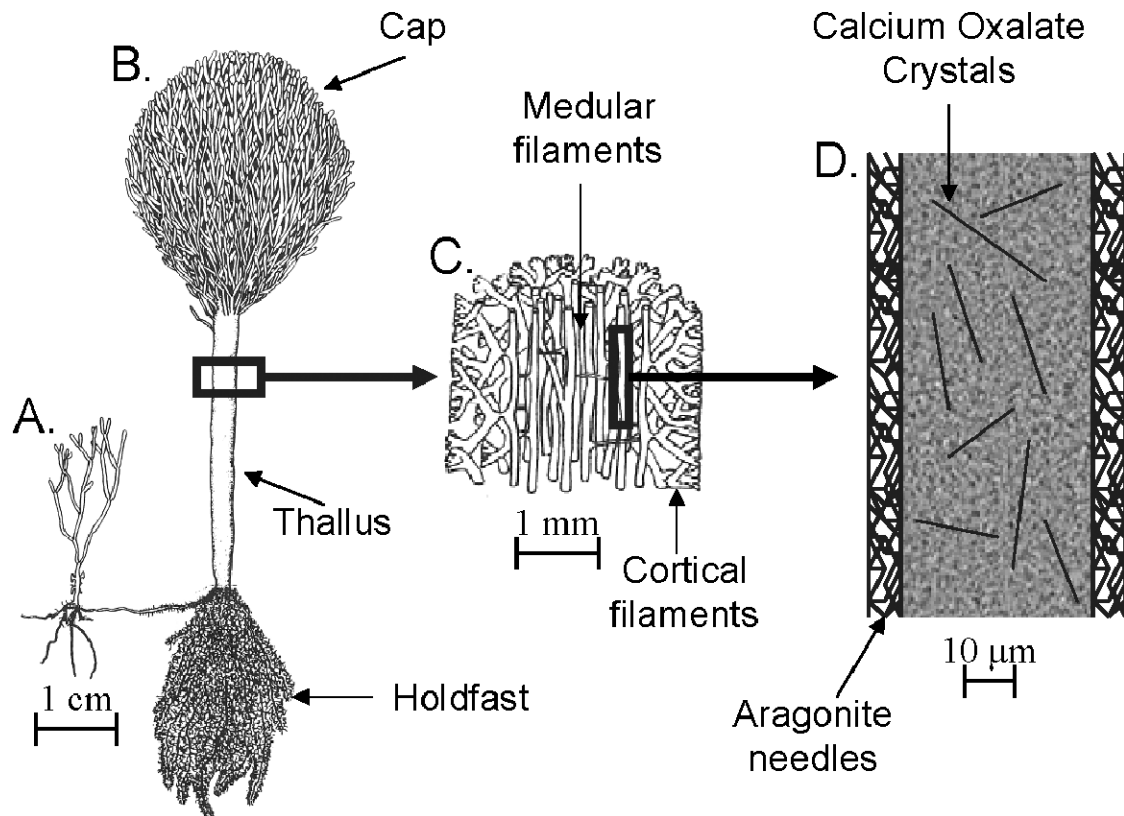


FIGURE 2. Anatomical detail of the alga *Penicillus capitatus*. A, Young plant sprouting from rhizoids. B, Full grown plant revealing uncalcified holdfast, calcified thallus, and calcified cap. C, Magnified view of thallus revealing the constituent calcified medullar and cortical filaments. D, Magnified longitudinal cross-section of a medullar filament showing deposition of aragonite needles between its inner and outer walls, as well as distribution of calcium oxalate crystals within its cytoplasm (after Van den Hoek 1981).

known. Elliot (1978) claimed that species of *Ovulites*, existing from the Cretaceous to the Eocene, resembled *Penicillus* in their morphology and ecology. This is consistent with the close resemblance of the *Penicillus* ultrastructure to that of *Halimeda* (Mu 1991), which is also believed to have existed since the Cretaceous (Elliot 1978).

Anatomy.—*Penicillus* is an erect alga whose anatomy can be divided into three basic components: thallus, cap, and holdfast (Fig. 2B). The thallus (stalk) is composed of medullar filaments, which run parallel to the thallus's axis, and cortical filaments, which branch laterally from the medullar filaments to form the perimeter of the thallus (Fig. 2C). The cortical filaments are terminated by small swellings, called utricles, which form the external surface of the thallus. The medullar filaments terminate as a bundle of 1–4-cm capitular fila-

ments above the thallus, thereby forming the brushy cap from which *Penicillus* derives its name (Van den Hoek 1981). The holdfast, consisting of a network of uncalcified filaments that adhere to sand particles, is located at the base of the alga and serves to anchor it in the sediment (Hillis 1991). Offspring algae grow from rhizoids sent out from the holdfast within the sediment (Fig. 2A). The filaments that make up the thallus and cap bear pores up to 10 μm in diameter, which are distributed at intervals of 5–25 μm (Matthews 1966).

Calcification.—Calcification in *Penicillus* occurs as aragonitic needles (<15 μm long), prisms (0.5 μm long), and serrated crystals (1.0 μm long) precipitated between an outer cell wall sheath and the inner cell wall of the cortical, medullar, and capitular filaments (Fig. 2D) (Friedman et al. 1972; Borowitzka et al. 1974; Borowitzka and Larkum 1977; Flajs

1977; Böhm and Fütterer 1978; Borowitzka 1984). Mature thalli can contain between 25 and 59 wt% aragonite. Although the purpose of algal calcification has been debated, its most common explanation is for rigidity in turbulent hydraulic environments and protection from grazing predation (Wray 1977; Paul and Van Alstyne 1988; Schupp and Paul 1994). Calcium oxalate crystals, up to 150 μm long, are also reported to be intracellularly precipitated within the cytoplasm-filled vacuolar system of the alga (Fig. 2D) (Friedman et al. 1972). However, these crystals are sparsely distributed and, therefore, provide little structural support or protection for the alga. They are most likely involved in the storage of Ca to be used during Ca-deficient times or in the regulation of osmosis or pH (Borowitzka 1984).

Sedimentary Production.—The codiacean algae have been producing CaCO_3 since at least the Ordovician (Roux 1991). Three modern aragonite-producing genera of the codiacean family (*Halimeda*, *Penicillus*, and *Udotea*) are believed to be among the most important carbonate sediment producers and bioherm-builders in modern tropical marine environments (Lowenstam 1955; Milliman 1977; Hillis-Colinvaux 1980; Wefer 1980; Drew 1983; Hudson 1985; Hine et al. 1988; Marshall and Davies 1988; Multer 1988; Orme and Salama 1988; Payri 1988; Phipps and Roberts 1988; Roberts et al. 1988; Mu 1991). Estimates of Recent carbonate accretionary rates in algae-dominated tropical environments range from 0.18 to 5.9 $\text{m } 1000 \text{ yr}^{-1}$ (Hillis 1991). *Penicillus*, *Halimeda*, and *Udotea* grow rapidly, attaining heights of up to 20 cm over their one- to three-month life spans. *Penicillus* densities of 76–108 alga m^{-2} have been reported in southern Florida (Stockman et al. 1967). The algae are globally distributed, with greatest densities occurring in the Caribbean Sea, followed by the Mediterranean Sea (Hillis-Colinvaux 1980), the Great Barrier Reef (Drew and Abel 1988), and restricted Indo-Pacific Ocean localities (Hillis 1991). Such rapid growth rates, short life spans (i.e., rapid turnover), dense populations, and widespread geographic distributions of the algae suggest that their production of aragonite needles could account for most of the carbonate mud deposited in Re-

cent tropical environments (Stockman et al. 1967; Neumann and Land 1975; Hillis 1991). Carbon and oxygen isotopes have also been used to show that Recent carbonate mud is algal in origin (Lowenstam and Epstein 1957). Others have estimated that the algal contribution to carbonate sediments, based on recognizable skeletal debris in sediment cores, is only between 11 and 29 wt% (Cloud 1962; Bathurst 1975).

Unfortunately, the architecture of *Penicillus* does not lend itself to identifiable preservation in the sedimentary and rock records; therefore, recognizable skeletal debris may underestimate the contribution of algae to carbonate sediment production. It should also be noted that while the role of codiacean algae as sedimentary producers in Recent tropical seas appears unrivaled in the geologic past, it has been suggested that they produced significant amounts of carbonate at other times throughout the Phanerozoic, as well (Høeg 1927; Johnson 1961; Jux 1966; Wray 1977; Segonzak 1986; Flügel 1988; Mankiewicz 1988). The record of such production may be obscured by the previously discussed preservation issues.

Seawater Chemistry.—The Mg/Ca ratio of seawater has varied significantly over the Phanerozoic, as a function of the rate of ocean crust production (Hardie 1996). As mid-ocean ridge basalt comes in contact with brine, it is converted to greenstone; thereby releasing Ca^{2+} and K^+ to the seawater and removing Mg^{2+} and SO_4^{2-} from it. The rate of ocean crust production controls the rate of this ion exchange and, therefore, the relative concentrations of these ions in the oceans. This is evidenced in synchronized transitions between MgSO_4 and KCl evaporites and aragonite and calcite precipitates (both biotic and abiotic) (Sandberg 1983; Hardie 1996; Stanley and Hardie 1998, 1999), 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; Ries 2004) (Fig. 1).

Füchtbauer and Hardie (1976, 1980) showed that in laboratory experiments on the system $\text{MgCl}_2\text{—CaCl}_2\text{—Na}_2\text{CO}_3\text{—H}_2\text{O}$, the precipitation of calcite versus aragonite + high-Mg calcite is determined by the solution's Mg/Ca ra-

tio, ionic strength and temperature. The experiments yielded a Mg/Ca molar ratio of 2 (± 0.5) as the boundary between the calcite (molar Mg/Ca < 2) and aragonite + high-Mg calcite (Mg/Ca > 2) nucleation fields (Leitmeier 1910, 1915; Lippman 1960; Müller et al. 1972; Folk 1974) for chloride solutions under laboratory conditions approximating modern values of ionic strength ($I = 0.7$), temperature (28°C), pressure (1 atm total pressure), and atmospheric $p\text{CO}_2$. Ancient Mg/Ca ratios calculated from rates of ocean crust production (Hardie 1996) predict that the oceans would have passed between the aragonite + high-Mg calcite and low-Mg calcite nucleation fields four times throughout the Phanerozoic. This predicted pattern is supported by the mineralogical record of ooids and marine cements throughout the Phanerozoic (Sandberg 1983) (Fig. 1).

Methods

Artificial Seawater Preparation.—Three 30-liter artificial seawater treatments, contained in ten-gallon glass aquaria, were formulated at molar Mg/Ca ratios of 1.0 (low-Mg calcite nucleation field), 2.5 (boundary nucleation field), and 5.2 (aragonite + high-Mg calcite nucleation field; modern seawater). The ionic strength of the artificial seawaters was held constant at the modern value of 0.7. The Mg/Ca ratios remained within 5% of their initial values throughout the duration of the experiments. Excluding the Mg/Ca ratios, the seawaters were chemically formulated at normal marine values (Bidwell and Spotte 1985). The seawater treatments were fertilized with 20.0 mg per liter NaNO_3 , 1.3 mg per liter $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$, and 0.025 ml per liter EDTA, all within the normal range for nearshore tropical marine waters (Spotte 1979). All three treatments were continuously filtered with Millennium 2000 Wet-Dry Multi-filters (rate of filtration = 600 liters per hour), maintained at $25 \pm 1^\circ\text{C}$ using 50-watt electric heaters, and provided with ten hours per day of identical irradiance (19 watts).

Specimen Collection.—Young *P. capitatus* specimens were collected from the Florida Bay and the back-reef lagoon of Caye Caulker, Belize. Specimens were stored in plastic bags filled

with natural seawater from these locations and transported by plane to the laboratory at Johns Hopkins University the following day. After transport, the algae were placed in a holding tank of normal salinity for seven days. The algae were acclimated to the artificial seawater treatments in stages, being moved every three days to seawater treatments of successively lower Mg/Ca ratios, so as to minimize any chemical shock they may experience.

Mineralogical Analysis.—Three *P. capitatus* specimens were grown from equal-sized parent algae for 60 days in each of the three seawater treatments (for a total of nine specimens). After growth, the organisms were removed from the seawater treatments, briefly washed with distilled water, and sectioned parallel to their thallus axes. The sectioned specimens were dried in an oven for four hours at 100°C . The three specimens from each of the seawater treatments were secured on carbon mounts with carbon paint, and carbon coated for ten second. The filaments constituting the *P. capitatus* specimens were thoroughly examined in a JEOL 8600 scanning electron microscope for CaCO_3 precipitates. Portions of the thalli and accompanying mineral precipitates were photomicrographed in the SEM. The specimens were then ground to a fine powder and analyzed individually in an X-ray diffractometer to determine carbonate polymorph mineralogy. The proportion of calcite to aragonite was calculated as the ratio of the area under the primary calcite peak ($2\theta = 29.4\text{--}29.5^\circ$) to the area under the primary aragonite peak ($2\theta = 26.2^\circ$) (Milliman 1974).

Linear Growth.—Forty equal-sized parent algae were grown for 60 days in each of the three seawater treatments (for a total of 120 specimens). The *P. capitatus* specimens were photographed every seven days. Linear growth of the parent and offspring algae was measured from the weekly photographs. Average linear growth rates were calculated for the algae over the weeks that they exhibited measurable linear growth.

Calcification and Primary Productivity.—Twenty equal-sized parent algae were grown for 80 days in each of the three seawater treatments (for a total of 60 specimens). The first appearances of offspring algae were noted

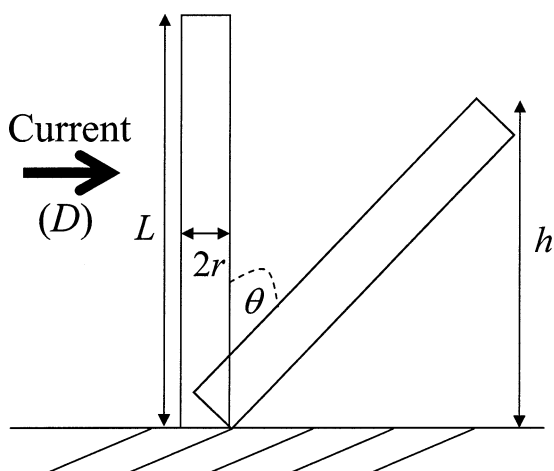


FIGURE 3. Free body diagram of a decapitated *Penicillus* stalk modeled as a cantilever beam stressed by a unidirectional current. Stress (σ) is calculated as $4Dh/(\pi r^3)$, where D is the current velocity, h is the height of the stalk, and r is the radius of the stalk. Note that height (h) decreases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

throughout the experiment. After 80 days, the offspring were harvested and their ages determined relative to the date of their first appearance. The offspring algae were oven dried at 100°C for 24 hours to remove all water content, after which the dry weight of the specimens was determined. The specimens were then baked in an oven at 450°C for four hours to combust all organic matter. The weight of the residual carbonate material was determined and then recorded as their total calcification. The difference between the weight of the residual carbonate material and the original dry weight was recorded as their primary productivity (i.e., organic matter removed by combustion).

Biomechanical Analysis.—The mechanical stiffness of the *Penicillus* thallus can be quantified as the slope of its stress-strain curve during elastic deformation experienced under varying flow regimes in a unidirectional current tank. The cylindrical shape of the *P. capitatus* thallus (Fig. 3) suggests that its stress can be modeled by using a variation on the basic formula of beam theory (Wainwright et al. 1976; Baumiller and Ausich 1996):

$$\sigma = My/I, \quad (1)$$

where σ is stress, M is the bending moment, y

is the distance of the outermost fiber in longitudinal cross-section, and I is the second moment of area (Appendix). Strain can be approximated by the angle of deflection of the thallus when subjected to the current stress.

Three replicate sets of *P. capitatus*, containing three specimens each (nine total), were grown for 60 days in the three artificial seawater treatments formulated at the various Mg/Ca ratios. Each of the *P. capitatus* specimens was photographed and measured after growth (Fig. 4C). The algae were decapitated, clamped with vice grips at their holdfasts, and secured to the bottom of a unidirectional current tank with an ordinary house brick. The current tank is an oval plexiglass loop that circulates water by using a revolving paddle wheel, which can be adjusted to produce varying current velocities.

Because stress-strain analyses of beams typically require an initial dummy unit-load to bring the material into a state of tension (Gaylord and Gaylord 1990), the *P. capitatus* thalli were prestressed with a current velocity sufficient to attain an initial deflection of 5° (Fig. 4A). Once this initial deflection was achieved, the current velocities were increased in increments of 5 cm/second until the thalli exhibited plastic deformation, as stiffness (stress/strain) is only calculated over the range of nonplastic (elastic) deformation. The deflection was photographed after each increase in current velocity (Fig. 4B).

Results

Mineralogical Analysis.—SEM images of the *Penicillus* specimens raised in the three seawater treatments of varying Mg/Ca illustrate that all specimens precipitated the majority of their CaCO_3 as aragonite needles (Fig. 5). However, X-ray diffraction of the powdered specimens revealed that algae grown in the artificial calcite seawater (molar Mg/Ca = 1) produced $22 \pm 3\%$ of their CaCO_3 as low-Mg calcite (4 ± 0.4 mole % MgCO_3) and $78 \pm 3\%$ as aragonite (Fig. 6), whereas specimens grown in the artificial aragonite seawaters produced their CaCO_3 exclusively as aragonite (Table 1).

The aragonite needles ranged from 1 to 4 μm in length and were bundled in apparently

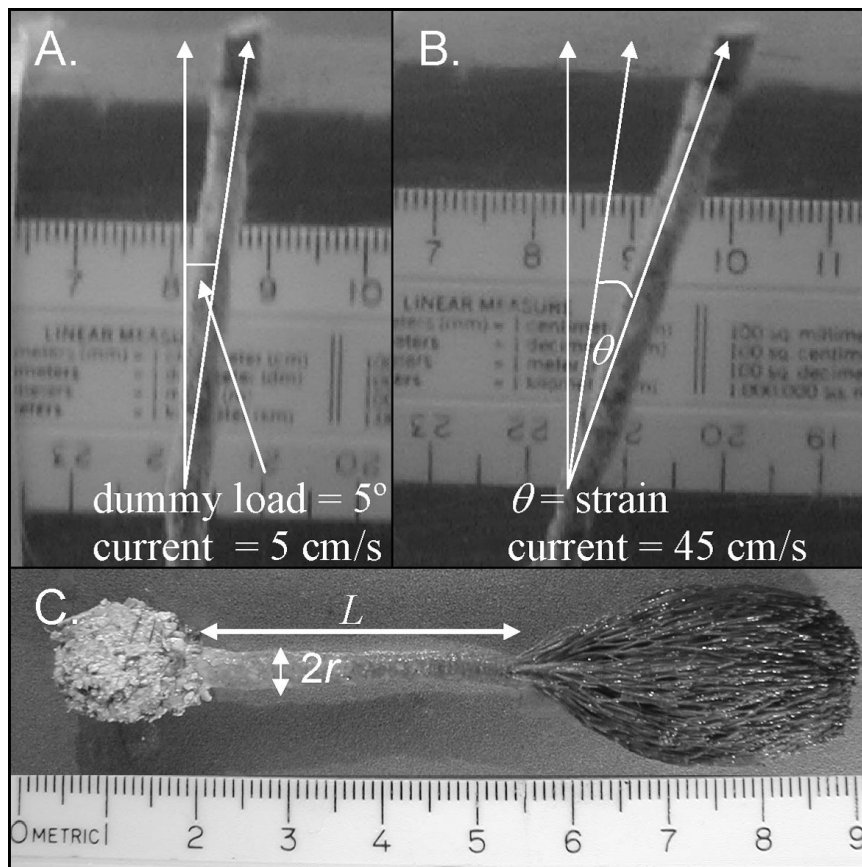


FIGURE 4. A, Decapitated *P. capitatus* thallus pre-strained to 5° deflection with the dummy load (current velocity = 5 cm/s). B, Decapitated *P. capitatus* alga strained beyond the 5° pre-strain dummy load (current velocity = 45 cm/s). Angles of deflection (θ) beyond the 5° pre-strain were used in the stress-strain analyses. C, Photograph of a *P. capitatus* alga depicting the length (L) and radius (r) dimensions used in modeling its thallus as a cantilever beam.

random arrangements in a $10\text{-}\mu\text{m}$ -thick zone between the outer walls of the capitular, medular, and cortical filaments (Fig. 5). The two-dimensional perspective of the SEM made it nearly impossible to quantitatively differentiate between the crystal arrangements of the *Penicillus* raised in the three seawater treatments. However, the aragonite needles produced by all of them were of approximately the same size and shape.

Linear Growth Rates.—Linear growth rates increased significantly ($p < 0.01$) with seawater Mg/Ca (Fig. 7). *Penicillus* grown in the lowest, intermediate and highest Mg/Ca treatments had average linear growth rates (\pm SE) of $0.14 (\pm 0.02)$, $0.75 (\pm 0.07)$, and $1.00 (\pm 0.11)$ mm per day, respectively (Table 1, Fig. 7).

The total number of algae exhibiting growth also varied with Mg/Ca among the seawater treatments. Twenty-six algae exhibited growth in the lowest (molar ratio ~ 1.0) Mg/Ca treatment, whereas 36 and 39 algae exhibited growth in the intermediate (molar ratio ~ 2.5) and highest (molar ratio ~ 5.2) Mg/Ca treatments, respectively.

Calcification and Primary Productivity.—The ages of the offspring algae at the time of harvest were plotted against their total calcification and primary productivity. These results can be interpreted as a timeline of these variables throughout the life span of a single *Penicillus* alga. Rates of calcification and primary productivity were calculated as the slopes of the least-squared linear regressions through

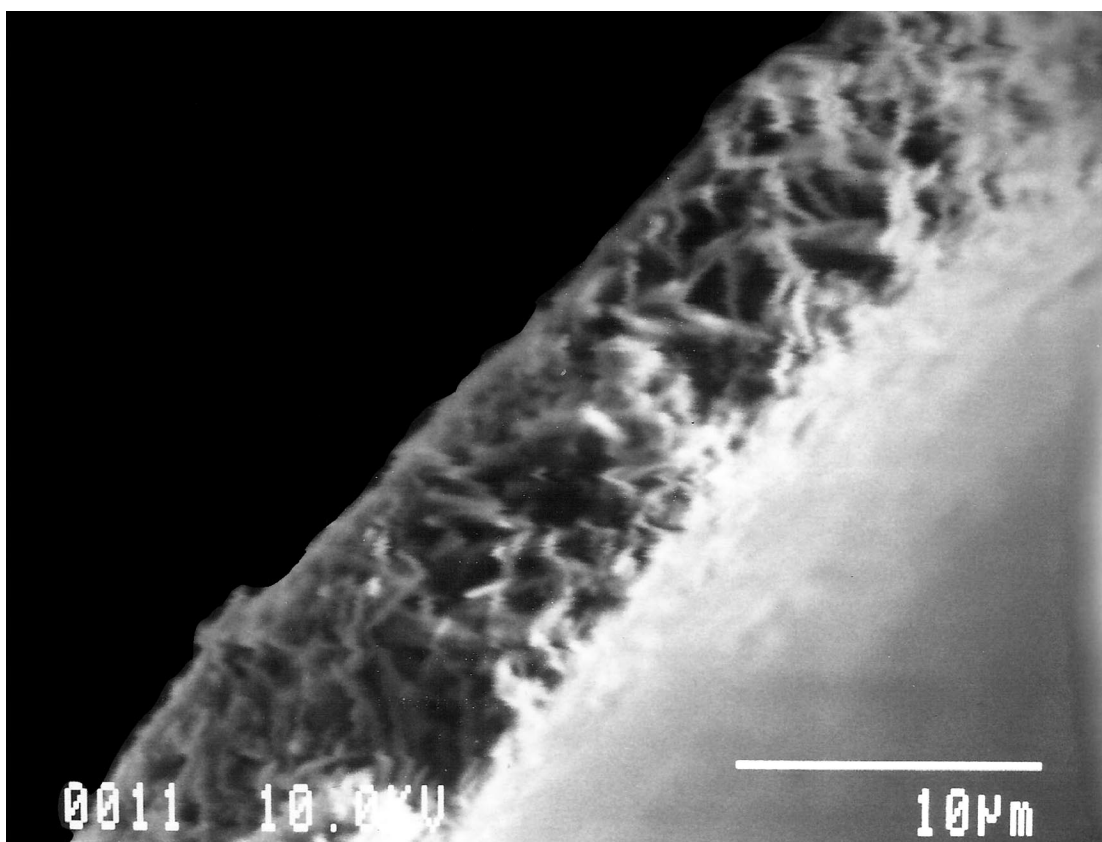


FIGURE 5. Scanning electron micrograph of the calcifying chamber between the inner and outer walls of a medullar filament in a *P. capitatus* thallus grown in seawater of molar Mg/Ca ≈ 1.0 . Despite having grown in artificial seawater favoring the inorganic precipitation of calcite (molar Mg/Ca < 2), the algae precipitated mostly ($78 \pm 3\%$) aragonite needles.

the calcification and primary productivity data (Table 1, Figs. 8, 9).

In the low molar Mg/Ca seawater (~ 1.0), 13 *Penicillus* offspring grew and ranged in age from 32 to 80 days. In the intermediate molar Mg/Ca seawater (~ 2.5), 29 *Penicillus* offspring grew and ranged in age from ten to 60 days. In the high molar Mg/Ca seawater (~ 5.2), 16 *Penicillus* offspring grew and ranged in age from 15 to 61 days. These differences in the age distributions among the three seawater treatments are due to the simultaneous harvest of specimens that vary in their dates of origination. The negative impact of using non-standardized age distributions should be mitigated by the construction of calcification and primary productivity timelines for these populations, where non-standard ages simply define different portions of the same rate curve.

Rates of calcification and primary produc-

tivity increased significantly ($p \ll 0.001$) with seawater Mg/Ca. *Penicillus* grown in the lowest, intermediate, and highest Mg/Ca treatments produced CaCO_3 at average rates ($\pm \text{SE}$) of 0.059 (± 0.034), 0.424 (± 0.065), and 0.697 (± 0.062) mg per day, respectively; and organic matter at average rates ($\pm \text{SE}$) of 0.152 (± 0.044), 0.358 (± 0.039), and 0.869 (± 0.095) mg per day, respectively (Table 1, Figs. 8, 9).

Biomechanical Analysis.—Stress-strain curves were derived for the *Penicillus* specimens by plotting the stress exerted on the thallus against the resulting deflection or strain (occurring beyond the initial 5° dummy-load strain). Strain can be measured as thallus deflection here because all such deflection was due solely to current stress. The thallus stiffness for each *Penicillus* was then calculated as the slope of the least-squared linear regression through this stress-strain curve (Table 2, Fig.

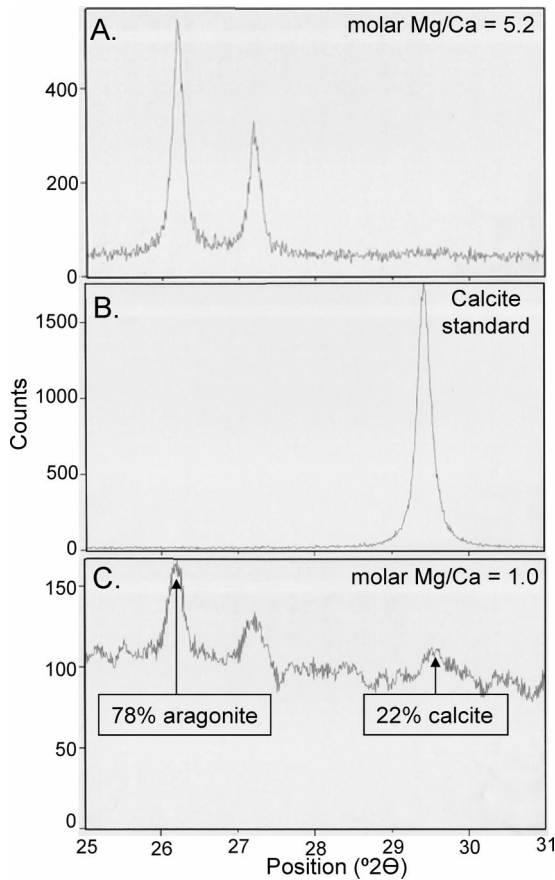


FIGURE 6. A, X-ray diffraction pattern for a *P. capitatus* alga which produced pure aragonite when grown in seawater which favors the nucleation of the aragonite polymorph (molar Mg/Ca = 5.2). Primary aragonite peak occurs at $2\theta = 26.2^\circ$. B, X-ray diffraction pattern for pure calcite, revealing primary calcite peak at $2\theta = 29.4^\circ$. C, X-ray diffraction pattern for a *P. capitatus* alga which produced $22 \pm 3\%$ calcite and $78 \pm 3\%$ aragonite, as calculated from the relative areas under the primary calcite peak ($2\theta = 29.4\text{--}29.5^\circ$) and the primary aragonite peak ($2\theta = 26.2^\circ$).

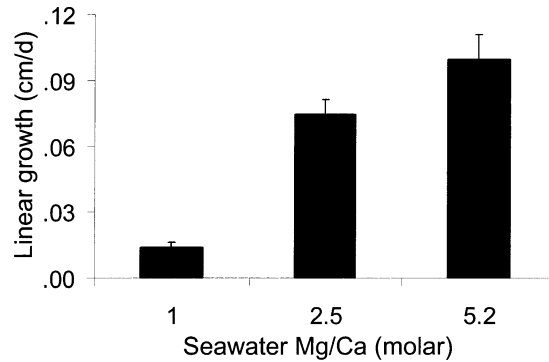


FIGURE 7. Linear growth rates for *P. capitatus* algae grown in all three artificial seawater nucleation fields. Algae grown in the calcite nucleation field (molar Mg/Ca ~ 1.0), which did not favor their aragonite mineralogy, maintained the slowest linear growth rates \pm SE (0.14 ± 0.02 mm per day). Algae grown in the boundary (molar Mg/Ca ~ 2.5) and aragonite + high-Mg calcite (molar Mg/Ca ~ 5.2) nucleation fields exhibited significantly ($p < 0.01$) increasing rates of growth (0.75 ± 0.07 and 1.00 ± 0.11 mm per day respectively).

10). The thallus stiffnesses were averaged for each of the seawater treatments and plotted against the seawater Mg/Ca molar ratio (Fig. 11).

The stiffness of the *Penicillus* thalli increased significantly ($p < 0.001$) with the Mg/Ca ratio of the ambient seawater (Fig. 11). *Penicillus* raised in the lowest Mg/Ca seawater (~ 1.0 ; low-Mg calcite nucleation field) exhibited the lowest stiffness with an average value of 773 (range = 764–779; SD = ± 8.56). *Penicillus* raised in the medium Mg/Ca seawater (~ 2.5 ; just above the low-Mg calcite and high-Mg calcite + aragonite nucleation boundary) exhibited increased stiffness with an average value of 1006 (range = 957–1099; SD = ± 80.4). *Penicillus* raised in the highest Mg/Ca seawater (~ 5.2 ; modern ocean value in the high-Mg calcite + aragonite nucleation field) exhibited

TABLE 1. Summary of mineralogy, linear growth, calcification, primary production, and thallus stiffness for *Penicillus* algae raised in the three seawater treatments. The latter four variables significantly ($p < 0.01$) decrease with reductions in ambient Mg/Ca, ultimately yielding the lowest values in the artificial seawater that supports calcite nucleation (molar Mg/Ca ~ 1.0).

Seawater Mg/Ca (molar)	Mineralogy (% calcite: % aragonite \pm SE)	Linear growth \pm SE (mm/day)	Calcification \pm SE (mg/day)	Primary production \pm SE (mg/day)	Stiffness \pm SD (arbitrary units)
~ 5.2	0:100 ± 3	1.00 ± 0.11	0.697 ± 0.062	0.869 ± 0.095	1310 ± 115.9
~ 2.5	0:100 ± 3	0.75 ± 0.07	0.424 ± 0.065	0.358 ± 0.039	1010 ± 80.42
~ 1.0	22:78 ± 3	0.14 ± 0.02	0.059 ± 0.034	0.152 ± 0.044	773 ± 8.56

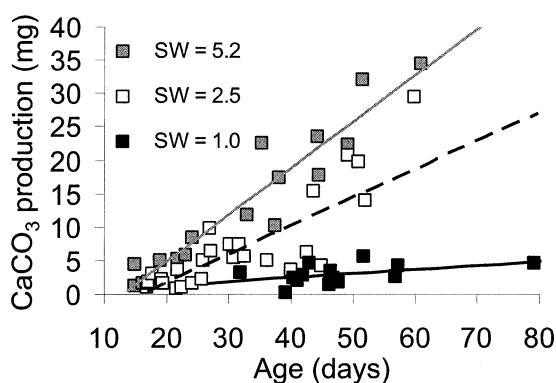


FIGURE 8. Calcification by *P. capitatus* algae of increasing age in the three seawater treatments. Average calcification rates were derived from linear regressions fit to the data using the least-squares method. The solid gray ($y = 0.697x - 9.050$, $R^2 = 0.900$, $SE = 0.062$), broken black ($y = 0.424x - 6.749$, $R^2 = 0.615$, $SE = 0.065$), and solid black ($y = 0.059x + 0.102$, $R^2 = 0.215$, $SE = 0.034$) curves correspond to *P. capitatus* algae raised in the molar Mg/Ca ~ 5.2 , ~ 2.5 , and ~ 1.0 treatments, respectively, and reveal average calcification rates decreasing significantly ($p \ll 0.001$) in that order.

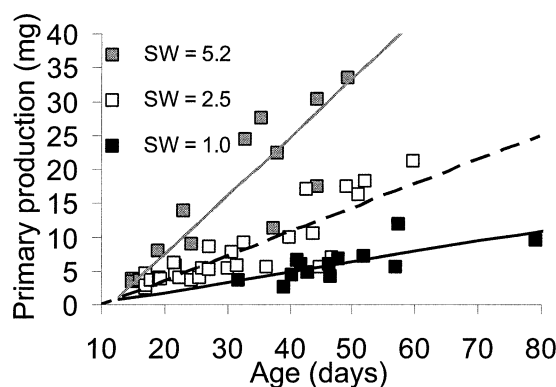


FIGURE 9. Primary productivity by *P. capitatus* algae of increasing age in the three seawater treatments. Average primary production rates were derived from linear regressions fit to the data using the least-squares method. The solid gray ($y = 0.8685x - 9.961$, $R^2 = 0.856$, $SE = 0.095$), broken black ($y = 0.358x - 3.584$, $R^2 = 0.754$, $SE = 0.039$), and solid black ($y = 0.152x - 1.224$, $R^2 = 0.517$, $SE = 0.044$) curves correspond to *Penicillus* algae raised in the molar Mg/Ca ~ 5.2 , ~ 2.5 , and ~ 1.0 treatments, respectively, and reveal primary production rates decreasing significantly ($p \ll 0.001$) in that order.

the greatest stiffness with an average value of 1307 (range = 1221–1439; $SD = \pm 116$).

Discussion

It is significant that the *P. capitatus* algae grown in the low-Mg calcite nucleation field still precipitated most of their CaCO_3 as aragonite needles ($78 \pm 3\%$). The kinetics of CaCO_3 precipitation from seawater dictate that the abiotic precipitation of aragonite should occur only when the molar Mg/Ca ratio is greater than two, whereas calcite precipitation should occur only when the molar Mg/Ca ratio is less than two (Leitmeier 1910, 1915; Lippman 1960; Müller et al. 1972; Folk 1974;

Füchtbauer and Hardie 1976, 1980). It therefore seems reasonable that the biologically mediated precipitation of aragonite in the low-Mg calcite nucleation field would proceed at a slower rate than it would in the aragonite + high-Mg calcite nucleation field. This explains why the calcification rate of the *Penicillus* specimens was greatest in the aragonite + high-Mg calcite nucleation field, lower in the boundary field, and lowest in the low-Mg calcite nucleation field. However, this does not explain why linear growth and primary productivity were also reduced in seawater treatments of decreased Mg/Ca. The answer may concern CO_2 .

TABLE 2. Linear regressions and statistics used to calculate stiffnesses of nine *Penicillus* thalli grown in the three seawater treatments. Stiffness decreases significantly ($p < 0.001$) with reductions in ambient Mg/Ca.

Nucleation field	Specimen	Linear regression	R^2	Stiffness	Avg. stiffness	SD
Aragonite + high-Mg calcite (Mg/Ca ~ 5.2)	5.2(a)	$y = 1439x + 1003.3$	0.9788	1439	1307	± 115.9
	5.2(b)	$y = 1221x + 1311$	0.9865	1221		
	5.2(c)	$y = 1262x - 119.9$	0.9810	1262		
Boundary (Mg/Ca ~ 2.5)	2.5(a)	$y = 1099x + 396.7$	0.9959	1099	1006	± 80.42
	2.5(b)	$y = 956.5x + 284.4$	0.9832	956.5		
	2.5(c)	$y = 963.5x + 636.4$	0.9654	963.5		
Low-Mg calcite (Mg/Ca ~ 1.0)	1.0(a)	$y = 763.5x + 707.1$	0.9459	763.5	773.3	± 8.555
	1.0(b)	$y = 777.3x + 293.3$	0.9887	777.3		
	1.0(c)	$y = 779.2x - 451.4$	0.9174	779.2		

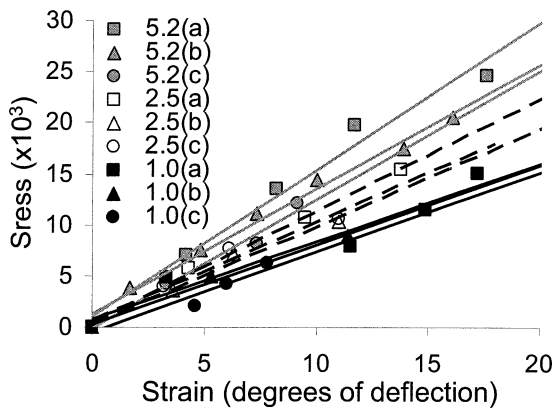


FIGURE 10. Stress-strain data generated for the thalli of nine *Penicillus* algae grown in the three seawater treatments. Stress-strain curves were generated by fitting linear regressions to the data using the least-squares method. The solid gray, broken black, and solid black curves correspond to *Penicillus* thalli grown in the molar Mg/Ca ~5.2, ~2.5, and ~1.0 artificial seawater treatments, respectively, and reveal thallus stiffness decreasing significantly ($p < 0.001$) in that order. Average stiffness was calculated from the slopes of these stress-strain curves (Table 2).

It has been shown that the codiacean algae *Udotea* and *Halimeda* will increase primary productivity (photosynthesis) when subjected to elevated levels of CO_2 (Reiskind et al. 1988, 1989):



Furthermore, the precipitation of CaCO_3 releases CO_2 to the ambient seawater:



Therefore, it has been proposed that calcareous green algae such as the Codiaceae (Borowitzka and Larkum 1976; Borowitzka 1977) and the coccolithophores (Paasche 1968; Sikes et al. 1980; Stanley et al. in press) utilize CO_2 liberated by calcification to support their own photosynthesis. This would explain the synchronicity between calcification and linear growth/primary productivity, with respect to ambient Mg/Ca, as observed in the present study. *Penicillus* precipitates aragonite more slowly outside of the aragonite + high-Mg calcite nucleation field, thereby liberating less CO_2 in seawater adjacent to the alga and producing less organic matter via reduced photosynthesis.

The fact that *Penicillus* still produces mostly

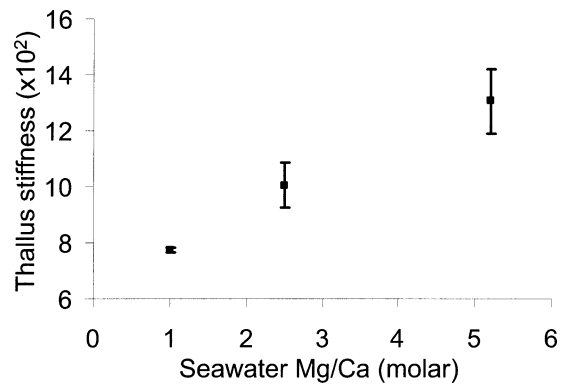


FIGURE 11. Plot of ambient molar Mg/Ca vs. average thallus stiffness for three replicate sets of *Penicillus* algae. Thallus stiffness is greatest in algae grown in seawater that supports their inherent aragonitic mineralogy (molar Mg/Ca ~5.2), least in seawater that supports calcite nucleation (molar Mg/Ca ~1.0), and intermediate in seawater near the nucleation field boundary (molar Mg/Ca ~2.5). Error bars are SD.

aragonite in the low-Mg calcite nucleation field suggests that the alga somehow forces the precipitation of the aragonite polymorph. This could be accomplished either by transcellular pumping of cations to re-create the aragonite nucleation field or by employment of an organic template which fosters the nucleation of the orthorhombic aragonite crystal structure (Borowitzka 1984). However, the observation that 22% of the alga's CaCO_3 is precipitated as the kinetically-favored low-Mg calcite polymorph suggests that the alga's biological control over its carbonate mineralogy is somewhat limited and can be partially overridden by ambient seawater chemistry.

The biomechanical analysis of *Penicillus* raised in the various seawater treatments empirically tests the physiological impact of an organism precipitating a CaCO_3 polymorph from seawater outside of that polymorph's natural nucleation field. The stress tests show that *Penicillus* thalli grown in the boundary and low-Mg calcite nucleation fields exhibited progressively decreasing stiffnesses. The results of the other experiments presented in this paper suggest that such decreased stiffness is attributable to depressed rates of calcification, linear growth, and primary productivity associated with the precipitation of aragonite from seawater outside (or on the boundary) of the aragonite nucleation field.

Such findings suggest that *Penicillus*, and possibly other aragonite-precipitating codiacean algae, would have been slower-growing, smaller, less calcified, and less stiff prior to 30 Ma, when seawater did not support the aragonite polymorph (molar Mg/Ca <2). These disadvantages would have had significant biological implications for *Penicillus* and related aragonitic algae. Their slow growth rates and small size would have handicapped them with respect to competition for space and sunlight on the shallow tropical seafloor. Their weak calcification and reduced stiffness would have made them more susceptible to predation by grazing fish, which in modern seas are deterred by the algae's high CaCO₃ content (Wray 1977; Paul and Van Alstyne 1988; Schupp and Paul 1994). Such reduced stiffness could have prevented some algae from standing upright to receive maximum light on the seafloor, although such an extreme condition was not observed in the present study.

Low Mg/Ca ratios in seawater would also have had sedimentological implications for aragonitic algae. Reduced rates of calcification would have reduced the algae's contribution of biogenic aragonitic needles to carbonate mud during times of low oceanic Mg/Ca. In contrast, Recent carbonate muds, deposited in tropical seas that supported the nucleation of aragonite, are primarily composed of aragonitic needles believed to be algal in origin (Lowenstam and Epstein 1957; Stockman et al. 1967; Neumann and Land 1975; Hillis 1991).

Conclusions

The following conclusions can be drawn from the present study:

1. *Penicillus capitatus* algae precipitate most of their CaCO₃ as aragonite needles, even in artificial seawater which favors the nucleation of the low-Mg calcite polymorph (molar Mg/Ca <2). This suggests that codiacean algae either control local Mg/Ca by pumping cations or employ an organic template to specify precipitation of the aragonite polymorph (Borowitzka 1984). The partial precipitation of low-Mg calcite (22 ± 3%) in the calcite seawater suggests that the algae's mineralogical control is somewhat limited and can be partially overridden by the Mg/Ca ratio of ambient seawater.
2. Linear growth, calcification, and primary productivity decreased for *P. capitatus* specimens grown in seawater that does not support the nucleation of the aragonite polymorph. Reduced liberation of CO₂ through reduced calcification may result in the reduced rates of linear growth and primary productivity observed in the experiments (Borowitzka and Larkum 1976; Borowitzka 1977).
3. Thallus stiffness decreased for *P. capitatus* specimens grown in seawater that does not support the aragonite polymorph. This physiological consequence of reduced Mg/Ca may be the result of decreased calcification and associated reductions in growth rate and primary productivity.
4. The results of the present study support Stanley and Hardie's (1998, 1999) assertion that the dominant ecological and sedimentological roles of codiacean algae in Recent tropical seas is due to the Mg/Ca ratio of seawater supporting the algae's aragonitic mineralogy during this time. It appears that producing aragonite in seawater that does not support that polymorph would have reduced the competitiveness of these algae, made them more susceptible to predation, and reduced their contribution to carbonate sedimentation.

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Appendix

Modeling the *Penicillus* Thallus as a Beam

The cylindrical shape of the *P. capitatus* thallus suggests that its stress-strain properties can be modeled using the basic formula of beam theory (Wainwright et al. 1976; Baumiller and Ausich 1996):

$$\sigma = My/I, \quad (1)$$

where σ is stress, M is the bending moment, y is the distance of the outermost fiber in longitudinal cross-section, and I is the second moment of area.

Because the *P. capitatus* thallus is circular in cross-section and consists of a relatively homogeneous matrix of organic filaments that are encased in micrometer-scale aragonite crystals (Fig. 2) (Wray 1977), y in equation (1) may be replaced with the radius (r) of the *P. capitatus* thallus:

$$\sigma = Mr/I. \quad (4)$$

The second moment of area (I) for a circular section of radius (r) is

$$I = (\pi r^4)/4. \quad (5)$$

Therefore, substituting equation (5) into equation (4) yields

$$\sigma = Mr/[(\pi r^4)/4], \text{ or } \sigma = 4M/(\pi r^3). \quad (6)$$

Furthermore, the *Penicillus* thallus can be modeled as a simple cantilever whose bending moment is given by

$$M = Dh, \quad (7)$$

where D is the drag (due to water current) exerted on the thallus and h is its height above ground (Fig. 3). Therefore, substituting equation (7) into equation (6) yields the stress formula that is the basis of this biomechanical analysis:

$$\sigma = 4Dh/(\pi r^3). \quad (8)$$

In this experiment, where drag (D) on the thallus is due to water current, the water current velocity can be substituted as a proxy for drag.

The stress function (σ) of a specimen with a given radius (r) will vary with respect to the current drag (D) exerted on the specimen. However, height (h), or the vertical component of the structure, will also vary with respect to the angle of deflection (θ), so that

$$h = L \cos \theta, \quad (9)$$

where L is the length of the *Penicillus* stalk (Fig. 3). Therefore, the height value (h) must be recalculated for successive angles of deflection.