

ARAGONITIC ALGAE IN CALCITE SEAS: EFFECT OF SEAWATER Mg/Ca RATIO ON ALGAL SEDIMENT PRODUCTION

JUSTIN B. RIES

Morton K. Blaustein Department of Earth and Planetary Sciences, Johns Hopkins University, Baltimore, Maryland 21218, U.S.A.
e-mail: jries@jhu.edu

ABSTRACT: Secular variation in seawater Mg/Ca would have subjected the aragonite-producing codiacean algae to two intervals of low-Mg calcite seas ($m\text{Mg}/\text{Ca} < 2$) and two intervals of aragonite + high-Mg calcite seas ($m\text{Mg}/\text{Ca} > 2$) seas since their origin in the Ordovician. It is asserted that the aragonite + high-Mg calcite affinity of modern and Recent tropical seas ($m\text{Mg}/\text{Ca} > 2$) has enabled the aragonitic Codiaceae to act as major carbonate sediment producers in these seas. To test this assertion, specimens of the sediment-producing codiacean alga *Udotea flabellum* were grown in artificial seawaters formulated at $m\text{Mg}/\text{Ca}$ ratios (1.0, 2.5, 5.2) that have occurred in the oceans throughout the geologic history of the Codiaceae.

While the *U. flabellum* algae produced exclusively aragonite in both the artificial boundary seawater ($m\text{Mg}/\text{Ca} = 2.5$) and the artificial aragonite + high-Mg calcite seawater (modern seawater; $m\text{Mg}/\text{Ca} = 5.2$), the algae produced a portion ($25 \pm 3\%$) of their CaCO_3 as low-Mg calcite ($\leq 4 \text{ mol}\% \text{ MgCO}_3$) in the artificial calcite seawater ($m\text{Mg}/\text{Ca} = 1.0$), suggesting that their CaCO_3 polymorph control can be partially overridden by ambient seawater chemistry.

Primary productivity, calcification, and linear growth of the algae decreased with reductions in ambient Mg/Ca, despite increases in absolute Ca concentration of the seawater. Reduced calcification in the lower Mg/Ca seawaters is probably due to kinetic difficulties of producing aragonite from seawater that favors the nucleation of calcite. The decreased linear growth and primary production are likely associated with reductions in the ambient CO_2 available for photosynthesis, resulting from the reduced calcification.

These findings support the assertion that the dominant ecological and sedimentological roles of codiacean algae in Recent tropical seas is facilitated by a seawater Mg/Ca ratio that favors the nucleation of aragonite over calcite. Furthermore, producing aragonite in seawater that favors the nucleation of low-Mg calcite ($m\text{Mg}/\text{Ca} < 2$) may have reduced the rates of growth and calcification of codiacean algae, making them less competitive for space on the shallow tropical seafloor and more susceptible to predatory grazing, thereby reducing their contribution to carbonate sedimentation.

INTRODUCTION

The polymorph mineralogies of the major reef-building and sediment-producing calcareous marine organisms have tracked transitions in the polymorph mineralogies of ooids and marine cements, the so-called calcite and aragonite seas (Sandberg 1983), throughout the Phanerozoic (Stanley and Hardie 1998, 1999) (Fig. 1). Secular variation in the Mg/Ca ratio of seawater, driven mainly by fluctuations in the rate of ocean crust production and believed to be responsible for the observed calcite–aragonite sea pattern throughout the Phanerozoic (Hardie 1996), would have subjected the codiacean algae to three transitions between high-Mg calcite + aragonite ($m\text{Mg}/\text{Ca} > 2$) and low-Mg calcite ($m\text{Mg}/\text{Ca} < 2$) nucleation fields in the oceans since their origin in the Ordovician (Roux 1991a; Stanley and Hardie 1998, 1999) (Fig. 1). It has been proposed that the role of the codiacean algae as major producers of carbonate sediment in Recent tropical seas has been permitted by the molar Mg/Ca of Recent seawater (~ 5.2) remaining within the nucleation field of the aragonite polymorph, thereby supporting the inherent aragonitic mineralogy of these algae (Stanley and Hardie 1998, 1999). This assertion is particularly intriguing in that it connects plate tectonics to carbonate sedimentology, via marine geochemistry and paleobiology (Montañez 2002).

Here I evaluate the relationship between seawater Mg/Ca and algal biomineralization experimentally by growing a modern aragonite-producing codiacean alga, *Udotea flabellum*, in artificial seawaters formulated at Mg/Ca ratios believed to have existed (Hardie 1996) since the apparent origination of the Codiaceae in the Ordovician.

This study complements previous work (Ries 2005) showing that the growth and calcification of the codiacean alga *Penicillus capitatus*, another major sediment producer in Recent tropical seas, was significantly reduced when grown in artificial calcite seawater. Other related work on the subject has revealed that coralline algae (Stanley et al. 2002; Ries in press), echinoids, serpulid worms, crabs, shrimp (Ries 2004), and some species of coccolithophores (Stanley et al. 2005), which naturally secrete high-Mg calcite in modern aragonite seas, actually change their mineralogy to low-Mg calcite when grown in artificial seawaters formulated at Mg/Ca ratios that characterize calcite seas ($m\text{Mg}/\text{Ca} < 2$).

BACKGROUND

Anatomy

Udotea is an upright-standing, fan-shaped alga whose anatomy can be divided into three basic components: fan; thallus; and holdfast (Fig. 2A).

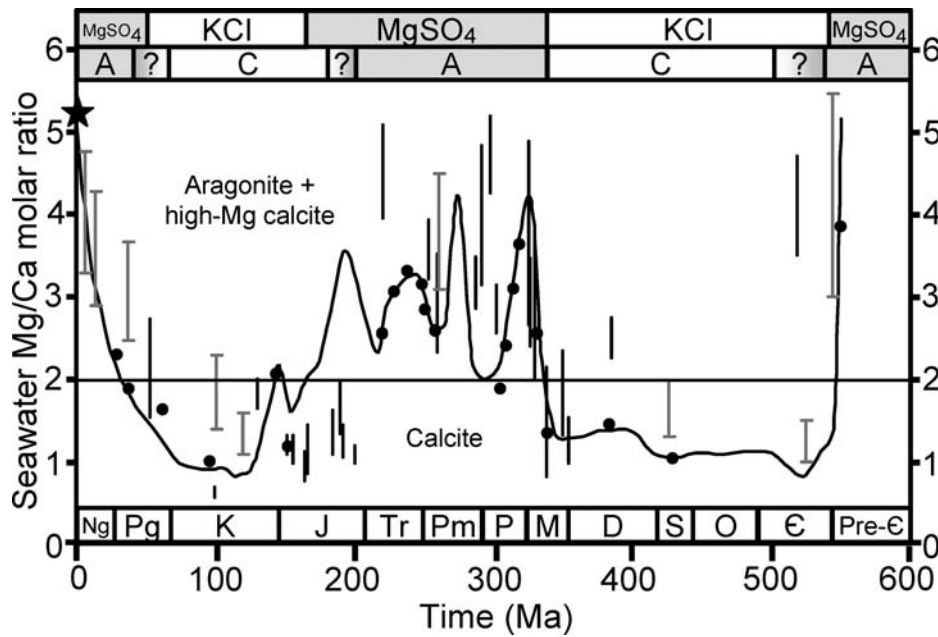


FIG. 1.—Evidence and predictions of secular variation in the Mg/Ca of seawater throughout the Phanerozoic that supported three periods of aragonite + high-Mg calcite nucleation and two periods of calcite nucleation. Curve is molar Mg/Ca ratio predicted from established rates of ocean crust production (Hardie 1996). Black vertical bars are molar Mg/Ca ranges calculated from the Mg content of fossil echinoderms (Dickson 2002, 2004). Solid black circles are molar Mg/Ca values estimated from Br in basal marine halite (Siemann 2003). Gray vertical bars with t-tops are molar Mg/Ca ranges estimated from fluid inclusions in marine halite (Lowenstein et al. 2001, 2003). The star represents modern seawater chemistry ($m\text{Mg}/\text{Ca} = 5.2$). The horizontal line divides the calcite ($\text{Mg}/\text{Ca} < 2$) and aragonite + high-Mg calcite ($\text{Mg}/\text{Ca} > 2$) nucleation fields in seawater of 25°C . Intervals of abiotic aragonite (“A”) and calcite (“C”) precipitates (Sandberg 1983) and KCl and MgSO_4 marine evaporites (Hardie 1996) are plotted along the top of the figure (modified from Lowenstein et al. 2001).

The thallus (stalk) comprises medullar filaments, which run parallel to the thalial axis, and cortical filaments, which branch laterally from the medullar filaments (Fritsch 1948; Colombo 1978). The cortical filaments are terminated by small swellings, called utricles, which form the external surface of the thallus. The medullar filaments in the fan (Fig. 2A) are heavily branched and lobed (Fig. 2C). These lobate filaments interweave and coalesce to form the apparently continuous surface (cortex) of the mature fan (Fig. 2E) (Fritsch 1948). Both the cortical and medullar filaments have an inner (Fig. 2D, *iw*) and outer filament wall (*ow*), which are divided by an organic layer (*ol*). The two filament walls and the space

between them are collectively referred to as the filament sheath (*f*). Unlike *Halimeda* and *Penicillus*, the filament sheaths within *Udotea flabellum* lack pores (Böhm et al. 1978). The holdfast (Fig. 2A), 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 (Fig. 2B) grow from rhizoids sent out from the holdfast within the sediment.

Photosynthesis occurs within chloroplasts contained in the cytoplasm within the medullar and cortical filaments. *Udotea* is considered the most primitive plant with a C4-like method of photosynthesis, and has called

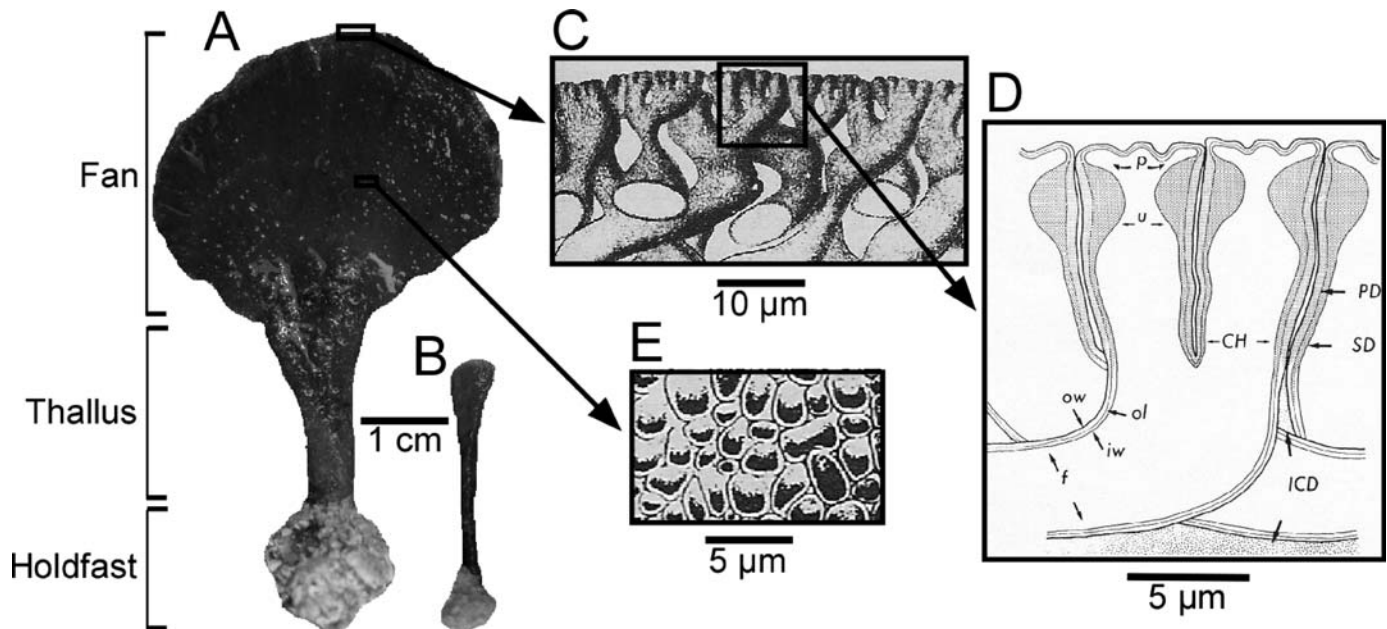


FIG. 2.—Anatomical detail of the alga *Udotea flabellum*. A) Full-grown plant revealing uncalcified holdfast, calcified thallus, and calcified fan. B) Young alga. C) Vertical section of surface of fan showing cortex and individual utricles. D) Vertical section through cortical layer; *u* = utricles, *p* = utricles protrusions, *f* = filament, *ow* = outer filament wall, *iw* = inner filament wall, *ol* = organic layer within filament wall, *CH* = chimney system, *PD* = primary deposit, *SD* = secondary deposit, *ICD* = intercellular deposit (after Böhm et al. 1978; Fritsch 1948). E) Cortication of surface of thallus.

into question the terrestrial origin of this CO₂-efficient process (Reiskind et al. 1988, 1989; Reiskind and Bowes 1991)

Calcification

Calcification in *U. flabellum* occurs as aragonitic needles (< 15 µm long), prisms (0.5 µm long), and serrated crystals (1.0 µm long) precipitated intracellularly within the filament sheath (between the inner and outer filament walls) and intercellularly in the space between the filaments themselves (Fig. 2D). The filament sheath contains an organic layer (*ol*) that divides the space (Fig. 2D). Aragonite deposited between the outer filament wall (*ow*) and the organic layer (*ol*) has been termed primary deposit (*PD*), while aragonite deposited between the inner filament wall (*iw*) and the organic layer (*ol*) has been termed secondary deposit (*SD*) (Fig. 2D) (Friedman et al. 1972; Borowitzka et al. 1974; Borowitzka and Larkum 1977; Flajs 1977; Böhm et al. 1978; Borowitzka 1984; Kooistra 2002). Mature thalli can contain between 25 and 59 wt % aragonite. While the purpose of algal calcification has been debated, its most common explanation is for rigidity in turbulent hydraulic environments and for protection from grazing predation, especially when combined with acidic, toxic secondary compounds and nocturnal growth (Wray 1977; Paul and Van Alstyne 1988; Hay et al. 1994; Schupp and Paul 1994; Hay 1997; Kooistra 2002).

Geologic History of *Udotea*

The codiacean algae have existed since at least the Ordovician, inasmuch as the Ordovician alga *Dimorphosiphon* demonstrates a level of organization very similar to that of the modern *Halimeda* (Mu 1991). Subsequent to their origin in the Early Ordovician, the Codiaceae have exhibited high levels of diversity and abundance in the Silurian–Devonian, the Permian, and the Cenozoic (Chuvashov and Riding 1984; Barattolo 1991; Flügel 1991; Mamet 1991; Mu 1991; Riding and Guo 1991; Roux 1991a, 1991b; Kooistra 2002). However, the acme of diversity and abundance of known *aragonitic* Codiaceae began in the early–middle Cenozoic and has continued until the present (Elliot 1984; Flügel 1988, 1991; Hillis 1991), an interval over which the Mg/Ca ratio of seawater has favored the precipitation of aragonite over calcite.

While it is evident that some Codiaceae have flourished in purported calcite-sea intervals, our poor understanding of the original polymorph mineralogy and phylogenetic relationships of these ancient groups precludes our meaningful interpretation of them in the context of long-term secular variation in seawater chemistry. This study is concerned primarily with the more recent transition from coccolithophore (calcite)-dominated carbonate production (Stanley et al. 2005) to Codiaceae (aragonite)-dominated carbonate production, which occurred concomitantly with the transition from calcite to aragonite seas in the early–middle Cenozoic (Stanley and Hardie 1998, 1999).

The most abundant codiacean algae in modern tropical seas are *Udotea*, *Penicillus*, and *Halimeda* (Wray 1977; Hillis 1991). However, analysis of nuclear-encoded ribosomal DNA (Zechman et al. 1990) reveals that *Penicillus* and *Udotea* are the most closely related, suggesting that the brush of the former alga is merely the uncorticated blade of the latter. Alternatively, *Halimeda* was shown to be the most phylogenetically distant.

Ecology and Biogeography

Udotea typically grows in the tropics (> 25°C) on unconsolidated substrata in low energy backreef, lagoon, and bay environments up to 40 m in depth (Hillis 1991). It is less stenothermic than other codiacean algae (such as *Penicillus* and *Halimeda*), inasmuch as three *Udotea* species have been identified growing in the subtropical Atlantic waters off the coast of North Carolina (Hillis 1991). The alga is 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 tropical Indian, Pacific, and Atlantic Ocean localities (Hillis 1991). The alga grows rapidly, attaining a height of up to 20 cm over its 1 to 3 month lifespan. *Udotea* densities up to 8 algae m⁻² have been reported in southern Florida (Neumann and Land 1975).

Sedimentary Production

The codiacean algae have been contributing to carbonate sedimentation since at least Ordovician time (Mu 1991; Roux 1991a). Modern codiacean algae of the genera *Halimeda*, *Penicillus*, and *Udotea* are among the most important carbonate sediment producers and bioherm builders in Recent and 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; Hillis 1991; Mu 1991).

Rates of carbonate sediment production in Recent codiacean algae-dominated marine environments are estimated to range from 0.18 to 5.9 m 1000 y⁻¹ (Hillis 1991). Such rapid rates of carbonate accretion by these algae, attributable to their relatively large size (up to 20 cm in height), short lifespans (1–3 months; i.e., rapid turnover), high rates of growth (up to 2 mm d⁻¹), high population densities (76–109 algae m⁻²), and global distribution throughout the shallow tropical environments of the Caribbean and Mediterranean Seas (Hillis-Colinvaux 1980), Great Barrier Reef (Drew and Abel 1988), and Indo-Pacific Ocean (Hillis 1991), suggest that they could be responsible for much of the aragonite mud deposited in Recent tropical marine environments (Stockman et al. 1967; Neumann and Land 1975; Hillis 1991). Carbon and oxygen isotopes support this assertion (Lowenstam and Epstein 1957). However, recent studies have shown that unicellular green algae and cyanobacteria are also capable of producing significant quantities of calcium carbonate sediments (Yates and Robbins 1998, 2001).

It should also be noted that estimates of algal contribution to carbonate sedimentation based solely on recognizable skeletal debris in sediment cores are only between 11 and 29 wt % (Cloud 1962; Bathurst 1975). This may be attributable to the codiacean algae's lack of discrete anatomical components that are easily recognized in sediment samples. Unlike coral, urchin, and mollusk fragments, most codiacean algae rapidly break down into ambiguous aragonite needles, unidentifiable at the organismal level. Therefore, the quantification of *Udotea*'s contribution to carbonate sediment production, based solely on recognizable skeletal debris, may be low.

Seawater Chemistry

The molar Mg/Ca ratio of seawater has fluctuated between approximately 1.0 and 5.2 throughout the Phanerozoic, probably 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 Ca²⁺ and K⁺ to the seawater and removing Mg²⁺ and SO₄²⁻ 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. Therefore, high rates of ocean crust production result in relatively low seawater Mg/Ca ratios, as existed during the Cretaceous Period. The secular variation of oceanic Mg/Ca is revealed by the coupling of MgSO₄ evaporites with aragonite biotic and abiotic precipitates (favored by low concentrations of Ca relative to SO₄ at the point of gypsum saturation and high Mg/Ca ratios, respectively) and the coupling of KCl evaporites with calcite biotic and abiotic precipitates (favored by high concentrations of Ca relative to SO₄ at the point of gypsum saturation and low Mg/Ca ratios, respectively) (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).

Laboratory experiments on the $\text{MgCl}_2\text{-CaCl}_2\text{-Na}_2\text{CO}_3\text{-H}_2\text{O}$ system revealed that ambient Mg/Ca ratio, ionic strength, and temperature determine the precipitation of calcite versus aragonite + high-Mg calcite from seawater (Füchtbauer and Hardie 1976, 1980). The Mg/Ca mole ratio value of 2 (± 0.5) was determined to be the boundary between the calcite ($m\text{Mg}/\text{Ca} < 2$) and aragonite + high-Mg calcite ($m\text{Mg}/\text{Ca} > 2$) 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 values calculated from established rates of ocean crust production (Hardie 1996) predict that the oceans would have transitioned between the aragonite + high-Mg calcite and low-Mg calcite nucleation fields four times throughout the Phanerozoic, thereby predicting a pattern of aragonite and calcite seas that is consistent with the mineralogical record of ooids and marine cements (Sandberg 1983) and skeletal carbonates (Stanley and Hardie 1998, 1999) throughout the Phanerozoic.

METHODS

Preparation of Artificial Seawater

Three 10-gallon glass aquaria were each filled with 30 L of artificial seawater 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). Excluding the concentrations of Mg and Ca, the artificial seawaters were identically formulated at normal marine values (Bidwell and Spotte 1985). Their ionic strengths were held constant at the modern value of 0.7. Mg/Ca ratios remained within 5% of their initial values throughout the duration of the experiments. The aquaria were fertilized with 20.0 mg/L NaNO_3 , 1.3 mg/L $\text{NaH}_2\text{PO}_4\cdot\text{H}_2\text{O}$, and 0.025 mL/L EDTA, all within the normal range for nearshore tropical marine waters (Spotte 1979). The aquaria were maintained at $25 \pm 1^\circ\text{C}$ using 50-watt electric heaters, illuminated with 10 hours/day of identical irradiance (19 watts), and continuously filtered with Millennium 2000 Wet-Dry Multi-filters (rate of filtration = 600 L/hour).

Specimen Collection

Young *U. flabellum* algae were collected from the back-reef lagoon of Caye Caulker, Belize. Specimens were stored in plastic bags filled with natural seawater from these locations and transported by airplane to the laboratory at Johns Hopkins University the following day. After transport, the algae were placed in a holding tank of normal salinity for 7 days. The algae were acclimated to the artificial seawater treatments in stages, being moved every 3 days to seawater treatments of successively lower Mg/Ca ratios, so as to minimize any chemical shock.

Mineralogical Analysis

Three *U. flabellum* offspring specimens were grown from comparably sized parent algae in each of the three seawater treatments (nine specimens total). After 60 days of growth, the organisms were removed from the seawater treatments and lightly rinsed for 10 seconds with distilled water. The specimens were sectioned parallel to their thallus axes, from their holdfasts to the upper tips of their fans, and dried in an oven for 4 hours at 100°C . Carbon paint was used to secure the specimens to cylindrical SEM carbon mounts, which were then carbon coated for 1 min. The *U. flabellum* specimens were thoroughly examined in a JEOL

8600 scanning electron microscope for CaCO_3 precipitates. Back-scatter electron images of the mineral precipitates within the thalli of the algae were obtained in the SEM. Each of the algae was ground to a fine powder and mixed with ethyl alcohol to create a suspension that was allowed to dry overnight on a glass slide, forming an equally thick layer of CaCO_3 crystals, which was analyzed for polymorph mineralogy using powder X-ray diffraction. The proportion of calcite to aragonite was calculated from the X-ray diffraction pattern as the ratio of the area under the primary calcite peak [$d(104)$; 3.03–3.04 Å; $2\theta = 29.4\text{--}29.5^\circ$] to the area under the primary aragonite peak [$d(111)$; 3.40 Å; $2\theta = 26.2^\circ$].

Linear Growth, Calcification, and Primary Productivity

Forty equal-sized parent algae were grown for 80 days in each of the three seawater treatments (for a total of 120 specimens). These specimens were grown simultaneously and in the same aquaria as those analyzed for their mineralogical attributes. Over the duration of the experiment, most of the parent algae produced offspring algae. The first appearances of offspring algae were noted throughout the experiment. The parent and offspring *U. flabellum* specimens were scale-photographed every seven days. Linear growth of the offspring algae was measured from the weekly photographs. Average linear growth rates were calculated for the offspring algae over the weeks that they exhibited measurable growth.

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

RESULTS

Mineralogical Analysis

Back-scatter electron images of the *U. flabellum* offspring algae reveal that they all precipitated aragonite needles throughout their organic tissue, regardless of the Mg/Ca ratio of the artificial seawater in which they were grown (Fig. 3). The needles are mostly between 1 and 4 μm in length and are packed in apparently random arrangements throughout a 10- μm -thick zone between the outer walls of their medular and cortical filaments (Fig. 2). However, as indicated in Figure 3 (A, B), there is evidence of another mineral precipitate intermixed with the aragonite needles that clearly lacks the acicular habit of the aragonite crystals. Powder X-ray diffraction of the mineral precipitates produced by the algae reveals that the specimens grown in the artificial calcite seawater actually produced 25 (± 3) % of their CaCO_3 as the low-Mg calcite polymorph (≤ 4 mol% MgCO_3) and 75 (± 3) % as the aragonite polymorph (Fig. 4). XRD patterns (Fig. 4A) and SEM imaging (Fig. 3C–D) of the algae grown in the aragonite and boundary artificial seawaters reveal that they produced aragonite exclusively.

Linear Growth Rates, Calcification, and Primary Productivity

The total number of offspring algae produced varied among the different artificial seawater treatments. Twenty-three offspring algae grew in the normal Mg/Ca (~ 5.2) seawater treatments, while only 16 and 17 algae grew in the low (~ 1.0) and intermediate (~ 2.5) Mg/Ca seawater treatments, respectively.

Linear growth rates increased significantly ($p < 0.005$) with increases in seawater Mg/Ca (Fig. 5). *U. flabellum* grown in the lowest,

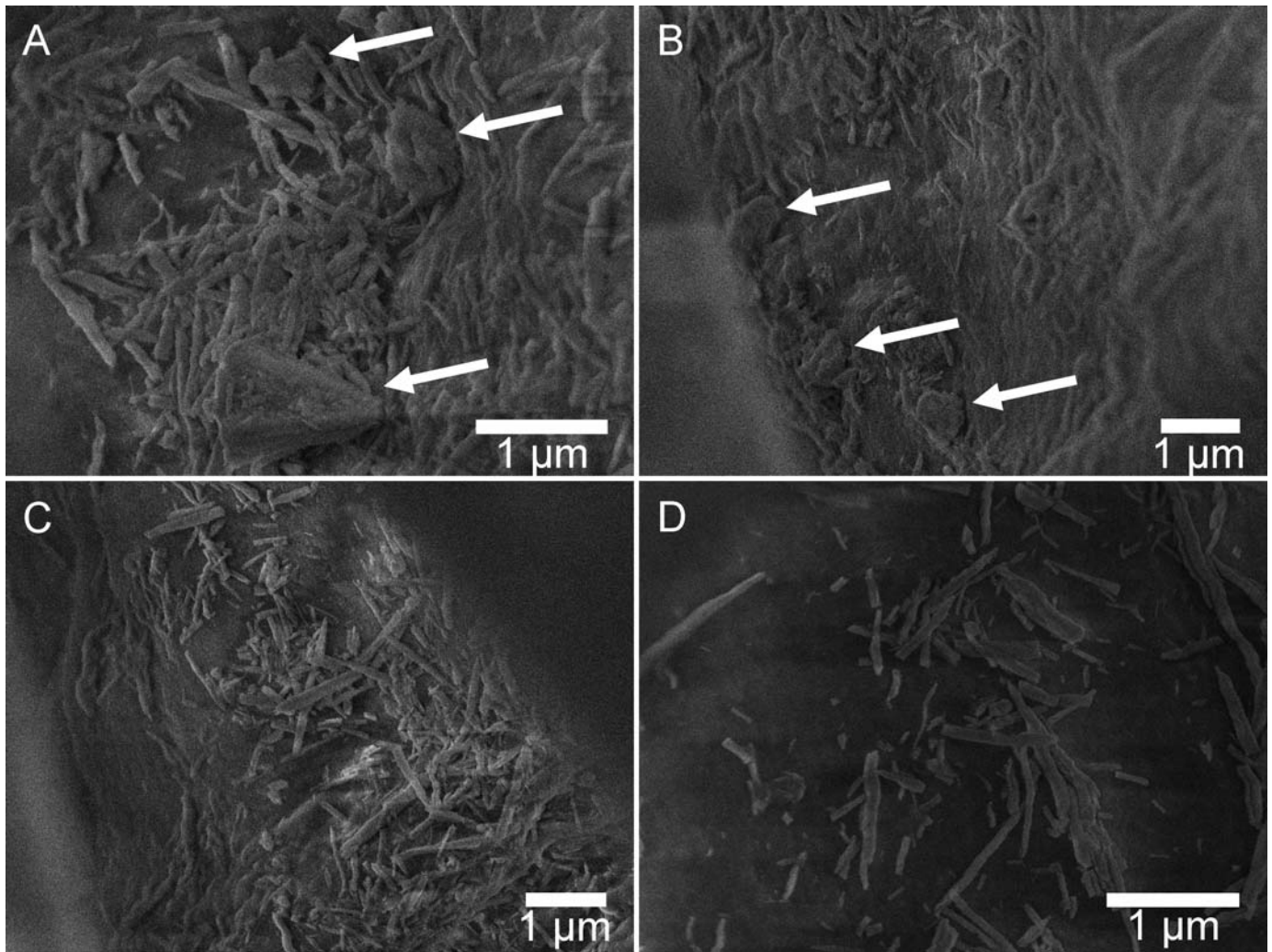


FIG. 3.—A, B) Back-scatter electron images of the calcifying chamber between the inner and outer walls of filaments within a *U. flabellum* alga grown in seawater of $m\text{Mg}/\text{Ca} = 1.0$ (calcite seawater). Arrows point to possible calcite crystals, interspersed among the more numerous aragonite needles. C, D) Back-scatter electron images of a comparable region of a *U. flabellum* alga grown in seawater of $m\text{Mg}/\text{Ca} = 5.2$ (aragonite seawater). Note absence of the purported calcite crystals identified in parts A and B.

intermediate, and highest Mg/Ca treatments had average linear growth rates (\pm standard error) of $0.104 (\pm 0.016)$, $0.195 (\pm 0.024)$, and $0.288 (\pm 0.052)$ mm d^{-1} , respectively (Table 1).

In the low Mg/Ca (~ 1.0) seawater, *U. flabellum* offspring ranged in age from 5 to 24 days. In the intermediate Mg/Ca (~ 2.5) seawater, *U. flabellum* offspring ranged in age from 5 to 40 days. In the high Mg/Ca (~ 5.2) seawater, *U. flabellum* offspring ranged in age from 6 to 54 days. These differences in the ages among the algae are due to the simultaneous harvest of specimens that vary in their dates of origination.

The ages of the offspring *U. flabellum* algae were plotted against their total calcification and primary production, resulting in a timeline of these variables representing the lifespan of an “idealized” alga raised in seawater with the given Mg/Ca ratio. This was the only way to obtain a continuous measure of calcification and primary production throughout the life of an alga, because measurement of these variables requires combustion and, therefore, destruction of the specimen. The rates of calcification (Fig. 6) and primary production (Fig. 7) of the algae (Table 1) were calculated as the slopes of the least-squares linear regressions through the respective data.

Rates of calcification and primary productivity increased significantly ($p \ll 0.001$) with seawater Mg/Ca. *U. flabellum* algae grown in the lowest, intermediate, and highest Mg/Ca treatments produced CaCO_3 at average rates (\pm SE) of $0.116 (\pm 0.025)$, $0.305 (\pm 0.030)$, and $0.551 (\pm 0.044)$ mg d^{-1} , respectively; and organic matter at average rates of $0.087 (\pm 0.034)$, $0.138 (\pm 0.028)$, and $0.383 (\pm 0.048)$ mg d^{-1} , respectively (Table 1).

DISCUSSION

The precipitation of mostly aragonitic needles by *U. flabellum* algae grown in the seawater treatment that favors the abiotic nucleation of low-Mg calcite is significant in that it implies that the algae have biological control over which polymorph of calcium carbonate they precipitate. However, it would be expected that this biologically mediated precipitation of aragonite from seawater that favors the nucleation of low-Mg calcite ($m\text{Mg}/\text{Ca} < 2$) would proceed slower than it would in seawater that naturally favors the nucleation of aragonite ($m\text{Mg}/\text{Ca} > 2$). This may explain the variation in the rate of calcification of

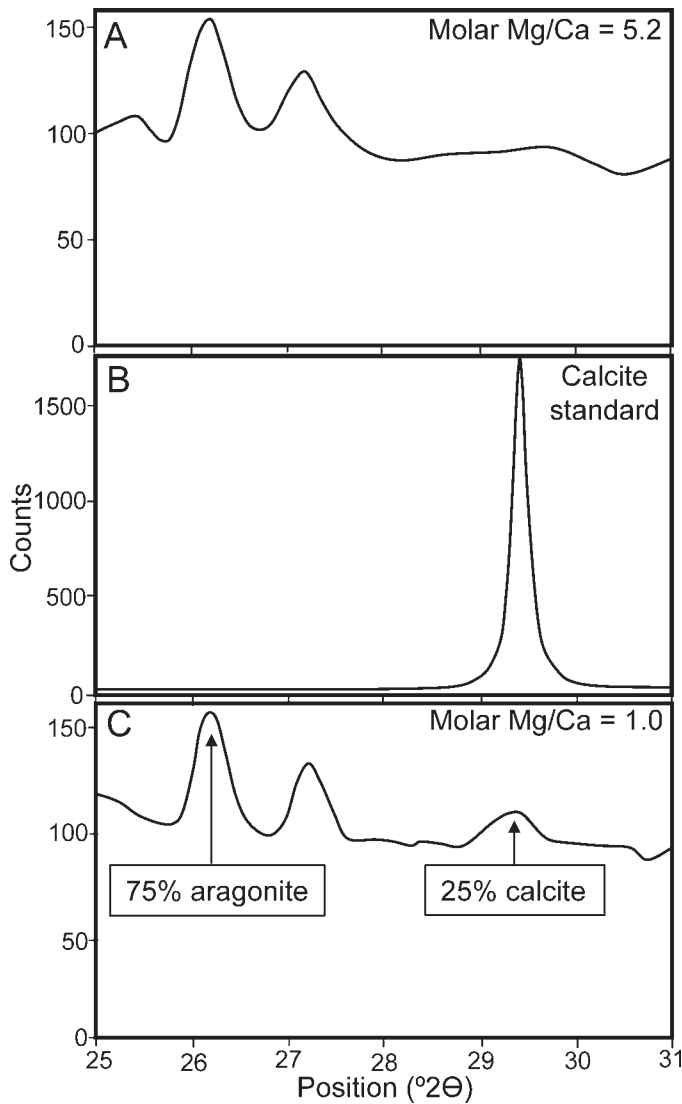


FIG. 4.— A) X-ray diffraction pattern for a *U. flabellum* alga that produced 100% aragonite when grown in seawater that favors the nucleation of the aragonite polymorph ($m\text{Mg}/\text{Ca} = 5.2$). Primary aragonite peak [d(111)] occurs at $2\theta = 26.2^\circ$ (3.40 Å). B) X-ray diffraction pattern for pure calcite, revealing primary calcite peak [d(104)] at $2\theta = 29.4\text{--}29.5^\circ$ (3.03–3.04 Å). C) X-ray diffraction pattern for a *U. flabellum* alga that produced $25 \pm 3\%$ low-Mg calcite and $75 \pm 3\%$ aragonite, as calculated from the respective areas beneath the primary calcite peak [d(104); 3.03–3.04 Å; $2\theta = 29.4\text{--}29.5^\circ$] and the primary aragonite peak [d(111); 3.40 Å; $2\theta = 26.2^\circ$].

U. flabellum algae among the three seawater treatments: high in the aragonite + high-Mg calcite nucleation field; lower in the boundary field; and lowest in the low-Mg calcite nucleation field. However, this fails to explain why rates of linear growth and primary productivity follow the

same pattern. The explanation may concern CO_2 (Ries 2005; Stanley et al. 2005).

Precipitation of CaCO_3 by the *Udotea* algae releases CO_2 to the ambient seawater:



This CO_2 may fertilize the algae's photosynthesis:



thereby resulting in the observed correlation of calcification with primary production and linear growth (Paasche 1968; Borowitzka and Larkum 1976; Borowitzka 1977; Sikes et al. 1980; Reiskind et al. 1988, 1989; Ries 2005; Stanley et al. 2005).

The observation that the *U. flabellum* alga precipitates most of its calcium carbonate as aragonite in the low-Mg calcite nucleation field suggests that the alga is able to specify the polymorph of calcium carbonate that it precipitates. This may be accomplished via transcellular pumping of cations to maintain an internal nucleation field within the aragonite range ($m\text{Mg}/\text{Ca} > 2$) or with mechanical and/or chemical templates that specify the nucleation of the orthorhombic aragonite crystal structure (Borowitzka 1984). The precipitation of one-quarter of its mineral component as low-Mg calcite, however, indicates that the alga's biomineralogical control is somewhat limited, and can be partially superseded by the Mg/Ca ratio of ambient seawater.

A previous study similar to the present one found that the primary productivity, calcification, and linear growth rates of the codiacean alga *Penicillus capitatus* decreased 82%, 91%, and 86%, respectively, when switched from the high Mg/Ca (~ 5.2) seawater to the low Mg/Ca (~ 1.0) seawater (Ries 2005). These results are mostly consistent with the outcome of the present study, which shows that primary productivity, calcification, and linear growth rates of the *U. flabellum* algae decreased 77%, 79%, and 64%, respectively, when switched from the high Mg/Ca to the low Mg/Ca seawater.

The main discrepancy between the two studies concerns linear growth rates, in which case the *Penicillus* algae appears to be more negatively affected by low ambient Mg/Ca ratios than the *Udotea* algae. This may be attributable to *Udotea*'s C4-like mode of photosynthesis, which would have sustained the algae's growth more successfully amid reduced CO_2 liberation resulting from reduced calcification in the low Mg/Ca seawater (Reiskind and Bowes 1991). Likewise, the *Penicillus* algae, which apparently do not use a C4-like mode of photosynthesis, would be more adversely affected by reductions in available CO_2 .

The previous study on *Penicillus capitatus* also included a stress-strain biomechanical analysis of the algae which revealed that the stiffness of their thalli decreased when grown in artificial seawater of depressed Mg/Ca, probably because of the observed concomitant reductions in primary productivity and calcification (Ries 2005). This suggests that the *U. flabellum* alga, which exhibits comparably reduced rates of primary production and calcification in reduced Mg/Ca seawater, would also have had a lower stiffness in such seawater.

The results of the present study suggest that *Udotea*, and possibly other aragonite-precipitating codiacean algae, would have been less calcified,

TABLE 1.— Summary of mineralogy, linear growth, calcification, and primary productivity for *Udotea flabellum* algae raised in the three artificial seawater treatments.

| Seawater Mg/Ca (molar) | Mineralogy (%cal : %arag) | Linear growth \pm SE (mm/day) | Calcification \pm SE (mg/day) | Primary production \pm SE (mg/day) |
|------------------------|---------------------------|---------------------------------|---------------------------------|--------------------------------------|
| ~ 5.2 | 0 : 100 | 0.288 ± 0.052 | 0.551 ± 0.044 | 0.383 ± 0.048 |
| ~ 2.5 | 0 : 100 | 0.195 ± 0.024 | 0.305 ± 0.030 | 0.138 ± 0.028 |
| ~ 1.0 | 25 : 75 | 0.104 ± 0.016 | 0.116 ± 0.025 | 0.087 ± 0.034 |

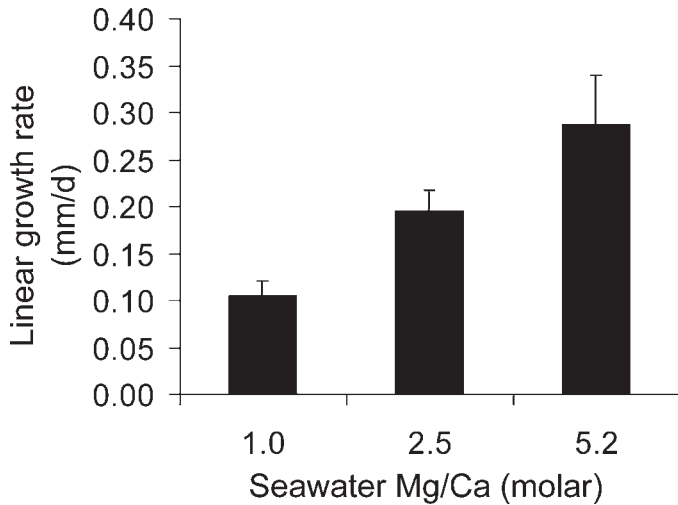


FIG. 5.—Linear growth rates for *U. flabellum* algae grown in the three artificial-seawater nucleation fields. Algae grown in the calcite nucleation field ($mMg/Ca = 1.0$), which does not favor their aragonite mineralogy, maintained the slowest linear growth rates \pm SE ($0.104 \pm 0.016 \text{ mm d}^{-1}$). Algae grown in the boundary ($mMg/Ca = 2.5$) and aragonite + high-Mg calcite ($mMg/Ca = 5.2$) nucleation fields exhibited rates of linear growth (0.195 ± 0.024 and $0.288 \pm 0.052 \text{ mm d}^{-1}$, respectively) increasing significantly ($p < 0.005$) with ambient Mg/Ca. Error bars correspond to the standard error of the data.

slower growing, smaller, and probably less stiff in the calcite seas of the geologic past. This, of course, assumes that ancient codiacean algae inhabiting such seas were not better adapted than modern codiacean algae at producing aragonite (or perhaps even calcite) in seawater favoring the nucleation of calcite. Such chemically induced reductions in the fitness of these algae would have had significant biological implications for *Udotea* and related codiacean algae. Their slow growth rates and small size would have made them less competitive for space and sunlight on the shallow tropical seafloor. Their reduced calcification and stiffness would have made them more susceptible to predation by grazing

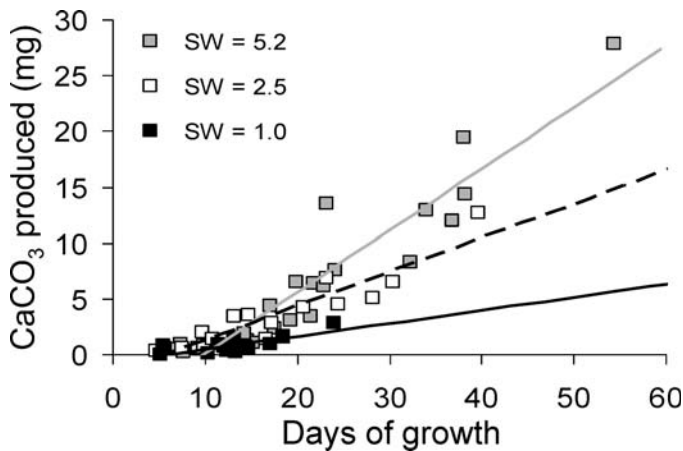


FIG. 6.—Calcification by *U. flabellum* algae of increasing age in the three seawater treatments. Average calcification rates are the slopes of the least-squares linear regressions through the data. The solid gray ($y = 0.551x - 5.395$, $R^2 = 0.88$, $SE = 0.044$), broken black ($y = 0.305x - 1.734$, $R^2 = 0.87$, $SE = 0.030$), and solid black ($y = 0.116x - 0.665$, $R^2 = 0.61$, $SE = 0.025$) curves correspond to *U. flabellum* algae raised in the aragonite ($mMg/Ca = 5.2$), boundary ($mMg/Ca = 2.5$), and calcite ($mMg/Ca = 1.0$) seawater treatments, respectively, and reveal average primary production rates that decrease significantly ($p \ll 0.001$) in that order.

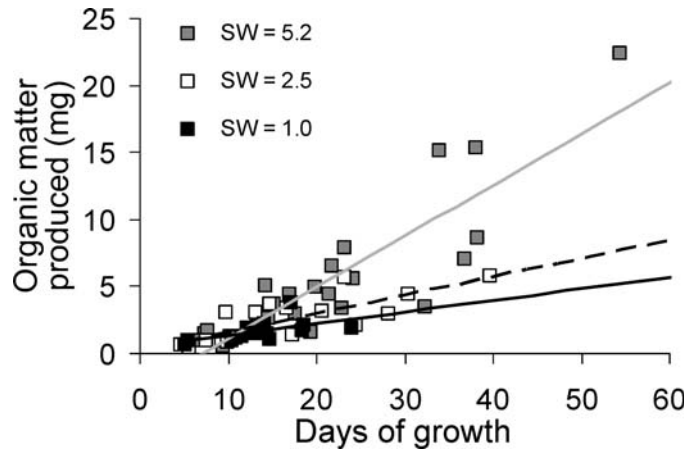


FIG. 7.—Primary productivity of *U. flabellum* algae of increasing age in the three seawater treatments. Average primary production rates are the slopes of the least-squares linear regressions through the data. The solid gray ($y = 0.383x - 2.738$, $R^2 = 0.75$, $SE = 0.048$), broken black ($y = 0.138x + 0.241$, $R^2 = 0.62$, $SE = 0.028$), and solid black ($y = 0.087x + 0.477$, $R^2 = 0.32$, $SE = 0.034$) curves correspond to *U. flabellum* algae raised in the aragonite ($mMg/Ca = 5.2$), boundary ($mMg/Ca = 2.5$), and calcite ($mMg/Ca = 1.0$) seawater treatments, respectively, and reveal average calcification rates that decrease significantly ($p \ll 0.001$) in that order.

fish, which are deterred by the algae's high $CaCO_3$ content in modern aragonitic seas (Wray 1977; Paul and Van Alstyne 1988; Schupp and Paul 1994). Such reduced calcification, primary productivity, and population density would have decreased the algae's contribution of biogenic aragonite needles to shallow tropical carbonate platforms during calcite seas.

The negative effects of reduced CO_2 , with respect to photosynthetic tissue growth, associated with reduced calcification for algae producing aragonite in calcite seas, may have been mitigated by elevated atmospheric pCO_2 (Royer et al. 2001; Yates and Robbins 2001) associated with elevated rates of ocean crust production, ultimately believed to be the principal cause of calcite seas. If this is the case, then the low rates of primary production observed in the present study may not be applicable to Codiaceae inhabiting high- CO_2 calcite seas of the geologic past. Additional experimental work on the combined effects of seawater CO_2 and Mg/Ca are required to explore this issue further.

CONCLUSIONS

U. flabellum algae, when grown in artificial seawater that favors the abiotic precipitation of low-Mg calcite ($mMg/Ca < 2$), continue to precipitate most of their calcium carbonate as aragonite needles, thereby suggesting that codiacean algae either control local Mg/Ca by pumping cations or employ a mechanical and/or chemical template to specify precipitation of the aragonite polymorph (Borowitzka 1984). However, the partial precipitation of low-Mg calcite ($25 \pm 3\%$) in the calcite seawater suggests that the algae's mineralogical control is limited and can be partially superseded by the Mg/Ca ratio of ambient seawater.

Rates of linear growth, calcification, and primary production decrease for *U. flabellum* algae grown in seawater that favors the nucleation of low-Mg calcite over aragonite. Slower calcification results in reduced liberation of CO_2 available for algal photosynthesis, which may be responsible for the concomitant reductions in rates of linear growth and primary production observed in the experiments (Borowitzka and Larkum 1976; Borowitzka 1977; Ries 2005; Stanley et al. 2005).

The production of aragonite by ancient codiacean algae inhabiting calcite seas, assuming that they found it comparably difficult to grow and

calcify in calcite seawater as did the modern codiacean algae evaluated in this study, would have reduced the competitiveness of these algae, made them more susceptible to grazing predation, and diminished their contribution to carbonate sedimentation. Likewise, these results support the assertion that the dominant ecological and sedimentological roles of codiacean algae in Recent tropical seas is facilitated by the Mg/Ca ratio of seawater supporting the aragonitic mineralogy of these algae over this interval (Stanley and Hardie 1998, 1999).

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation Grant EAR-0202849 and the Petroleum Research Fund Grant 38468-AC2. I thank Steven M. Stanley and Lawrence A. Hardie for their ideas and suggestions regarding the subjects evaluated in this manuscript, Amy Ries for assistance with specimen collection, and Mark Koontz for aid in micro-imaging and mineralogical analyses. I gratefully acknowledge Leslie Melim, Kim Yates, and Neil Tabor for their helpful reviews of this manuscript.

REFERENCES

- BARATTOLO, F., 1991, Mesozoic and Cenozoic marine benthic calcareous algae with particular regard to Mesozoic Dasycladaleans, in Riding, R., ed., *Calcareous Algae and Stromatolites*: Berlin, Springer-Verlag, p. 504–540.
- BATHURST, R.G.C., 1975, *Carbonate Sediments and Their Diagenesis*: Amsterdam, Elsevier, 658 p.
- BIDWELL, J.P., AND SPOTTE, S., 1985, *Artificial Seawaters: Formulas and Methods*: Boston, Jones and Bartlett, 349 p.
- BÖHM, L., FÜTTERER, D., AND KAMINSKI, E., 1978, Algal calcification in some Codiciaeae (Chlorophyta): ultrastructure and location of skeletal deposits: *Journal of Phycology*, v. 14, p. 486–493.
- BOROWITZKA, M.A., 1977, Algal calcification: Annual Review of Oceanography and Marine Biology, v. 15, p. 189–223.
- BOROWITZKA, M.A., 1984, Calcification in aquatic plants: *Plant, Cell and Environment*, v. 7, p. 457–466.
- BOROWITZKA, M.A., AND LARKUM, A.W.D., 1976, Calcification in the green alga *Halimeda*. III. The sources of inorganic carbon for photosynthesis and calcification and a model of the mechanism of calcification: *Journal of Experimental Biology*, v. 27, p. 879–893.
- BOROWITZKA, M.A., AND LARKUM, A.W.D., 1977, Calcification in the green alga *Halimeda*. I. An ultrastructure study of thallus development: *Journal of Phycology*, v. 13, p. 6–16.
- BOROWITZKA, M.A., LARKUM, W.D., AND NOCKOLDS, C.E., 1974, A scanning electron microscope study of the structure and organization of the calcium carbonate deposits of algae: *Phycologia*, v. 13, p. 195–203.
- CHUVASHOV, B., AND RIDING, R., 1984, Principal floras of Paleozoic marine calcareous algae: *Palaeontology*, v. 27, p. 487–500.
- CLOUD, P.E. JR., 1962, Environment of calcium carbonate deposition west of Andros Island, Bahamas: U.S. Geological Survey, Professional Paper 350, 138 p.
- COLOMBO, P.M., 1978, An ultrastructural study of thallus organization in *Udotea petiolata*: *Phycologia*, v. 17, p. 227–235.
- DICKSON, J.A.D., 2002, Fossil echinoderms as monitor of the Mg/Ca ratio of Phanerozoic oceans: *Science*, v. 298, p. 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*, v. 74, p. 355–365.
- DREW, E.A., 1983, *Halimeda* biomass growth rate and sediment generation on reefs in the Central Great Barrier Reef Province: *Coral Reefs*, v. 2, p. 101–110.
- DREW, E.A., AND ABEL, K.M., 1988, Studies on *Halimeda*. 1. The distribution and species composition of *Halimeda* meadows throughout the Great Barrier Reef Province: *Coral Reefs*, v. 6, p. 195–205.
- ELLIOT, G.F., 1984, Climatic tolerance in some aragonitic green algae of the post-Paleozoic: *Palaeogeography, Palaeoclimatology, Palaeoecology*, v. 48, p. 163–169.
- FLAJS, G., 1977, Skeletal structures of some calcifying algae, in Flügel, E., ed., *Fossil Algae*: Berlin, Springer-Verlag, p. 225–231.
- FLÜGEL, E., 1988, *Halimeda*: paleontological record and palaeoenvironmental significance: *Coral Reefs*, v. 6, p. 123–130.
- FLÜGEL, E., 1991, Triassic and Jurassic marine calcareous algae: a critical review, in Riding, R., ed., *Calcareous Algae and Stromatolites*: Berlin, Springer-Verlag, p. 481–503.
- FOLK, R.L., 1974, The natural history of crystalline calcium carbonate: effect of magnesium content and salinity: *Journal of Sedimentary Petrology*, v. 44, p. 40–53.
- FRIEDMAN, E.I., ROTH, W.C., TURNER, J.B., AND McEWIN, R.S., 1972, Calcium oxalate crystals in the aragonite-producing green alga *Penicillus* and related genera: *Science*, v. 177, p. 891–893.
- FRIESEN, F.E., 1948, *The Structure and Reproduction of the Algae*: Cambridge, U.K., Cambridge University Press, p. 402–413.
- FÜCHTBAUER, H., AND HARDIE, L.A., 1976, Experimentally determined homogeneous distribution coefficients for precipitated magnesian calcites: application to marine carbonate cements (abstract): *Geological Society of America, Abstracts with Program*, v. 8, p. 877.
- FÜCHTBAUER, H., AND HARDIE, L.A., 1980, Comparison of experimental and natural magnesian calcites (abstract): *International Association of Sedimentologists, Meeting, Bochum, Germany, Abstracts*, p. 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*, v. 24, p. 279–283.
- HAY, M.E., 1997, Calcified seaweeds on coral reefs: complex defenses, trophic relationships, and value as habitats: *Eighth International Coral Reef Symposium, Proceedings*, p. 713–718.
- HAY, M.E., KAPPEL, Q.E., AND FENICAL, W., 1994, Synergism in plant defenses against herbivores: interactions of chemistry, calcification and plant quality: *Ecology*, v. 75, p. 1714–1726.
- HILLIS, L., 1991, Recent calcified *Halimeda*, in Riding, R., ed., *Calcareous algae and stromatolites*: Berlin, Springer-Verlag, p. 167–188.
- HILLIS-COLINVAUX, L., 1980, Ecology and taxonomy of *Halimeda*: Primary producer of coral reefs, in Blaxter, J.H.S., Russell, F.S., and Yonge, M., eds., *Advances in Marine Biology 11*: London, Academic Press, p. 1–327.
- HINE, A.C., HALLOCK, P., HARRIS, M.W., MULLINS, H.T., BELKNAP, D.F., AND JAAP, W.C., 1988, *Halimeda* bioherms along an open seaway: Miskito Channel, Nicaraguan Rise, SW Caribbean Sea: *Coral Reefs*, v. 6, p. 173–178.
- HUDSON, J.H., 1985, Growth rate and carbonate production in *Halimeda opuntia*: Marquesas Keys, Florida, in Toomey, D.F., and Nitecki, M.H., eds., *Paleoecology*: Berlin, Springer-Verlag, p. 257–263.
- KOOISTRA, W.H.C.F., 2002, Molecular phylogenies of Udoteaceae (Bryopsidales, Chlorophyta) reveal monophyly for *Udotea*, *Penicillus* and *Chlorodemis*: *Phycologia*, v. 41, p. 453–462.
- LEITMEIER, H., 1910, Zur kenntnis der carbonate, die dimorphie des Kohlensauren Kalkes. I. Teil: *Neues Jahrbuch für Mineralogie*, v. 1, p. 49–74.
- LEITMEIER, H., 1915, Zur kenntnis der carbonate. II. Teil: *Neues Jahrbuch für Mineralogie, Beilageband*, v. 40, p. 655–700.
- LIPPMAN, F., 1960, Versuche zur Aufklärung der Bildungsbedingungen von Calcit und Aragonit: *Fortschritte der Mineralogie*, v. 38, p. 156–161.
- LOWENSTAM, H.A., 1955, Aragonite needles secreted by algae and some sedimentary implications: *Journal of Sedimentary Petrology*, v. 25, p. 270–272.
- LOWENSTAM, H.A., AND EPSTEIN, S., 1957, On the origin of sedimentary aragonite needles of the Great Bahama Bank: *Journal of Geology*, v. 65, p. 364–375.
- LOWENSTEIN, T.K., TIMOFFEEFF, M.N., BRENNAN, S.T., HARDIE, L.A., AND DEMICCO, R.V., 2001, Oscillations in Phanerozoic seawater chemistry: evidence from fluid inclusions: *Science*, v. 294, p. 1086–1088.
- LOWENSTEIN, T.K., HARDIE, L.A., TIMOFFEEFF, M.N., AND DEMICCO, R.V., 2003, Secular variation in seawater chemistry and the origin of calcium chloride basinal brines: *Geology*, v. 31, p. 857–860.
- MAMET, B., 1991, Carboniferous calcareous algae, in Riding, R., ed., *Calcareous Algae and Stromatolites*: Berlin, Springer-Verlag, p. 370–451.
- MARSHALL, J.F., AND DAVIES, P.J., 1988, *Halimeda* bioherms of the Great Barrier Reef: *Coral Reefs*, v. 6, p. 139–148.
- MILLIMAN, J.D., 1977, Role of calcareous algae in Atlantic continental margin sedimentation, in Flügel, E., ed., *Fossil Algae*: Berlin, Springer-Verlag, p. 232–247.
- MONTAÑEZ, I.P., 2002, Biological skeletal carbonate records changes in major-ion chemistry of paleo-oceans: *National Academy of Sciences, Proceedings*, v. 99, p. 15852–15854.
- MU, X., 1991, Fossil Udoteaceae and Gymnocodiaceae, in Riding, R., ed., *Calcareous Algae and Stromatolites*: Berlin, Springer-Verlag, p. 146–166.
- MÜLLER, G., IRION, G., AND FÖRSTNER, U., 1972, Formation and diagenesis of inorganic Ca–Mg carbonates in the lacustrine environment: *Naturwissenschaften*, v. 59, p. 158–164.
- MULTER, H.G., 1988, Growth rate, ultrastructure and sediment contribution of *Halimeda incressata* and *Halimeda monile*, Nonsuch and Falmouth Bays, Antiqua, W.I.: *Coral Reefs*, v. 6, p. 179–186.
- NEUMANN, A.C., AND LAND, L.S., 1975, Lime mud deposition and calcareous algae in the Bight of Abaco, Bahamas: a budget: *Journal of Sedimentary Petrology*, v. 45, p. 763–786.
- ORME, G.R., AND SALAMA, M.S., 1988, Form and seismic stratigraphy of *Halimeda* banks in part of the northern Great Barrier Reef Province: *Coral Reefs*, v. 6, p. 131–137.
- PAASCHE, E., 1968, Biology and physiology of coccolithophorids: *Annual Review of Microbiology*, v. 22, p. 77–86.
- PAUL, V.J., AND VAN ALSTYNE, K.L., 1988, Chemical defense and chemical variation in some tropical Pacific species of *Halimeda* (Halimeda: Chlorophyta): *Coral Reefs*, v. 6, p. 263–269.
- PAYRI, C.E., 1988, *Halimeda* contribution to organic and inorganic production in a Tahitian reef system: *Coral Reefs*, v. 6, p. 251–262.
- PHIPPS, C.V.G., AND ROBERTS, H.H., 1988, Seismic characteristics and accretion history of *Halimeda* bioherms on Kalukalukuang Bank, eastern Java Sea (Indonesia): *Coral Reefs*, v. 6, p. 149–159.
- REISKIND, J.B., AND BOWES, G., 1991, The role of phosphoenolpyruvate carboxylase in a marine macroalga with C4-like photosynthetic characteristics: *National Academy of Sciences, Proceedings*, v. 88, p. 2883–2887.

- REISKIND, J.B., SEAMON, P.T., AND BOWES, G., 1988, Alternative methods of photosynthetic carbon assimilation in marine macroalgae: *Plant Physiology*, v. 87, p. 686–692.
- REISKIND, J.B., SEAMON, P.T., AND BOWES, G., 1989, Photosynthetic responses and anatomical features of two marine macroalgae with different CO₂ compensation points: *Aquatic Botany*, v. 33, p. 71–86.
- RIDING, R., AND GUO, L., 1991, Permian marine calcareous algae, in Riding, R., ed., *Calcareous Algae and Stromatolites*: Berlin, Springer-Verlag, p. 452–480.
- RIES, J.B., 2004, 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*, v. 32, p. 981–984.
- RIES, J.B., 2005, Aragonite production in calcite seas: effect of seawater Mg/Ca ratio on the calcification and growth of the calcareous alga *Penicillus capitatus*: *Paleobiology*, v. 31, p. 445–458.
- RIES, J.B., in press, Mg fractionation in crustose coralline algae: geochemical, biological, and sedimentological implications of secular variation in the Mg/Ca ratio of seawater: *Geochimica et Cosmochimica Acta*.
- ROBERTS, H.H., AHARON, P., AND PHIPPS, C.V., 1988, Morphology and sedimentology of *Halimeda* bioherms from the eastern Java Sea (Indonesia): *Coral Reefs*, v. 6, p. 161–172.
- ROUX, A., 1991a, Ordovician algae and global tectonics, in Riding, R., ed., *Calcareous Algae and Stromatolites*: Berlin, Springer-Verlag, p. 335–348.
- ROUX, A., 1991b, Ordovician to Devonian marine calcareous algae, in Riding, R., ed., *Calcareous Algae and Stromatolites*: Berlin, Springer-Verlag, p. 349–369.
- ROYER, D.L., BERNER, R.A., AND BEERLING, D.J., 2001, Phanerozoic atmospheric CO₂ change: evaluating geochemical and paleobiological approaches: *Earth-Science Reviews*, v. 54, p. 349–392.
- SANDBERG, P.A., 1983, An oscillating trend in Phanerozoic nonskeletal carbonate mineralogy: *Nature*, v. 305, p. 19–22.
- SCHUPP, P.J., AND PAUL, V.J., 1994, Calcium carbonate and secondary metabolites in tropical seaweeds: variable effects on herbivorous fishes: *Ecology*, v. 75, p. 1172–1185.
- SIEMANN, M.G., 2003, Extensive and rapid changes in seawater chemistry during the Phanerozoic: evidence from Br contents in basal halite: *Terra Nova*, v. 15, p. 243–248.
- SIKES, C.S., ROER, R.D., AND WILBUR, K.M., 1980, Photosynthesis and coccolith formation: inorganic carbon sources and net inorganic reaction of deposition: *Limnology and Oceanography*, v. 25, p. 248–261.
- SPOTTE, S.H., 1979, *Seawater Aquariums: the Captive Environment*: New York, Wiley & Sons, 413 p.
- STANLEY, S.M., AND 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*, v. 144, p. 3–19.
- STANLEY, S.M., AND HARDIE, L.A., 1999, Hypercalcification: paleontology links plate tectonics and geochemistry to sedimentology: *GSA Today*, v. 9, p. 1–7.
- STANLEY, S.M., RIES, J.B., AND HARDIE, L.A., 2002, Low-magnesium calcite produced by coralline algae in seawater of Late Cretaceous composition: *National Academy of Sciences, Proceedings*, v. 99, p. 15323–15326.
- STANLEY, S.M., RIES, J.B., AND HARDIE, L.A., 2005, Seawater chemistry, coccolithophore population growth, and the origin of Cretaceous chalk: *Geology*, v. 33, p. 593–596.
- STOCKMAN, K.W., GINSBURG, R.N., AND SHINN, E.A., 1967, The production of lime mud by algae in south Florida: *Journal of Sedimentary Petrology*, v. 37, p. 633–648.
- WEFER, G., 1980, Carbonate production by algae *Halimeda*, *Penicillus* and *Padina*: *Nature*, v. 285, p. 323–324.
- WRAY, J.L., 1977, *Calcareous Algae*: Amsterdam, Elsevier, *Developments in Paleontology and Stratigraphy*, v. 4, 185 p.
- YATES, K.K., AND ROBBINS, L.L., 1998, Production of carbonate sediments by a unicellular green alga: *American Mineralogist*, v. 83, p. 1503–1509.
- YATES, K.K., AND ROBBINS, L.L., 2001, Microbial lime-mud production and its relation to climate changes, in Gerhard, L.C., Harrison, W., and Hanson, B.M., eds., *Geological Perspectives of Global Climate Change*: American Association of Petroleum Geologists, *Studies in Geology*, v. 47, p. 267–283.
- ZECHMAN, F.W., THERIOT, E.C., ZIMMER, E.A., AND CHAPMAN, R.L., 1990, Phylogeny of the Ulvophyceae (Chlorophyta): Cladistic analysis of nuclear encoded rRNA sequence data: *Journal of Phycology*, v. 26, p. 700–710.

Received 5 April 2005; accepted 21 September 2005.