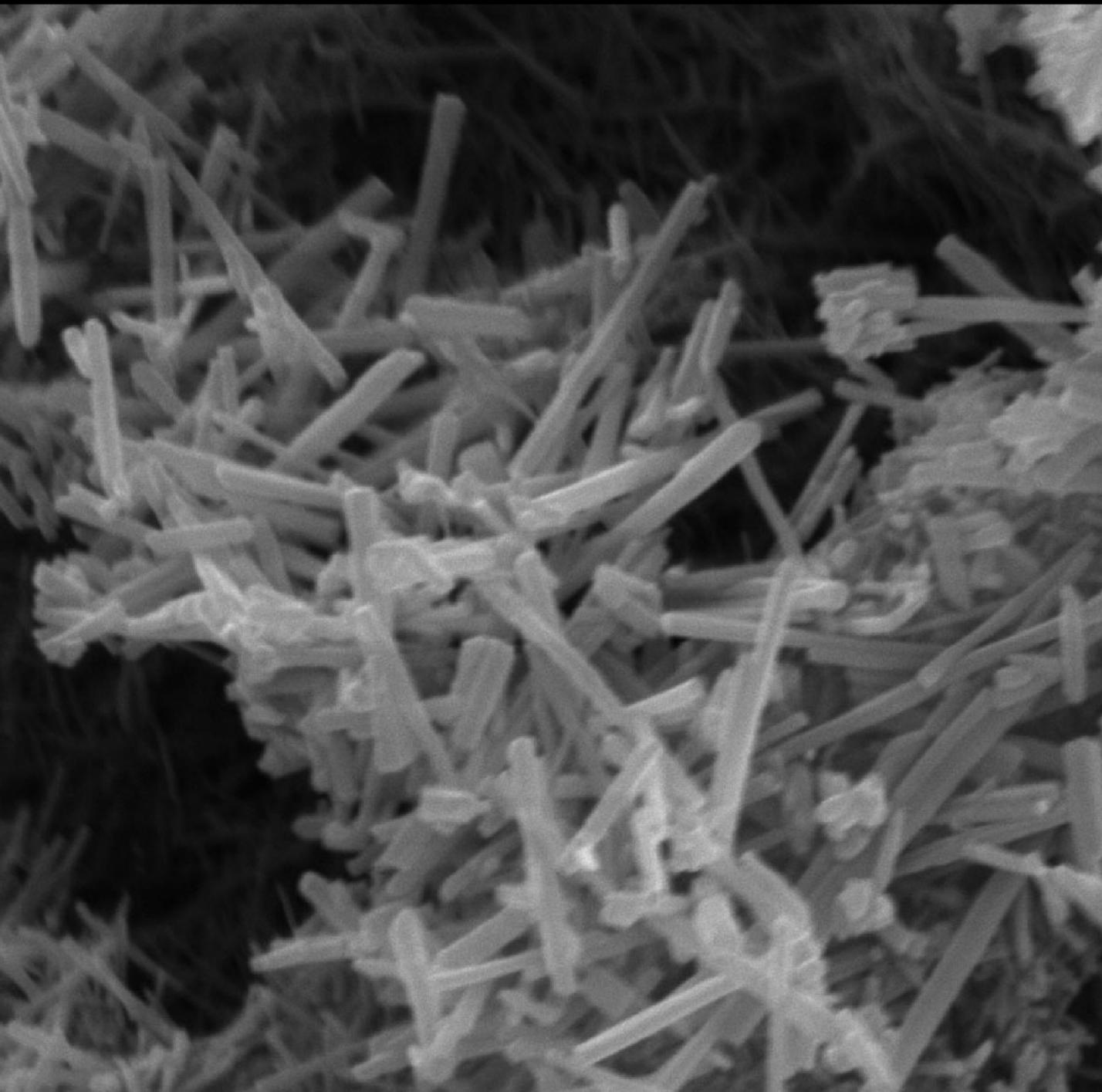


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REVIEW ARTICLE

Effects of secular variation in seawater Mg/Ca ratio (calcite–aragonite seas) on CaCO₃ sediment production by the calcareous algae *Halimeda*, *Penicillus* and *Udotea* – evidence from recent experiments and the geological record

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ABSTRACT

Independent lines of geological evidence suggest that fluctuations in the Mg/Ca ratio of seawater between 1.0 and 5.2 have caused the oceans to alternate between favouring the precipitation of the aragonite and high-Mg calcite polymorphs of calcium carbonate ($mMg/Ca > 2$; aragonite seas) and the low-Mg calcite polymorph ($mMg/Ca < 2$; calcite seas) throughout Phanerozoic time. The rise of aragonite-secreting bryopsidalean algae as major producers of carbonate sediments in middle Palaeogene time, a role that they maintained through to the present, has been attributed to a transition from calcite-to-aragonite seas in early Cenozoic time. Recent experiments on the modern, carbonate-sediment-producing bryopsidales *Halimeda*, *Penicillus* and *Udotea* reveal that their rates of calcification, linear extension and primary production decline when reared in experimental

calcite seawaters ($mMg/Ca < 2$). These normally aragonite-secreting algae also began producing at least one-quarter of their CaCO₃ as calcite under calcite sea conditions, indicating that their biomineralogical control can be partially overridden by ambient seawater chemistry. The observation that primary production and linear extension declined along with calcification in the mineralogically unfavourable seawater suggests that photosynthesis within these algae is enhanced by calcification via liberation of CO₂ and/or H⁺. Thus, the reduced fitness of these algae associated with their low rates of calcification in calcite seas may have been exacerbated by concomitant reductions in tissue mass and algal height.

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Introduction

Calcareous bryopsidalean algae are amongst the most important contributors of aragonite sediments to modern carbonate environments (Hillis, 1997; Rees *et al.*, 2007). The aragonite-secreting bryopsidalean algae assumed their role as important sediment producers in middle Palaeogene time (Hillis, 2001), around the time of the most recent calcite-to-aragonite sea transition (Hardie, 1996). They retained this role throughout the remainder of Cenozoic time, as seawater Mg/Ca ascended further into the aragonite domain (Hillis, 2001). There is mounting evidence that this protracted transition into the aragonite stability field played

an important role in the rise of calcareous bryopsidalean algae as important carbonate sediment producers in early Cenozoic time and enabled them to continue functioning as limestone-forming algae through to present time (Stanley and Hardie, 1998; Ries, 2005, 2006; Stanley *et al.*, 2009).

Multiple independent lines of evidence suggest that the Mg/Ca ratio of seawater fluctuated between 1.0 and the modern value of 5.2 throughout Phanerozoic time (Fig. 1), this evidence includes (1) secular variation in the ionic composition of fluid inclusions in primary marine halite (Lowenstein *et al.*, 2001), (2) secular variation in the mineralogy of late stage marine evaporites (MgSO₄ and KCl; Hardie, 1996), (3) secular variation in concentrations of Br in marine halite (Siemann, 2003) and (4) secular variation in the skeletal Mg/Ca ratio of fossil molluscs (Steuber and Rauch, 2005) and echinoderms (Dickson, 2002, 2004). Hardie (1996) and Demicco *et al.* (2005) suggest that this variation in seawater Mg/Ca has been

primarily driven by variations in the global rate of ocean crust production, which caused fluctuations in the mixing rates of the primary sources of seawater – Ca²⁺-rich hydrothermal brines and river water.

Variations in the Mg/Ca ratio of seawater is of particular interest to palaeobiologists and carbonate sedimentologists because experiments (Füchtbauer and Hardie, 1976, 1980) have shown that seawater Mg/Ca ratio controls which polymorph(s) of the skeleton-, sediment- and limestone-forming mineral CaCO₃ will be kinetically favoured. Molar Mg/Ca ratios (mMg/Ca) greater than 2 support precipitation of aragonite and high-Mg calcite (aragonite seas), while ratios less than 2 support precipitation of low-Mg calcite (calcite seas). Secular trends in the original polymorph mineralogy of ooids and marine cements (Fig. 1, Sandberg, 1983) reveal that these fluctuations in seawater Mg/Ca have had systematic effects on abiotic marine calcification throughout Phanerozoic time (Hardie, 1996).

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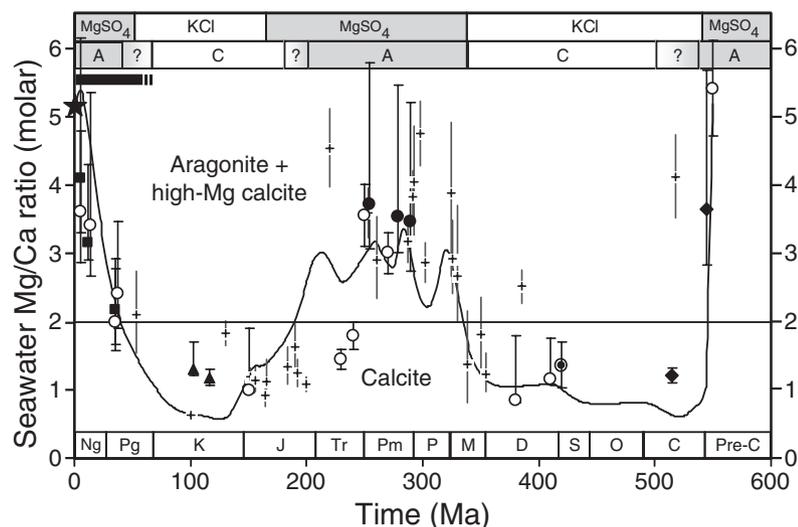


Fig. 1 Secular variation in seawater Mg/Ca throughout Phanerozoic time supported three intervals of predominantly aragonite + high-Mg calcite precipitation alternating with two intervals of predominantly calcite precipitation. Curve is Mg/Ca ratio of seawater (Demiccò *et al.*, 2005) calculated from a mid-ocean ridge hydrothermal brine/river water mixing model. Closed squares (Brennan, 2002), closed triangles (Timofeeff *et al.*, 2006), large closed circles (Lowenstein *et al.*, 2005), circumscribed small closed circle (Brennan and Lowenstein, 2002), closed diamonds (Brennan *et al.*, 2004) and open circles (Horita *et al.*, 2002) are seawater *m*Mg/Ca ranges estimated from fluid inclusions in primary marine halite. Crosses represent seawater Mg/Ca inferred from the Mg/Ca and dolomite content of fossil echinoderms (Dickson, 2002, 2004; Ries, 2004). Star represents modern seawater (*m*Mg/Ca = 5.2). Horizontal black bar represents temporal range over which bryopsidalean algae have been important contributors of carbonate sediments (Wray, 1977; Hillis, 2001). Horizontal line divides the calcite (*m*Mg/Ca < 2) and aragonite + high-Mg calcite (*m*Mg/Ca > 2) nucleation fields in seawater at 25 °C. Intervals of primarily aragonitic ('A') and calcitic ('C') abiogenic (ooids, marine cements, seafloor precipitates; Sandberg, 1983) and biogenic (hypercalcifying reef-building and sediment-producing organisms; Stanley and Hardie, 1998) precipitates, as well as KCl and MgSO₄ marine evaporites (Hardie, 1996), are plotted along the top of the figure.

There is mounting evidence that these fluctuations in seawater Mg/Ca also played a role in determining which groups of hypercalcifying marine organisms functioned as the dominant reef-builders and sediment-producers throughout Phanerozoic time (Stanley and Hardie, 1998; Porter, 2007; Kiesling *et al.*, 2008). One group of hypercalcifying marine organisms whose contribution to limestone formation is thought to have been particularly influenced by fluctuations in seawater Mg/Ca is the aragonite-secreting bryopsidalean algae (known to geologists as 'codiacean algae' or 'calcareous green algae'), which are major sediment producers in modern carbonate platform environments (Hillis, 1997; Rees *et al.*, 2007).

Although these calcifying algae have been identified in Permian-age limestones (Poncet, 1989), they did not

become important producers of carbonate sediments until middle Palaeogene time (Hillis, 2001), coincident with the rise of seawater *m*Mg/Ca above 2 into the aragonite stability field (Fig. 1; Hardie, 1996; Lowenstein *et al.*, 2001; Demiccò *et al.*, 2005). Significantly, they persisted in their role as major producers of carbonate sediments throughout Cenozoic time, as seawater Mg/Ca gradually ascended further into the aragonite stability field (Fig. 1). Their modern rate of carbonate sediment production is thought to represent a Cenozoic maximum (Hillis, 2001) and occurs in seawater conditions (*m*Mg/Ca = 5.2) that are more favourable for the nucleation of aragonite than at any other time in their geological past. The apparent susceptibility of the bryopsidalean algae to secular variation in seawater chemistry may be attributable to their relatively

rapid and uncontrolled mode of calcification, in which precipitation of aragonite needles proceeds mostly extracellularly, within invaginations of the algal cell wall.

It is perhaps important to note here that the Stanley-Hardie calcite–aragonite sea hypothesis (1998, 1999) does not address macroevolutionary trends within the bryopsidalean order. Indeed, there is no compelling evidence presented to date to suggest that compatibility between seawater Mg/Ca and the polymorph mineralogy of these algae played any part in their origination, diversification or extinction. Rather, the Stanley-Hardie hypothesis asserts that the ascendance of calcareous bryopsidalean algae as *important producers of carbonate sediments* in early-middle Cenozoic time was permitted by the coeval rise in seawater Mg/Ca into the aragonite stability field. Critically, these algae retained their role as important manufacturers of carbonate sediments throughout the remainder of Cenozoic time, as seawater Mg/Ca continued to rise further into the aragonite domain.

Here, I review the physiological, geological and experimental evidence that suggests that secular variation in seawater Mg/Ca has influenced bryopsidalean biomineralization and carbonate sediment production throughout Phanerozoic time. This review covers three general subjects: (1) anatomy, mechanisms of calcification, ecology and phylogeny of the calcareous bryopsidalean algae; (2) sedimentary and geological evidence in support of secular variation in seawater Mg/Ca and its effect on algal carbonate sedimentation and (3) recent experiments on living bryopsidalean algae (*Halimeda*, *Penicillus* and *Udotea*) that were conducted to empirically constrain the relationship between seawater Mg/Ca and algal calcification and growth.

Anatomy, mechanism of calcification, ecology and phylogeny

Anatomy

Halimeda, *Penicillus* and *Udotea* are upright-standing green algae with thalli that are anchored to the sediment with fibrous holdfasts. The *Halimeda* thallus is constructed from

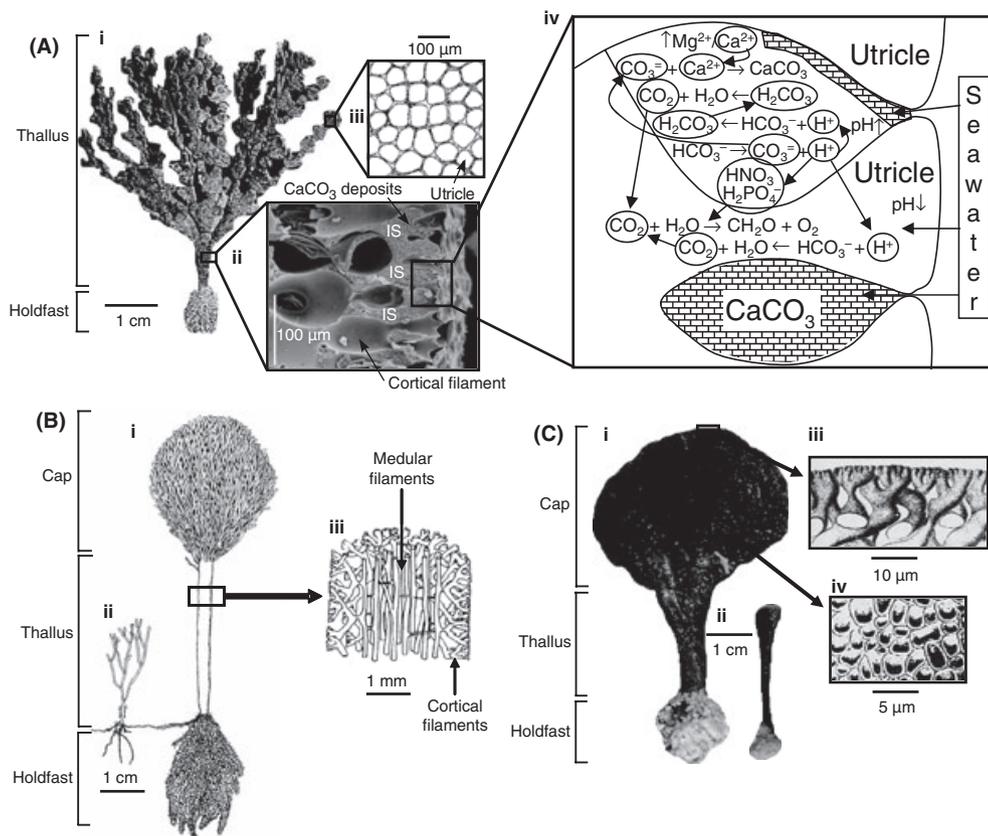


Fig. 2 Anatomy of the predominant CaCO₃-producing bryopsidalean algae in modern carbonate platform environments. (A) *Halimeda incrassata* showing (i) the thallus, the calcified segments, and the uncalcified holdfast; (ii) an SEM image of a vertical section through the cortical layer of the thallus, showing extracellular calcification in the interutricular space ('IS'), external to the outer algal wall; (iii) corticated surface of a calcified segment resulting from coalescence of utricles; (iv) diagram showing the chemical connectivity between the primary mass-forming reactions (calcification, photosynthesis), the primary carbonate system equilibria, nutrient shuttling, localized Mg/Ca ratios and pH within and between the coalescing utricles that form the calcified cortex of the *Halimeda*, *Penicillus* and *Udotaea* algae. (B) *Penicillus capitatus* showing (i) a full grown plant revealing uncalcified holdfast, calcified thallus and calcified cap; (ii) an offspring alga sprouting from rhizoids and (iii) magnified diagram of thallus revealing the constituent calcified medullar and cortical filaments. (C) *Udotaea flabellum* showing (i) full-grown alga revealing uncalcified holdfast, calcified thallus and calcified fan; (ii) an offspring alga; (iii) vertical section through the cortical layer of the fan, showing coalescence of the utricles and (iv) corticated surface of the fan (after Fritsch, 1948; Böhm *et al.*, 1978).

sub-centimetre scale calcified segments (Fig. 2A). Growth of the *Halimeda* alga occurs through the addition of new segments, as well as through the augmentation of previously formed segments. Segments are joined by flexible, non-calcified filaments that run the length of the thallus. Branching of the *Halimeda* thallus occurs when multiple segments grow from a single, pre-existing segment (Hillis, 1957; Hillis-Colinvaux, 1980; Macintyre and Reid, 1995). Unlike *Halimeda*, the *Penicillus* (Fig. 2B) and *Udotaea* (Fig. 2C) thalli are continuous, with the *Penicillus* thallus terminating as a cap and the *Udotaea* thallus terminating as a fan.

The *Halimeda*, *Penicillus* and *Udotaea* thalli comprise medullar filaments that

run the length of these algae. The medullar filaments trifurcate laterally to form cortical filaments that ramify into distally swollen structures termed utricles (Fig. 2). The appressed, swollen utricles coalesce to form the outer surface of these algae, effectively sealing off their interutricular regions from ambient seawater (Fig. 2). It is within these interutricular regions that most calcification occurs. Differences in thallus morphology are used to divide these genera into different species.

Mechanisms of calcification

The *Halimeda*, *Penicillus* and *Udotaea* algae each deposits CaCO₃ crystals primarily as the aragonite polymorph extracellularly within the interutri-

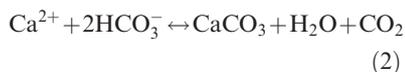
cular space (IS, Fig. 2) of the algae's medullar and cortical regions (Borowitzka and Larkum, 1976a, 1977; Borowitzka *et al.*, 1974). These algae also deposit a small portion of their aragonite intracellularly, between the inner and outer walls of their filaments. The precipitation of aragonite begins shortly after the appearance of chloroplasts (Wilbur *et al.*, 1969). The extent of calcification increases with the age of the alga, with mature portions of tissue containing up to 88 wt% CaCO₃ (Multer, 1988). *Halimeda*, *Penicillus* and *Udotaea* are thought to precipitate CaCO₃ within their tissue for increased rigidity in turbulent hydraulic regimes, for maintaining an erect posture to maximize exposure to sunlight and as a deter-

rent of predatory grazing, especially when combined with toxic, secondary metabolites and nocturnal growth of new, non-calcified segments (Paul and Fenical, 1984; Hay *et al.*, 1988, 1994; Paul and Van Alstyne, 1992; Schupp and Paul, 1994).

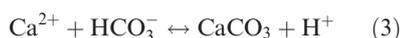
The primary substrate-forming reactions in calcifying algae (Fig. 2A) are photosynthesis:



and calcification:



and/or



and/or



As inorganic C is integral to each of these reactions, it is not surprising that experiments have revealed an intimate coupling between photosynthesis and calcification (Borowitzka and Larkum, 1976b; Borowitzka, 1977, 1982a,b; Pentecost, 1978; Smith and Roth, 1979; Gattuso *et al.*, 1999; De Beer and Larkum, 2001; Marshall and Clode, 2002). However, their relationship is complex and remains somewhat ambiguously defined.

An aqueous system's affinity for calcification can be quantified by its CaCO₃ saturation state (Ω_{CaCO_3}):

$$\Omega_{\text{CaCO}_3} = [\text{Ca}^{2+}][\text{CO}_3^{2-}]/K_{\text{sp}}^* \quad (5)$$

where $[\text{Ca}^{2+}]$ and $[\text{CO}_3^{2-}]$ are the concentrations of Ca²⁺ and CO₃²⁻ and K_{sp}^* is the stoichiometric solubility product of the appropriate polymorph of CaCO₃. If $\Omega_{\text{CaCO}_3} > 1$, calcification should occur; if $\Omega_{\text{CaCO}_3} < 1$, dissolution should occur.

The equilibrium reactions that govern the aqueous carbonate system can be summarized as follows:



and



Photosynthesis is thought to enhance calcification in the calcareous

bryopsidalean algae by removing CO₂ from the algae's intertricular fluid, which would shift the carbonate system equilibria of the algae's calcifying fluid towards increased $[\text{CO}_3^{2-}]$ and Ω_{CaCO_3} (Fig. 2A). Alternatively, calcification may be enhanced by photosynthesis within algae through the intracellular extraction of CO₂ from HCO₃⁻ by the enzyme carbonic anhydrase, which liberates OH⁻ that is extruded into the algae's intertricular fluid (Borowitzka and Larkum, 1976b; Axelsson *et al.*, 2000; Hellblom *et al.*, 2001; Hellblom and Axelsson, 2003; Uku *et al.*, 2005). This OH⁻ complexes with H⁺ in the intertricular fluid, thereby increasing the fluid's pH and therefore its $[\text{CO}_3^{2-}]$ and Ω_{CaCO_3} . The algae also utilize H⁺ ions from the intertricular fluid to shuttle HCO₃⁻, PO₄³⁻ and NO₃⁻ across the cell wall to fuel photosynthesis (Fig. 2A; McConnaughey and Whelan, 1997). Such photosynthetically driven removal of H⁺ ions from the algae's intertricular space effectively increases Ω_{CaCO_3} of the alga's intertricular fluid, thereby enhancing calcification. Photosynthesis may also enhance calcification by producing Ca²⁺-binding polysaccharide mucilage within cell walls that act as nucleation sites for CaCO₃ crystals (Borowitzka and Larkum, 1976a,b). It has also been suggested that the cation-binding properties of this polysaccharide influence the polymorph mineralogy of the nucleating CaCO₃ (Borowitzka, 1977).

Calcification may enhance photosynthesis in the calcareous bryopsidalean algae by removing CO₃²⁻ ions from the algae's intertricular fluid, thereby liberating CO₂ and H⁺ as the carbonate system re-equilibrates (see reactions 6, 7 and 8 above; Fig. 2A). CO₂ liberated within the intertricular calcifying fluid would diffuse across the algal cell wall, where it would fuel photosynthesis within chloroplasts (Borowitzka and Larkum, 1976b). Protons released to the intertricular fluid would complex with HCO₃⁻ and form H₂CO₃, some of which would be converted to CO₂ via cellular dehydration (see reactions 6 and 7 above; Fig. 2A; McConnaughey and Whelan, 1997; Hellblom *et al.*, 2001). Protons liberated by calcification in the intertricular fluid may also assist in the active transport of HCO₃⁻ and

nutrients such as NO₃⁻ and PO₄³⁻ across the algal cell wall by H⁺ symporters or co-transporters (Fig. 2A; Price and Badger, 1985; Price *et al.*, 1985; Badger and Price, 1994; Hellblom *et al.*, 2001; Hellblom and Axelsson, 2003). This would increase the alga's rate of photosynthesis directly via nutrient enrichment or indirectly via increased CO₂ liberation from the imported HCO₃⁻ by the enzyme carbonic anhydrase.

There is also evidence that a light-induced H⁺ pump controls pH within the *Halimeda* alga (Fig. 2A; De Beer and Larkum, 2001; Kangwe, 2006). This H⁺ pump is reported to regulate the distribution of so-called acid and alkaline zones, which promote dissolution and calcification of CaCO₃ respectively within the alga (Borowitzka, 1977; De Beer and Larkum, 2001; Kangwe, 2006).

Ecology and biogeography

Halimeda, *Penicillus* and *Udotea* are restricted to tropical and subtropical marine environments (> 20 °C), where they grow either on unconsolidated sediments or on the reef itself. They are pantropically distributed, with greatest densities occurring in the Caribbean Sea, followed by the Mediterranean Sea (Hillis-Colinvaux, 1980), the Great Barrier Reef Province (Drew and Abel, 1988) and restricted Indian (Kangwe, 2006), Pacific and Atlantic Ocean localities (Bach, 1979; Garrigue, 1985; Hillis, 1991). *Penicillus* and *Udotea* exist primarily in shallow, low-energy environments, while *Halimeda* algae tolerate a range of hydrodynamic regimes, flourishing from the back-reef lagoon to the fore-reef slope, at depths ranging from < 1 to 150 m (Moore *et al.*, 1976; Hillis-Colinvaux, 1980).

These algae grow rapidly, attaining heights up to 15 cm over their 1–3 month lifespan. Population densities of over 80 plants m⁻² have been observed in embayments off the coast of Antigua (Multer, 1988). Due to their high productivity, these calcareous algae are considered important geological and biological components of tropical and subtropical carbonate platform environments (Blair and Norris, 1988; Hillis, 1997).

Phylogeny

Halimeda, *Penicillus* and *Udotea* are the most abundant representatives of the carbonate producing bryopsidalean algae in modern tropical seas. These three algae are classified within the phylum *Chlorophyta*, class *Bryopsidophyceae* and order *Bryopsidales*. Analysis of 18S DNA sequences from these algae (Verbruggen *et al.*, 2009) reveals that *Penicillus* and *Udotea* are the more closely related genera and are both assigned to the udoteacean family. The more distant *Halimeda* genus is assigned to the halimedacean family.

Geological evidence

Secular variation in seawater Mg/Ca

Analysis of fluid inclusions (Lowenstein *et al.*, 2001, 2003, 2005; Horita *et al.*, 2002; Brennan *et al.*, 2004; Timofeeff *et al.*, 2006) trapped in primary marine halite crystals from the geological record indicates that the molar Mg/Ca ratio of seawater has varied between approximately 1.0 and 5.2 through the Phanerozoic Eon (Fig. 1). These estimates of ancient seawater Mg/Ca are consistent with multiple independent proxies of seawater Mg/Ca, including (1) secular variation in the polymorph mineralogy of abiogenic marine carbonates (Sandberg, 1983) and the dominant reef-building/sediment-producing marine organisms (Stanley and Hardie, 1998, 1999; Steuber, 2002; Porter, 2007; Kiessling *et al.*, 2008); (2) the precipitation of MgSO₄ evaporites during aragonite sea intervals ($m\text{Mg}/\text{Ca} > 2$) and KCl evaporites during calcite sea intervals ($m\text{Mg}/\text{Ca} < 2$; Sandberg, 1983; Hardie, 1996; Lasemi and Sandberg, 2000); (3) secular variation in concentrations of Br in marine halite (Siemann, 2003) and (4) secular variation in the skeletal Mg/Ca ratio of fossil molluscs (Steuber and Rauch, 2005) and echinoderms (Dickson, 2002, 2004).

Hardie (1996) and Demicco *et al.* (2005) suggested that this variation in seawater Mg/Ca was caused by fluctuations in the rate of ocean crust production (Engel and Engel, 1970; Gaffin, 1987; Vail *et al.*, 1991) that alter the flux of hydrothermal brine through mid-ocean-ridge and large-igneous-province zones of ocean crust production.

The fresh basalt in these systems is converted to greenstone as it reacts with the circulating hydrothermal brine, a reaction that effectively removes Mg²⁺ from the brine and releases Ca²⁺ to it. Ancient seawater Mg/Ca ratios calculated from this model are consistent with empirical estimates, suggesting that the principal tenants of the model are correct.

Laboratory experiments conducted at standard conditions (1 atm pressure, T = 25 °C, $p\text{CO}_2 = 380$ p.p.m.) have demonstrated that low-Mg calcite will precipitate from seawater when $m\text{Mg}/\text{Ca} < 2$ (± 0.5), whereas aragonite and high-Mg calcite will precipitate when $m\text{Mg}/\text{Ca} > 2$ (± 0.5 ; Leitmeier, 1910, 1915; Lippmann, 1960; Müller *et al.*, 1972; Berner, 1975; Füchtbauer and Hardie, 1976, 1980; Given and Wilkinson, 1985; Morse *et al.*, 1997). Therefore, the calcareous bryopsidalean algae would have experienced two transitions between aragonite and calcite seas since Permian time, which is the age of the oldest known fossils assigned to this order (Poncet, 1989).

Role of atmospheric $p\text{CO}_2$ and seawater temperature

Sandberg (1975) originally attributed his single calcite-to-aragonite shift in ocean state to a protracted increase in the Mg/Ca ratio of seawater throughout Phanerozoic time, driven by the selective removal of calcium ions via planktonic calcification. Mackenzie and Pigott (1981) later argued that Sandberg's single shift was driven by tectonically induced shifts in atmospheric $p\text{CO}_2$. As more ancient oolite and early marine cement data became available, Sandberg abandoned his single-shift hypothesis in favour of the currently accepted fourfold shift in carbonate mineralogy (Sandberg, 1983; Lasemi and Sandberg, 2000), which he attributed to Mackenzie and Pigott's (1981) $p\text{CO}_2$ mechanism.

Morse *et al.* (1997) and Stanley and Hardie (1998) discounted the $p\text{CO}_2$ mechanism on the ground that it could only effect a shift to calcite seas if it caused seawater to become simultaneously oversaturated with respect to calcite and undersaturated with respect to aragonite. As the stoichiometric

solubility coefficients (K_{sp}) of aragonite ($10^{-6.19}$) and calcite ($10^{-6.37}$) are relatively close, the range of CaCO₃ saturation states that yields simultaneous calcite oversaturation and aragonite undersaturation is correspondingly narrow ($1 < \Omega_{\text{calcite}} < 1.5$; $0.7 < \Omega_{\text{aragonite}} < 1$) and requires that seawater be near undersaturation with respect to calcite over protracted intervals of geological time. Given the ubiquity and abundance of both biogenic and abiogenic limestone deposits throughout the calcite seas of Early Cambrian – Late Mississippian time and Late Jurassic – Middle Palaeocene time, it is improbable that the CaCO₃ saturation state of seawater during these intervals was regularly constrained to such a low and narrow range, teetering on the edge of total CaCO₃ undersaturation ($\Omega_{\text{calcite}} < 1$). And unlike Hardie's (1996) seawater Mg/Ca model, atmospheric $p\text{CO}_2$ does not explain the simultaneous transitions in the mineralogy of late stage marine evaporites (KCl-to-MgSO₄) and abiogenic marine carbonates (calcite-to-aragonite) throughout Phanerozoic time.

However, Morse *et al.* (1997) showed experimentally that temperature can strongly influence which polymorph of CaCO₃ precipitates abiotically from seawater. In modern seawater ($m\text{Mg}/\text{Ca} = 5.2$), the calcite and aragonite nucleation fields are divided by a temperature of ~ 6 °C – which is of little consequence here since the carbonate forming environments relevant to the calcite–aragonite sea hypothesis have probably been confined to tropical waters that are inherently more saturated with respect to CaCO₃ throughout Phanerozoic time. However, for seawater with $m\text{Mg}/\text{Ca}$ ratios between 3.0 and 1.0, Morse *et al.* (1997) showed that the calcite and aragonite nucleation fields are divided by temperatures ranging from 15 to 25 °C respectively. Thus, a slight change in the temperature of tropical, carbonate-forming waters could effect a threshold change in oceanic state. It is therefore likely that $p\text{CO}_2$ -induced fluctuations in climate have modulated the effect of seawater Mg/Ca on oceanic state (calcite vs. aragonite seas) throughout Phanerozoic time, particularly when seawater $m\text{Mg}/\text{Ca}$ was in its lower range ($1.0 < m\text{Mg}/\text{Ca} < 3.0$).

Along these lines, Zhuravlev and Wood (2008) attributed an apparently short-lived aragonite sea interval in middle Cambrian time (late Atbadanian–Botoman), which occurred shortly after the commencement of the protracted Palaeozoic calcite sea, to the onset of global greenhouse conditions at a time when seawater *mMg/Ca* was near the calcite–aragonite boundary value of 2.

Modern carbonate sediment production

The role of *Halimeda*, *Penicillus* and *Udotea* as important producers of modern carbonate sediments is well documented (David and Sweet, 1904; Finckh, 1904; Halligan, 1904; Chapman and Mawson, 1906; Emery *et al.*, 1954; Ginsburg, 1956; Milliman, 1977, 1993; Hillis-Colinvaux, 1980; Drew, 1983; Drew and Abel, 1988; Payri, 1988, 1995; Hillis, 1991, 2001; Freile *et al.*, 1995; Rees *et al.*, 2007). These algae are reported to contribute 25 to 39% of carbonate sediments in the Bahama Banks (Emery *et al.*, 1954; Neumann and Land, 1975), 25% to 80% in parts of the Great Barrier Reef Province (Drew, 1983; Rees *et al.*, 2007), 80% in carbonate platforms of the Timor Sea, NW Australia (Heyward *et al.*, 1997), 28% off the Island of Moorea, Tahiti (Payri, 1988) and 20–30% in the Florida Keys (Ginsburg, 1956). Rates of carbonate deposition range from 0.18 to 5.9 m 1000 yr⁻¹ (Neumann and Land, 1975; Marshall and Davies, 1988; Orme and Salama, 1988; Roberts *et al.*, 1988; Searle and Flood, 1988; Hillis, 1991; Freile *et al.*, 1995). Sediment production by these algae occurs from shallow back-reef environments (Ginsburg, 1956) to the deep fore-reef (Goreau and Goreau, 1973).

Such rapid rates of sediment production are attributable to the algae's relatively large size (up to 20 cm), rapid turnover because of a short, 1–2 month lifespan (Wefer, 1980), massive standing biomasses (up to 1560 g-dw m⁻²; Kangwe, 2006) and high rates of growth (3–4 mm day⁻¹). Detailed field studies of *Halimeda* sedimentary production have yielded CaCO₃ sedimentation rates of 2227 g CaCO₃ m⁻² yr⁻¹ from a standing stock of 228.4 g-dw m⁻² in parts and of the Great Barrier Reef Complex

(Drew, 1983); 1400 g CaCO₃ m⁻² yr⁻¹ from a standing stock of 111 g-dw m⁻² off the Island of Moorea, Tahiti (Payri, 1988); 6205–20805 g m⁻² yr⁻¹ from a standing stock of 1560 g-dw m⁻² in Chkawa Bay of the Indian Ocean, off the coast of Tanzania (Kangwe, 2006), 2300 g CaCO₃ m⁻² yr⁻¹ in Moorea Island lagoon in Tahiti (Freile *et al.*, 1995), 2400 g CaCO₃ m⁻² yr⁻¹ in Western Great Bahama Bank (Freile and Hillis, 1997), 2300 g CaCO₃ m⁻² yr⁻¹ around the San Blas islands off the coast of Panama (Freile and Hillis, 1997) and 404.9 g CaCO₃ m⁻² yr⁻¹ off the coast of Guam (Merten, 1971).

Massive '*Halimeda* reefs' (Martin *et al.*, 1997), tens of metres thick, kilometres in width and consisting almost entirely of *Halimeda* segments that are cemented and bound by microbially precipitated micrite and marine cement, have been observed in the Great Barrier Reef Province (Orme *et al.*, 1978a,b; Marshall and Davies, 1988; Orme and Salama, 1988; Roberts *et al.*, 1988), the Timor Sea off the northwest coast of Australia (Heyward *et al.*, 1997), the Fly River Delta in the Gulf of Papua New Guinea (Harris *et al.*, 1996), Indonesia (Phipps and Roberts, 1988; Roberts *et al.*, 1988; Granier *et al.*, 1997), the Caribbean Sea (Hine *et al.*, 1988) and offshore western India (Rao and Veerya, 1994).

Significantly, Neumann and Land (1975) observed that although the CaCO₃ within living *Halimeda* algae constitutes half of the total CaCO₃ within all calcareous bryopsidalean algae in the Bight of Abaco (Bahamas), only 25% of the underlying CaCO₃ sediments contain recognizable *Halimeda* grains. This suggests that half of the *Halimeda* grains are either exported by currents and storms from the basin or remain within the basin and disaggregate into loose, unrecognizable aragonite needles. The tendency for calcareous bryopsidalean algae – particularly *Udotea* and *Penicillus* – to disaggregate rapidly into nondescript grains of aragonite may cause their contribution to carbonate sedimentation to be underestimated. In fact, Lowenstam and Epstein (1957) showed that the carbon and oxygen isotopic signatures of aragonitic carbonate muds are consistent with a predominantly algal origin. However, microbial precipita-

tion in the water column has also been shown to be capable of producing substantial quantities of carbonate mud in tropical marine environments (Yates and Robbins, 1998, 1999, 2001).

Geological history of the calcareous bryopsidalean algae

The oldest fossil representative of the bryopsidalean order to which *Halimeda*, *Penicillus* and *Udotea* belong is *Halimeda soltanensis* (Poncet, 1989; Bucur, 1994), which has been identified in Permian-age limestones. However, calcareous bryopsidalean algae did not exhibit extensive diversity until Late Cretaceous time (c. 80 Ma; Elliott, 1960, 1965, 1978, 1981, 1984; Conrad and Rioult, 1977; Bassoulet *et al.*, 1983; Flügel, 1988, 1991; Hillis, 1991, 2000, 2001). After a brief period of stasis that followed the Cretaceous/Tertiary mass extinction event (Hillis, 2001), the algae's contribution to sediment production increased markedly throughout early-middle Cenozoic time (Elliott, 1984; Flügel, 1988, 1991; Hillis, 2000, 2001), an interval marked by the ocean's transition into the aragonite nucleation field (seawater *mMg/Ca* > 2). Their high level of diversity, abundance and sediment production persisted throughout the latter half of the Cenozoic Era (Elliott, 1960; Bassoulet *et al.*, 1983; Flügel, 1988; Mankiewicz, 1988) as the *mMg/Ca* of seawater ascended further into the aragonite nucleation field (from ~3 in Miocene time to 5.2 in the modern ocean). Hillis (2001) showed that the abundance of calcareous bryopsidalean algae was punctuated by a burst of productivity in Holocene time, but he notes that this is probably an artefact of the high quality of the sedimentary record over this interval.

The emergence of calcareous bryopsidalean algae as important producers of carbonate sediments in early Cenozoic time is based on numerous yet largely qualitative observations by Elliott (1960, 1965, 1978, 1981, 1984), Wray (1977), Conrad and Rioult (1977), Bassoulet *et al.* (1983), Flügel (1988, 1991) and Hillis (1991, 2000, 2001). This generally qualitative approach to assessing these algae's contribution to carbonate sedimentation and their evolution in general may be

partly attributable to their tendency to disaggregate rapidly into nondescript grains of aragonite shortly after deposition on the sea floor (Hillis, 2001), which may preclude a more rigorous and systematic examination of their fossilized remains.

Experimental evidence

Multiple studies have been published over the past several years investigating the effects of seawater Mg/Ca and absolute Ca²⁺ on the polymorph mineralogy, primary production and calcification of calcareous bryopsidalean algae (Ries, 2005, 2006; Stanley *et al.*, 2009). The *Halimeda incrassata*, *Penicillus capitatus* and *Udotea flabellum* species were investigated in these studies because of their pantropical distribution (Wray, 1977; Hillis-Colinvaux, 1980) and relatively dense coverage (Bach, 1979; Garrigue, 1985), which makes them particularly important producers of carbonate sediments in modern carbonate platform environments. These studies are reviewed in the following section.

Overview of experimental designs

Specimens of *Halimeda incrassata* (Stanley *et al.*, 2009), *Penicillus capitatus* (Ries, 2005) and *Udotea flabellum* (Ries, 2006) were grown for up to 90 days in 10-gallon glass aquaria filled with 30 L of experimental seawater (Bidwell and Spotte, 1985) formulated with Mg/Ca ratios of 1.0–1.5, 2.5 and 5.2, corresponding to calcite sea, boundary calcite–aragonite sea and aragonite sea conditions respectively. For the experiments on *Halimeda*, additional experimental seawaters were employed to investigate the effects of absolute [Ca²⁺]. These experimental seawaters were formulated with identical Mg/Ca ratios and differed only in absolute [Ca²⁺], which was fixed at 25.3, 18.1 and 10.2 mM, as well as [Mg²⁺], which was adjusted to maintain the prescribed Mg/Ca ratio and [Na²⁺], which was adjusted to offset the prescribed variations in [Mg²⁺] and [Ca²⁺] so that salinity remained at the modern value of 35 PSU.

The polymorph mineralogy of the CaCO₃ precipitated by the algae was determined by scanning electron

microscopy (SEM) and powder x-ray diffraction (XRD). The proportion of aragonite-to-calcite was calculated from the ratio of the area under the primary aragonite peak [d (111): 3.39 Å; 2θ = 26.3°] to the area under the primary calcite peak [d(104): 2.98–3.03 Å; 2θ = 29.5–30.0°], using standardized mixtures to calibrate this relationship. The Mg/Ca ratio of calcite was determined from the d-spacing of the calcite crystal lattice (calibrated with Mg-calcite standards) and confirmed with EDS microprobe spot analysis in the SEM.

Rates of calcification, linear extension and primary production were calculated from the offspring algae that were produced from the parent algae via rhizoid extension. Linear extension was determined by direct measurement. Calcification and pri-

mary production were determined through a standard loss-on-combustion method (Heiri *et al.*, 2001).

Mineralogical analysis

Powder X-ray diffraction (XRD) of the mineral precipitates (Fig. 4) derived from the *Halimeda*, *Penicillus* and *Udotea* offspring algae from the normal seawater treatments (*mMg/Ca* = 5.2) confirms that these algae produce the majority of their CaCO₃ as aragonite (*Halimeda* = 92% aragonite, 8% Mg-calcite; *Penicillus* and *Udotea* = 100% aragonite) under these conditions. However, XRD analysis also revealed that all three species of algae produced a portion of their CaCO₃ as low-Mg calcite (*Halimeda* = 46%; *Penicillus* = 22%; and *Udotea* = 25%) under

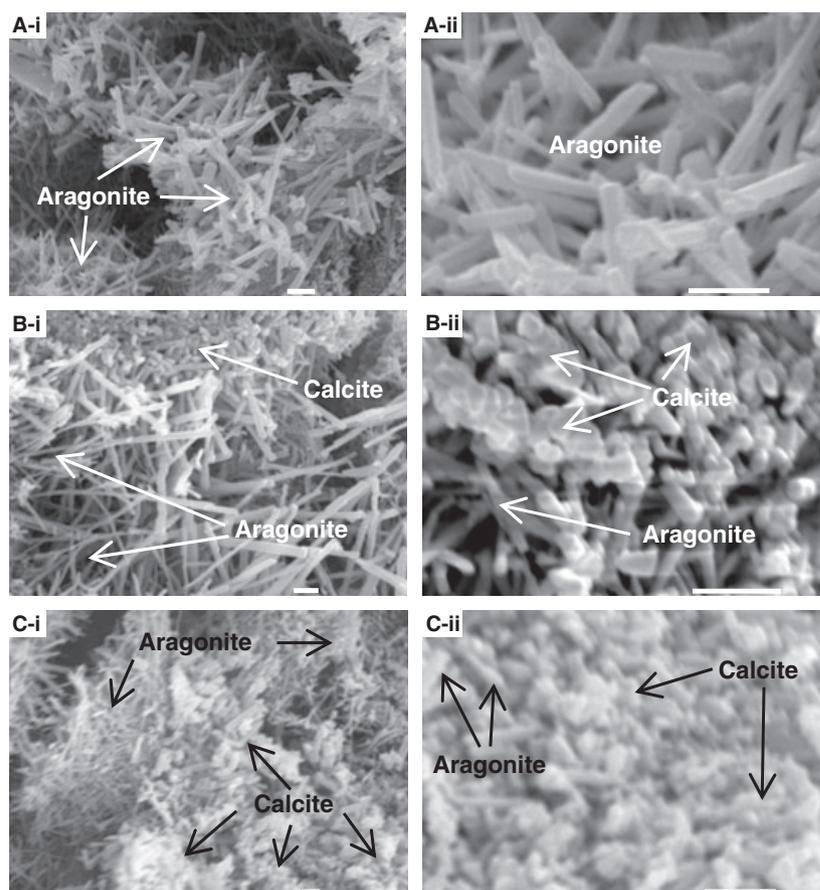


Fig. 3 Back-scatter electron images showing the distribution of the aragonite and calcite precipitated within the intertricular space of segments comprising the thallus of *Halimeda* grown in experimental seawaters with *mMg/Ca* = 5.2 and [Ca²⁺] = 10.2 mM (aragonite seawater; A-i, A-ii), *mMg/Ca* = 2.5 and [Ca²⁺] = 18.1 mM (aragonite-calcite boundary seawater; B-i, B-ii), and *mMg/Ca* = 1.5 and [Ca²⁺] = 25.3 mM (calcite seawater; C-i, C-ii). Scale bars are 1 μm (from Stanley *et al.*, 2009).

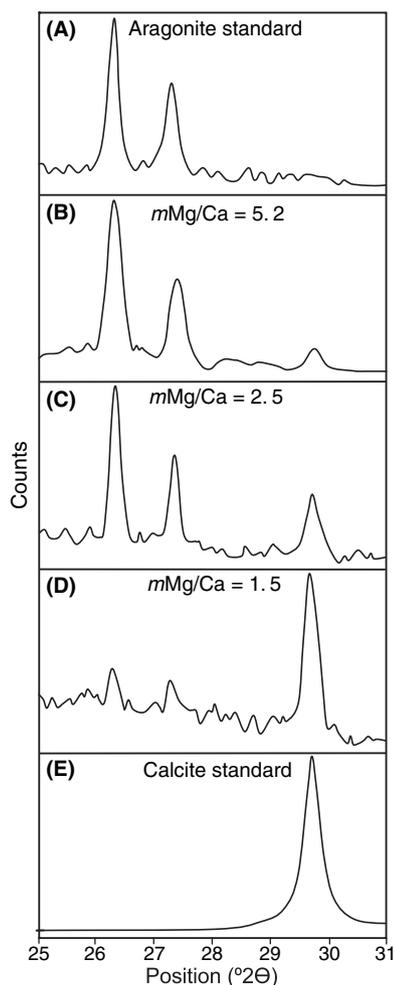


Fig. 4 X-ray diffraction patterns for: (A) pure aragonite, revealing primary aragonite peak [d(111)] at $2\theta = 26.3^\circ$ (3.39 Å); (B) a *Halimeda* alga that produced 92% aragonite and 8% calcite when grown in experimental seawater that favours the nucleation of the aragonite polymorph ($m\text{Mg}/\text{Ca} = 5.2$; $[\text{Ca}^{2+}] = 10.2$ mM); (C) a *Halimeda* alga that produced 84% aragonite and 16% calcite when grown in the boundary aragonite-calcite experimental seawater ($m\text{Mg}/\text{Ca} = 2.5$; $[\text{Ca}^{2+}] = 18.1$ mM); (D) a *Halimeda* alga that produced 54% aragonite and 46% calcite when grown in the experimental calcite seawater ($m\text{Mg}/\text{Ca} = 1.5$; $[\text{Ca}^{2+}] = 25.3$ mM); (E) pure calcite, revealing primary calcite peak [d(104); 3.01–3.02 Å; $2\theta = 29.6$ – 29.7°] (from Stanley *et al.*, 2009).

the experimental calcite sea conditions ($m\text{Mg}/\text{Ca} = 1.0$ – 1.5 ; Figs. 3–5). And *Halimeda* actually produced small amounts of high-Mg calcite in the boundary and aragonite sea condi-

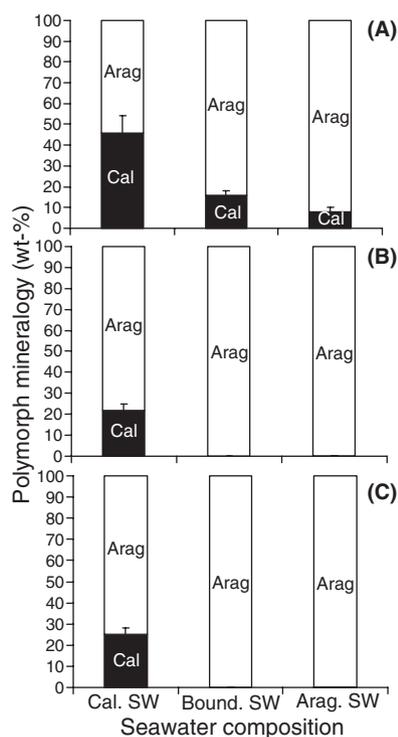


Fig. 5 Relative distribution (wt%) of the calcite and aragonite polymorphs of CaCO₃ precipitated within *Halimeda* (A), *Penicillus* (B), and *Udotea* (C) reared in the experimental seawaters ($m\text{Mg}/\text{Ca} = 1.5$, $[\text{Ca}^{2+}] = 25.3$ mM; $m\text{Mg}/\text{Ca} = 2.5$, $[\text{Ca}^{2+}] = 18.1$ mM; $m\text{Mg}/\text{Ca} = 5.2$, $[\text{Ca}^{2+}] = 10.2$ mM), as determined by powder X-ray diffraction. Error bars represent instrument error and variation within and amongst specimens (from Ries, 2005, 2006; Stanley *et al.*, 2009).

tions as well (Figs. 3–5). The proportion of calcite produced by the *Halimeda* alga increased significantly ($P < 0.001$) as the Mg/Ca ratio of the experimental seawater treatment decreased into the calcite stability field (Figs 3–5). Furthermore, the $m\text{Mg}/\text{Ca}$ ratio of the calcite produced by the *Halimeda* specimens increased proportionately ($P < 0.001$) with the $m\text{Mg}/\text{Ca}$ ratio of the experimental seawater treatment (Fig. 6).

Backscatter electron images of the *Halimeda* offspring algae from each of the seawater treatments reveal the distribution of aragonite and calcite precipitates within the intertricular space of the algae (Fig. 3). The aragonite crystals are acicular and euhedral, ranging in length from 1 to 10 μm , and packed in apparently

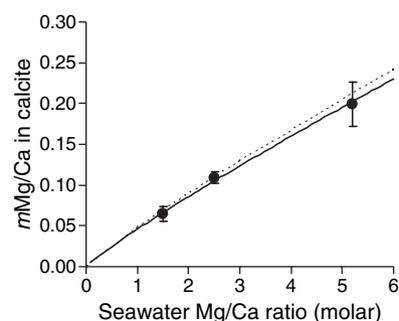


Fig. 6 Molar Mg/Ca of calcite precipitated by *Halimeda* algae in the experimental seawaters ($m\text{Mg}/\text{Ca} = 1.5$, $[\text{Ca}^{2+}] = 25.3$ mM; $m\text{Mg}/\text{Ca} = 2.5$, $[\text{Ca}^{2+}] = 18.1$ mM; $m\text{Mg}/\text{Ca} = 5.2$, $[\text{Ca}^{2+}] = 10.2$ mM), as determined by powder X-Ray diffraction and energy-dispersive spectrometry. Mg-fractionation algorithm (solid curve) is calculated using a least squares regression and is defined as $y = 0.0460x^{0.899}$ ($R^2 = 0.996$) at 25 °C. Dashed curve is Mg-fractionation curve for calcite precipitated abiotically from seawater at 25 °C ($y = 0.0482x^{0.898}$, $R^2 = 0.930$; Füchtbauer and Hardie, 1976). Error bars represent instrument error and variation within and amongst specimens (from Stanley *et al.*, 2009).

random orientations. The calcite crystals are rhombic and subhedral, less than one micron in diameter and generally clustered between the aragonite bundles. Both mineral phases exhibit clumped distributions.

Reproduction under experimental conditions

The total number of offspring algae produced by the parent algae varied amongst the different experimental seawater treatments. In the calcite, boundary and aragonite seawater treatments, *Halimeda* produced 18, 37 and 45 offspring algae, *Penicillus* produced 13, 29 and 16 offspring algae and *Udotea* produced 16, 17 and 23 offspring algae respectively. That the algae generally produced fewer offspring in the experimental seawaters formulated at lower Mg/Ca ratios suggests that the algae were stressed by producing a large portion of their CaCO₃ as aragonite in seawater favouring the nucleation of calcite. If the precipitation of aragonite under such conditions requires extra energy to manipulate the composition of the algae's calcifying fluid (e.g. to elevate Mg/Ca back into the aragonite domain) to produce aragonite under

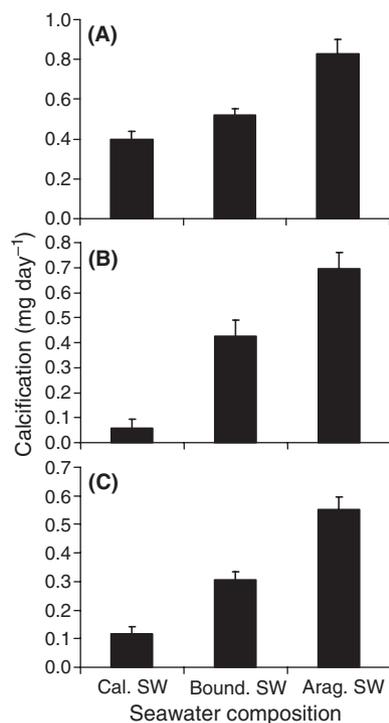


Fig. 7 Rates of linear extension for *Halimeda* (A), *Penicillus* (B) and *Udotea* (C) grown in the experimental calcite, boundary and aragonite seawaters. Rates of linear extension increase significantly ($P < 0.05$) with increasing seawater Mg/Ca. Error bars represent standard error (from Ries, 2005, 2006; Stanley *et al.*, 2009).

such conditions, this energy may be diverted away from other physiological activities, such as reproduction and tissue growth.

Rates of calcification, linear extension and primary production

Rates of calcification (Fig. 7), linear extension (Fig. 8) and primary production (Fig. 9) for the *Halimeda*, *Penicillus* and *Udotea* algae were the highest ($P < 0.05$) in the seawater treatments that favoured nucleation of their aragonite mineral ($mMg/Ca = 5.2$) and the lowest ($P < 0.05$) in the treatments that favoured nucleation of the calcite mineral ($mMg/Ca = 1.0$ – 1.5). These results are consistent with the hypothesis that the calcite-to-aragonite sea transition in early Cenozoic time facilitated the rise of these algae as important producers of CaCO₃ sediments across that interval of geological time.

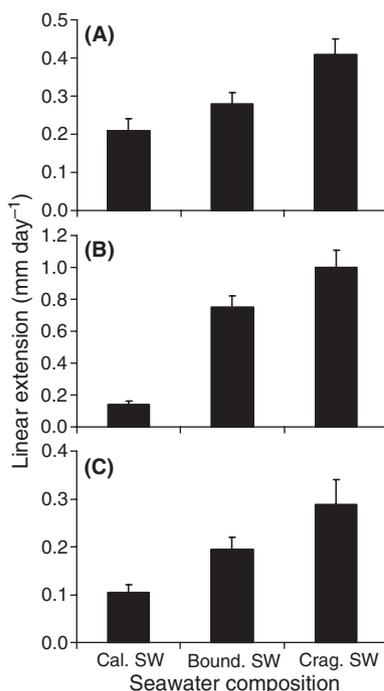


Fig. 8 Rates of calcification for *Halimeda* (A), *Penicillus* (B) and *Udotea* (C) grown in the experimental calcite, boundary and aragonite seawaters. Rates of calcification increase significantly ($P < 0.05$) with increasing seawater Mg/Ca. Error bars represent standard error (from Ries, 2005, 2006; Stanley *et al.*, 2009).

Effect of absolute [Ca²⁺] on linear extension, calcification and primary production in *Halimeda*

As variations in seawater Mg/Ca throughout the geological past are thought to be partially driven by inverse changes in [Ca²⁺], it is possible that the positive effects of elevated seawater Mg/Ca on bryopsidalean calcification (i.e. favouring nucleation of the algae's preferred aragonite mineral) would have been offset by the negative effects of reduced [Ca²⁺] [i.e. reducing the CaCO₃ saturation state ([Ca²⁺] × [CO₃²⁻]) of seawater]. To isolate the effects of [Ca²⁺] and Mg/Ca, the *Halimeda* algae were reared in an array of experimental seawaters specifically formulated to test for the effects of [Ca²⁺] when Mg/Ca is held constant and vice versa (Fig. 10). When mMg/Ca was held constant (at 1.5, 2.5 and 5.2), increases in [Ca²⁺] from 10.2 to 18.1, to 25.3 mM resulted in increased ($P < 0.05$) rates of linear extension,

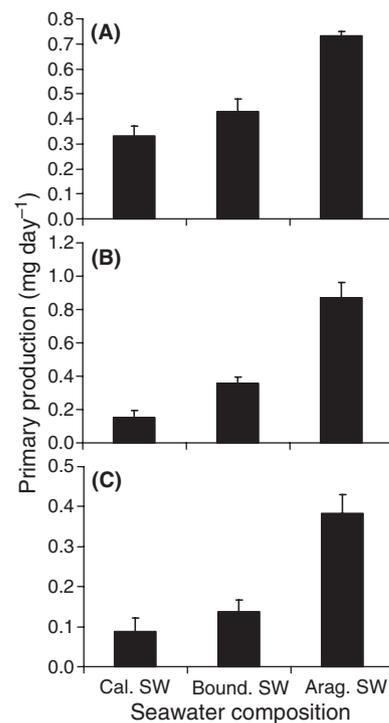


Fig. 9 Rates of primary production for *Halimeda* (A), *Penicillus* (B) and *Udotea* (C) grown in the experimental calcite, boundary and aragonite seawaters. Rates of primary production increase significantly ($P < 0.05$) with increasing seawater Mg/Ca. Error bars represent standard error (from Ries, 2005, 2006; Stanley *et al.*, 2009).

calcification and primary production (Fig. 10). And when [Ca²⁺] was held constant (at 10.2, 18.1 and 25.3 mM), increases in mMg/Ca from 1.5 to 2.5, to 5.2 resulted in increased ($P < 0.05$) rates of linear extension, calcification and primary production (Fig. 10). However, over the range of values that are thought to have occurred throughout the geologic history of the bryopsidalean algae, the magnitude of the effects of seawater Mg/Ca on linear extension, calcification and primary production of the *Halimeda* algae was greater than that of [Ca²⁺].

Discussion

These experiments show that bryopsidalean algae exhibit higher rates of calcification, linear extension and primary production when reared in experimental seawaters that favour nucleation of their preferred aragonite polymorph of CaCO₃ ($mMg/Ca > 2$).

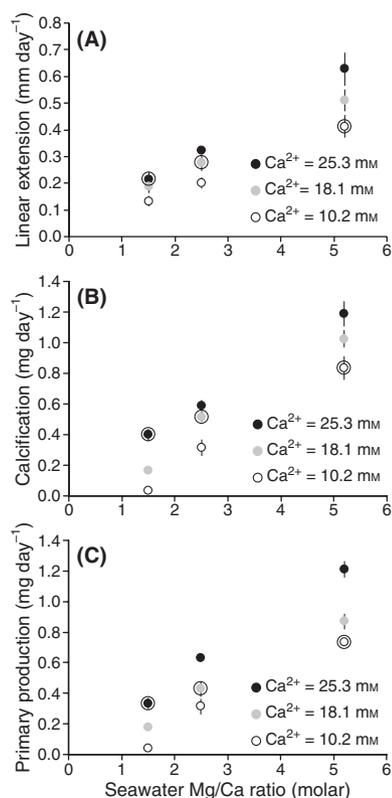


Fig. 10 Rates of linear extension (A), calcification (B) and primary production (C) for *Halimeda* grown in the nine experimental seawaters formulated to isolate the effects of seawater Mg/Ca and [Ca²⁺]. Rates of linear extension, calcification and primary production increase significantly ($P < 0.05$) with both increasing seawater Mg/Ca ([Ca²⁺] fixed) and increasing seawater [Ca²⁺] (Mg/Ca fixed). Rates of linear extension, calcification and primary production also increase significantly ($P < 0.05$) with elevations in seawater Mg/Ca that are formulated with geologically realistic (Hardie, 1996; Demicco *et al.*, 2005) reductions in [Ca²⁺] (circumscribed data). Error bars represent standard error (from Stanley *et al.*, 2009).

This observation is consistent with the assertion that the steady elevation of seawater *m*Mg/Ca ratios (from 1.0 to 5.2) throughout Cenozoic time has fostered their role as major sediment producers in carbonate platform environments throughout this interval.

Relationship between calcification and primary production

Although the observed relationship between seawater Mg/Ca and calcifi-

cation of the *Halimeda*, *Penicillus* and *Udotea* algae may be expected, it is less obvious why seawater Mg/Ca would also affect primary production and linear extension of these algae. It has been proposed that some calcareous bryopsidalean algae and coccolithophores utilize CO₂ liberated via calcification directly in their own photosynthesis (Fig. 2A; see equation 2; Paasche, 1968; Borowitzka and Larkum, 1976b; Borowitzka, 1977; Sikes *et al.*, 1980; Reiskind *et al.*, 1988, 1989; Ries, 2005, 2006; Stanley *et al.*, 2005). Thus, elevated rates of calcification would increase CO₂ within the intertricular calcification space of the *Halimeda*, *Penicillus* and *Udotea* algae (Fig. 2), thereby increasing the rate of photosynthesis within adjacent cells, resulting in increased rates of primary production and linear extension for the algae. While calcification is certainly not the sole source of CO₂ for photosynthesis within calcareous bryopsidalean algae (as many non-calcifying bryopsidalean algae exist), its role in CO₂ liberation may be sufficient to explain the observed connection between calcification and primary production/linear extension.

The negative impact of low intertricular CO₂ on primary production, resulting from reduced calcification in low Mg/Ca seawater, could have been partially offset by the elevated atmospheric *p*CO₂ (Berner and Kothavala, 2001; Royer *et al.*, 2001, 2004; Yates and Robbins, 2001; Tyrrell and Zeebe, 2004; Pagani *et al.*, 2005) that may have accompanied the tectonically forced reductions in seawater Mg/Ca. If this offset occurred, then the low rates of primary production and linear extension observed in the experimental calcite and boundary seawater treatments of the present study, for which *p*CO₂ was fixed at the relatively low modern value of 385 p.p.m., may not be applicable to calcareous bryopsidalean algae inhabiting the potentially high-CO₂ calcite seas of the geological past. Under such elevated *p*CO₂ conditions, photosynthesis by these algae would likely not have been limited by ambient CO₂ and thus would have been less affected by reductions in the amount of CO₂ liberated within the algae's intertricular space by calcification. Thus, although their role as carbonate sediment producers would have been

diminished under such low Mg/Ca-high *p*CO₂ conditions, they may still have been important constituents of shallow tropical ecosystems if they were able to resist predation in their weakly calcified state.

An alternative mechanism that explains why algal linear extension and primary production would track calcification is based on the release of H⁺ ions during calcification (see equation 3; Fig. 2A). In one model, the liberated H⁺ ions complex with HCO₃⁻ ions within the algae's intertricular space, thus facilitating CO₂ extraction by dehydration of H₂CO₃ within the algal cell (Fig. 2A; McConnaughey and Whelan, 1997; Hellblom *et al.*, 2001; Hellblom and Axelsson, 2003). In another model, H⁺ ions liberated by the alga as symporters or co-transporters of HCO₃⁻ and nutrients, such as NO₃⁻ and PO₄⁻³, across the algal cell wall (Fig. 2A; Price and Badger, 1985; Price *et al.*, 1985; McConnaughey and Whelan, 1997; Hellblom *et al.*, 2001). Increased rates of assimilation of these typically limiting substrates could effectively increase the algae's rates of photosynthesis and primary production as their rates of calcification increase.

Mg/Ca ratio versus CaCO₃ saturation state

The results of the study on *Halimeda* reveal that both elevated Mg/Ca ratios and elevated [Ca²⁺] promote calcification, primary production and linear extension within this alga. The elevated Mg/Ca ratios evidently translate into higher rates of calcification by creating ambient chemical conditions favourable for the precipitation of the alga's preferred aragonite biomineral. Elevated [Ca²⁺] probably fosters higher rates of calcification by increasing the CaCO₃ saturation state of the alga's ambient seawater.

Over the range of *m*Mg/Ca ratios (1.0–5.2) and absolute [Ca²⁺] (10.2–25.3 mM) that are believed to have occurred throughout Phanerozoic time, the favourable effects of elevated Mg/Ca on bryopsidalean algal calcification are generally greater in magnitude than the unfavourable effects of reduced CaCO₃ saturation state caused by concomitant reductions in

[Ca²⁺]. Thus, Mg/Ca ratio appears to be the primary determinant of how calcareous bryopsidalean algae will respond to calcite–aragonite sea transitions. However, it should be noted that at least one scenario was identified in which increasingly favourable Mg/Ca ratios were outweighed by increasingly unfavourable CaCO₃ saturation states (via decreasing [Ca²⁺]), in terms of their relative effects on calcification rate. This was evident (Fig. 10) when experimental seawater conditions shifted from $m\text{Mg}/\text{Ca} = 1.5$, [Ca²⁺] = 25.2 mM to $m\text{Mg}/\text{Ca} = 2.5$, [Ca²⁺] = 10.2 mM.

Biominerological control

The observation that the *Halimeda*, *Penicillus* and *Udotea* algae each precipitate the majority of their CaCO₃ as the aragonite polymorph in the experimental calcite seawater suggests that these algae exhibit some control over the Mg/Ca ratio of their intertricular calcifying fluid. Yet because, as these algae commence producing a portion of their CaCO₃ as the kinetically favoured calcite polymorph under such conditions, it is evident that their biominerological control can be partially overridden by ambient seawater Mg/Ca.

The distribution of aragonite and calcite clusters precipitated within *Halimeda* (Fig. 3), *Penicillus* and *Udotea* grown in the experimental calcite seawater occurs on a spatial scale that is comparable to that of the purported acid and alkaline zones within these algae (De Beer and Larkum, 2001). Both conditions may reflect the algae's spatially limited control over the chemical milieu of their intertricular fluid.

It has been suggested that *Halimeda* algae control calcification solely through pH regulation (Borowitzka, 1987; De Beer and Larkum, 2001). If this assertion is correct, then *Halimeda* algae grown in the experimental calcite seawater should precipitate exclusively calcite which they did not. De Beer and Larkum's (2001) conclusion that Ca²⁺ is not actively transported into the intertricular space of *Halimeda* is based on their observation that the alga's rate of calcification remains unaffected by inhibition of the Ca-ATPase enzyme. While their findings show that *Halimeda* are not actively transporting Ca²⁺ into the calcifying space, it is conceivable that *Halimeda*, as well as *Penicillus* and *Udotea*, pumps Ca²⁺ out of the intertricular space, thereby maintaining the Mg/Ca ratio of certain regions of the algae's intertricular space within the aragonite nucleation field ($m\text{Mg}/\text{Ca} > 2$). Alternatively, the drawdown of Ca²⁺ via calcification (Fig. 2A) may also be sufficient to maintain the Mg/Ca of the intertricular fluid at an elevated steady-state (favouring precipitation of aragonite), despite low ambient Mg/Ca. These scenarios, of course, require that the CaCO₃ saturation state of the intertricular fluid is maintained at a level sufficient to promote calcification, even after Ca²⁺ is reduced via cation transport or calcification, perhaps by increasing [CO₃²⁻] by removing CO₂ via photosynthesis (Fig. 2A; Borowitzka, 1982b, 1987) or by increasing pH through H⁺-pumping (Fig. 2A; De Beer and Larkum, 2001). Alternatively, the same outcome could be achieved by actively transporting Mg²⁺ ions into the algae's intertricular space, thereby

elevating the Mg/Ca ratio into the aragonite nucleation field. However, a mechanism capable of such rapid transport of Mg²⁺ across the algal cell wall is yet to be identified in the bryopsidalean algae.

Comparison of biominerological control amongst *Halimeda*, *Udotea* and *Penicillus*

The degree of biominerological control appears to vary amongst the three genera of calcareous bryopsidalean algae, with *Halimeda* exerting the least control and *Penicillus* and *Udotea* the most. This is evidenced by the observation that the *Halimeda* algae (Stanley *et al.*, 2009) produced 46 (±8) wt% calcite in the experimental calcite seawater treatment, whereas *Penicillus* (Ries, 2005) and *Udotea* (Ries, 2006) produced only 22 (±3) and 25 (±3) wt% of their CaCO₃ as calcite in the experimental calcite seawater. More limited biominerological control by *Halimeda* is also evidenced by the surprising observation that it produced a portion of its CaCO₃ as magnesian calcite even in the boundary [16.2 (±1.8) wt%] and experimental aragonite [8.1 (±1.9) wt%] seawaters (Figs 3–5). *Penicillus* and *Udotea*, in contrast, precipitated exclusively aragonite under these conditions (Table 1). Furthermore, the Mg²⁺ fractionation pattern for calcite precipitated by the *Halimeda* algae in the various seawater treatments (Fig. 6) mimics Mg²⁺ incorporation in abiotically precipitated calcite (Füchtbauer and Hardie, 1976, 1980), supporting the assertion that precipitation of calcite by the *Halimeda* algae proceeds in an uncontrolled, nearly abiotic manner.

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

Alga	SW $m\text{Mg}/\text{Ca}^*$	Mineralogy (%cal:%arag)	Calcification ±SE (mg day ⁻¹)	Linear extension ±SE (mm day ⁻¹)	Primary production ±SE (mg day ⁻¹)	Study
<i>Halimeda incrassata</i>	5.2	8: 92 ± 2	0.83 ± 0.07	0.41 ± 0.04	0.73 ± 0.02	Stanley <i>et al.</i> , 2009
<i>Halimeda incrassata</i>	2.5	16: 84 ± 2	0.52 ± 0.03	0.28 ± 0.03	0.43 ± 0.05	Stanley <i>et al.</i> , 2009
<i>Halimeda incrassata</i>	1.5	46: 54 ± 8	0.40 ± 0.04	0.21 ± 0.03	0.33 ± 0.04	Stanley <i>et al.</i> , 2009
<i>Penicillus capitatus</i>	5.2	0: 100 ± 3	0.70 ± 0.06	1.00 ± 0.11	0.87 ± 0.10	Ries, 2006
<i>Penicillus capitatus</i>	2.5	0: 100 ± 3	0.42 ± 0.07	0.75 ± 0.07	0.36 ± 0.04	Ries, 2006
<i>Penicillus capitatus</i>	1.0	22: 78 ± 3	0.06 ± 0.03	0.14 ± 0.02	0.15 ± 0.04	Ries, 2006
<i>Udotea flabellum</i>	5.2	0: 100 ± 3	0.55 ± 0.04	0.29 ± 0.05	0.38 ± 0.05	Ries, 2005
<i>Udotea flabellum</i>	2.5	0: 100 ± 3	0.30 ± 0.03	0.20 ± 0.02	0.14 ± 0.03	Ries, 2005
<i>Udotea flabellum</i>	1.0	25: 75 ± 3	0.12 ± 0.03	0.10 ± 0.02	0.09 ± 0.03	Ries, 2005

* $m\text{Mg}/\text{Ca} = 1.0$, [Ca²⁺] = 31.6 mM; $m\text{Mg}/\text{Ca} = 1.5$, [Ca²⁺] = 25.3 mM; $m\text{Mg}/\text{Ca} = 2.5$, [Ca²⁺] = 18.1 mM; $m\text{Mg}/\text{Ca} = 5.2$, [Ca²⁺] = 10.2 mM.

Analysis of nuclear-encoded ribosomal DNA reveals that the *Penicillus* and *Udotea* algae are more closely related to each other than they are to the *Halimeda* algae (Verbruggen *et al.*, 2009). The phylogenetic relationships amongst these algae are consistent with their apparently varying degrees of biomineralogical control.

Nonetheless, the observation that three genera of bryopsidalean algae, belonging to two separate families (udoteacea and halimedacea), each exhibited highly similar responses to reductions in seawater Mg/Ca – in terms of their rates of calcification, primary production and linear extension and their control over polymorph mineralogy – suggests that these responses are indeed representative of most aragonite-secreting algae assigned to this order.

Palaeoecological implications

The results of the experimental studies suggest that the predominant carbonate-producing bryopsidalean algae – *Halimeda*, *Penicillus* and *Udotea* – would have been slower growing, smaller and less calcified during calcite seas of the geological past. Such geochemically induced reductions in the fitness of these algae would have had important ecological implications for these algae and for carbonate platform environments, in general. Their slower growth rates and smaller size would have reduced their ability to compete for space and sunlight on the substrate-limited shallow tropical seafloor; and their reduced calcification would have rendered them more susceptible to predation by grazing fish, which, in modern aragonite seas, are largely deterred by the algae's high CaCO₃ content (Hay *et al.*, 1994). The algae's contribution of biogenic CaCO₃ to shallow tropical carbonate platforms would have been comparably diminished by such reductions in calcification, primary production and population density during calcite sea intervals.

Needless to say, such extrapolation from the laboratory aquarium to the geological past assumes that the modern *Halimeda*, *Penicillus* and *Udotea* species employed in these experiments are sufficiently representative of the ancient species and that these ancient species were not better adapted for

producing aragonite, or even calcite, in seawater favouring the precipitation of calcite.

Additional factors contributing to increased carbonate sedimentation by bryopsidalean algae in early Cenozoic time

Resistance to herbivory is an important determinant of the distribution and abundance of calcareous bryopsidalean algae. The two main defences employed by these algae to deter herbivory are calcification and production of secondary metabolic toxins (see Hay *et al.*, 1994 for review). Although the timing of the evolution of toxic compounds within calcareous bryopsidalean algae is not known, it is possible that this contributed to their increased abundance and sediment production in early Cenozoic time. Alternatively, increased predation pressure in early Cenozoic time (e.g. from the diversification of reef fish in Eocene time; Bellwood, 1996) may have given algae that possessed defences such as calcification and toxicity a competitive advantage. Increased carbonate production by these algae in early Cenozoic time may have also resulted from the existence of warm, greenhouse conditions at that time (Pagani *et al.*, 2005), which would have favoured the nucleation of the aragonite mineral (Morse *et al.*, 1997), and enhanced the primary productivity of tropical marine algae, in general. However, none of these variables should have continuously fostered elevated rates of carbonate sediment production by the bryopsidalean algae throughout the latter half of the Cenozoic Era. Only seawater Mg/Ca, which continued ascending further into the aragonite stability field throughout Cenozoic time, is consistent with the bryopsidalean algae's late Neogene apex in carbonate sediment production (Hillis, 2001).

Conclusions

1 The *mMg/Ca* ratio of seawater has varied between approximately 1.0 and 5.2 throughout Phanerozoic time. This is evidenced from the composition of fluid inclusions in primary marine halite, the Mg content of fossil echinoids and molluscs

and synchronized transitions in the mineralogy of ooids and marine cements (aragonite and high-Mg calcite vs. low Mg calcite) and late stage marine evaporites (MgSO₄ vs. KCl).

- 2 A mid-ocean ridge hydrothermal brine/river water mixing model driven by global rates of ocean crust production predicts fluctuations in seawater Mg/Ca ratios throughout Phanerozoic time that are consistent with the geological record of seawater Mg/Ca (i.e. fluid inclusions, Mg-contents of echinoids and molluscs and primary mineralogy of abiotic CaCO₃ deposits and marine evaporites). This suggests that the principal tenants of the model are correct and that seawater Mg/Ca has generally varied inversely with the global rate of ocean crust production.
- 3 When seawater *mMg/Ca* was greater than 2, precipitation of the aragonite and high-Mg calcite polymorphs was favoured. When seawater *mMg/Ca* was less than 2, precipitation of low-Mg calcite was favoured. This relationship is reflected in the primary polymorph mineralogy of ooids and marine cements and in the skeletal mineralogy of the major reef-building and sediment-producing calcareous marine organisms throughout Phanerozoic time.
- 4 Today, calcifying bryopsidalean algae are among the most important contributors of aragonite sediments to carbonate platform environments. These aragonite-secreting algae assumed their important sediment-producing roles in early Cenozoic time, coincident with the most recent transition from calcite-to-aragonite seas. Significantly, they retained their sediment-producing roles throughout the remainder of Cenozoic time, as seawater continued to rise further into the aragonite stability field. However, this trend is based largely on qualitative descriptions of the algae's contribution to Cenozoic limestones. Evaluation of these trends in the context of the calcite–aragonite sea hypothesis would be substantially improved by a more quantitative assessment of the algae's geological record of sediment production. This repre-

sents an important area of future research.

- 5 Experiments on modern *Halimeda*, *Penicillus* and *Udotea* algae revealed that their rates of calcification, primary production and linear extension declined in experimental seawaters formulated with reduced Mg/Ca ratios that favour nucleation of the calcite polymorph over the algae's preferred aragonite polymorph. Assuming that these modern algae mimic the response of ancient related taxa to modified seawater Mg/Ca, these experimental studies suggest that calcareous bryopsidalean algae would have been smaller, less abundant, less competitive for space on the seafloor and less resistant to grazing when seawater Mg/Ca did not favour their inherently aragonitic mineralogy. This is consistent with the assertion that a shift from calcite-to-aragonite seas in early-to-middle Cenozoic time enabled the aragonite-secreting bryopsidalean algae to flourish and to become the important producers of CaCO₃ sediments that they are today.
- 6 Experiments on *Halimeda* revealed that the elevation of Mg/Ca and [Ca²⁺] both result in increased rates of calcification, primary production and linear extension. During calcite seas intervals, low Mg/Ca would have been accompanied by relatively high [Ca²⁺]. Thus, their effects on algal calcification, primary production and linear extension would have partially offset each other. However, the experiments revealed that over the range of coupled seawater Mg/Ca ratios and [Ca²⁺] that are believed to have occurred throughout the geological history of the bryopsidalean algae, seawater Mg/Ca was probably the controlling variable. Simultaneous, inverse variations in [Ca²⁺] appear only to moderate the effects of seawater Mg/Ca.
- 7 The concomitant variations in calcification, primary production, and linear extension of the *Halimeda*, *Penicillus* and *Udotea* algae suggest that there are important connections amongst these processes within the algae. Seawater Mg/Ca appears to directly influence calcification via CaCO₃ polymorph com-

patibility. Calcification, in turn, may influence primary production and linear extension by liberating CO₂ for photosynthesis and/or supplying H⁺ ions for various cellular functions that support photosynthesis, such as the transcellular proton-shuttling of nutrients or HCO₃⁻ and the formation of intracellular H₂CO₃, from which CO₂ can be efficiently extracted via dehydration.

- 8 *Halimeda*, *Penicillus* and *Udotea* each produced a portion (< 50%) of their CaCO₃ as the calcite polymorph in the experimental calcite seawater. This indicates that the algae's biomineralogical control can be partially overridden by ambient seawater chemistry and suggests that these algae may have produced a mixture of aragonite and calcite throughout Cretaceous time, when ocean chemistry favoured nucleation of calcite rather than aragonite (mMg/Ca < 2). Nonetheless, the observation that the algae precipitated the majority of their CaCO₃ as aragonite in experimental seawater that favours the precipitation of calcite indicates that these algae must actively specify nucleation of the aragonite polymorph. This may be accomplished by controlling Mg/Ca of their intertricular fluid through cation pumping or with chemical and/or mechanical templates that specify nucleation of the aragonite polymorph (Borowitzka, 1987). Regardless of the mechanism, the observation that calcification, primary production, linear extension and reproduction each declined for the algae reared under calcite sea conditions suggests that their active specification of the aragonite polymorph in mineralogically unfavourable seawater comes at a substantial energetic cost.
- 9 The similarity amongst the responses of the three genera of bryopsidalean algae (belonging to two separate families) to the experimental calcite seawater – i.e. reduced rates of calcification, primary production and linear extension and partial precipitation of low-Mg calcite – suggests that these responses are representative of most aragonite-secreting algae assigned to this order.

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