Influence of seawater chemistry on biomineralization throughout phanerozoic time: Paleontological and experimental evidence

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Abstract

Although some organisms exercise considerable control over their biomineralization, seawater chemistry has affected skeletal secretion by many taxa. Secular changes in the magnesium/calcium ratio and absolute concentration of calcium in seawater, driven by changes in rates of deep-sea igneous activity, have influenced the precipitation of nonskeletal carbonates: low-Mg calcite forms when the ambient Mg/Ca molar ratio is <1, high-Mg calcite forms when the ratio is 1–2, and high-Mg calcite and aragonite form when the ratio is above 2. Reef builders and other simple organisms that are highly productive biomineralizers have tended to respond to changes in seawater chemistry in ways that mirror patterns for nonskelatal carbonates. Also, changes in the concentration of silicic acid in seawater have affected the ability of organisms to secrete siliceous skeletons. In laboratory experiments, organisms that secrete high-Mg calcite in the modern aragonite sea incorporate progressively less Mg in their skeletons with a reduction in the ambient Mg/Ca ratio, producing low-Mg calcite in "Cretaceous" seawater (Mg/Ca molar ratio=1.0). Because algae that liberate CO_2 through calcification use it in their photosynthesis, an increase in the ambient Mg/Ca ratio results in accelerated aragonite secretion and overall growth for codiacean algae, and a decrease in the Mg/Ca ratio results in greatly accelerated growth rates for calcitic coccolithophores. Controlled experiments show that the increased concentration of Ca that accompanies a reduction of the ambient Mg/Ca ratio also accelerates coccolithophore population growth. Coccolithophores' production of vast chalk deposits in Late Cretaceous time can be attributed to the low Mg/Ca ratio and high Ca concentration in ambient seawater. The high Mg/Ca ratio and low Ca concentration in modern seawater apparently limit population growth for the large majority of modern coccolithophore species: ones that fail to respond to nitrate, phosphate or iron fertilization and are confined to oligotrophic waters. Presumably the low Mg/Ca ratio of ambient seawater was at least partly responsible for reduced reef-building by scleractinian corals in Late Cretaceous time. Some taxa have secreted more robust skeletons when seawater chemistry has favored their skeletal mineralogy. Strong intrinsic control of biomineralization can buffer a taxon against secular changes in seawater chemistry. Mollusks, for example, evolved the ability to severely limit the incorporation of Mg in their skeletal calcite in seawaters with Mg/Ca ratios as high as that of the present, but not in seawaters with still higher ratios. The ability to exclude Mg is useful because Mg reduces the rate of step growth of calcite crystals. On the other hand, labile skeletal mineralogy has permitted some taxa to respond to secular changes in the Mg/Ca ratio of seawater via phenotypic or evolutionary shifts of skeletal mineralogy. Sponges and bryozoans have apparently undergone evolutionary shifts of this kind polyphyletically. Increased incorporation of Mg in skeletal calcite with secular increases in the concentration of Mg in seawater has had little effect on

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seawater chemistry. In contrast, removal of Si by diatoms beginning in late Mesozoic time lowered the concentration of silicic acid in seawater, forcing siliceous sponges to secrete less robust skeletons.

1. Introduction

The relative importance of *biologically induced* biomineralization, in which the environment plays a dominant role, and *biologically controlled* biomineralization, in which cellular activities exert a powerful control has been a subject of much controversy (Lowenstam and Weiner, 1989, p. 26–27; Mann, 2001, p. 24–27; Weiner and Dove, 2003). At issue here are the factors that govern the mineralogy of skeletons and the rate at which skeletons form. Organisms have the potential to control the mineralogy of their skeletons in either of two ways: (1) they can employ organic templates that specify or favor a particular crystal structure (e.g. Borowitzka, 1984; Teng et al., 1998; Mount et al., 2004), or (2) they can control the chemistry of the medium from which their skeletal material is derived; mollusks exemplify this level of evolution, secreting their shell in fluid compartments that are physically isolated from external seawater and employ separate compartments to secrete calcite and aragonite (Wilbur, 1972).

Considerations of the importance of biologically induced biomineralization have often focused on photosynthetic organisms, which by consuming CO_2 can cause calcium carbonate to precipitate. In this paper, however, I review evidence that throughout the Phanerozoic Eon the cationic composition of seawater has also powerfully influenced skeletal formation, not only by photosynthesizers but also by animals. The magnesium/calcium (Mg/Ca) ratio and absolute concentration of Ca in seawater have played important roles in biocalcification. In addition, the concentration of silica in the ocean has influenced skeletal secretion by siliceous sponges.

In particular, I will review evidence that changes in the chemistry of ambient seawater:

(1) have induced phenotypic changes in the mineralogy of organisms,
(2) have influenced the rate at which organisms have grown their skeletons without mineralogical changes—and have thereby enabled certain organisms to function as major reef builders and sediment producers during particular intervals,

(3) may have induced organisms to evolve so as to produce minerals whose formation is compatible with seawater chemistry, and
(4) have apparently altered seawater chemistry in ways that have fed back to influence biomineralization.

1.1. Biocalcification and seawater chemistry

Much of the biocalcification research summarized in this paper is an outgrowth of the modeling of seawater chemistry by Hardie (1996), which was modified slightly in Stanley and Hardie (1998) and Demicco et al. (2005). Hardie's seminal work addressed the important discovery by Sandberg (1983, 1985) that the composition of nonskeletal carbonate precipitates (early marine cements and ooliths) has undergone oscillations during Phanerozoic time: there have been three intervals of aragonite seas, including the present, and two intervals of calcite seas (Fig. 1). Petrographic and chemical analyses indicate that lime muds have also adhered to this pattern (Lasemi and Sandberg, 2000).

Folk (1974) and Berner (1975) showed that the Mg/Ca ratio of aqueous fluids determines what form of calcium or calcium magnesium carbonate precipitates inorganically, and Hardie (1996) made a convincing case that the alternation between aragonite and calcite seas has resulted from oscillations in the Mg/Ca ratio of seawater. Füchtbauer and Hardie (1976, 1980) documented how the mole percent of Mg substituting for Ca in nonskeletal calcite increases with the Mg/Ca ratio of ambient seawater (Fig. 1). They showed that nonskeletal precipitation produces low-Mg calcite (<4 mol% Mg substituting for Ca) when the Mg/Ca molar ratio is below 1.0, high-Mg calcite when this ratio is above 1.0, and both high-Mg calcite and aragonite when the ratio is above 2.0. Thus, high-Mg calcite and aragonite precipitate in modern seas, in which the Mg/Ca molar ratio is 5.2.

As Hardie (1996) based his model of secular changes in seawater chemistry on marine hydrothermal brine/river flux mass balance calculations that show the rate of ocean crust formation to be the dominant control of the Mg/Ca ratio of seawater. In areas of seafloor formation, Mg is removed from seawater and Ca is released to it through hydrothermal
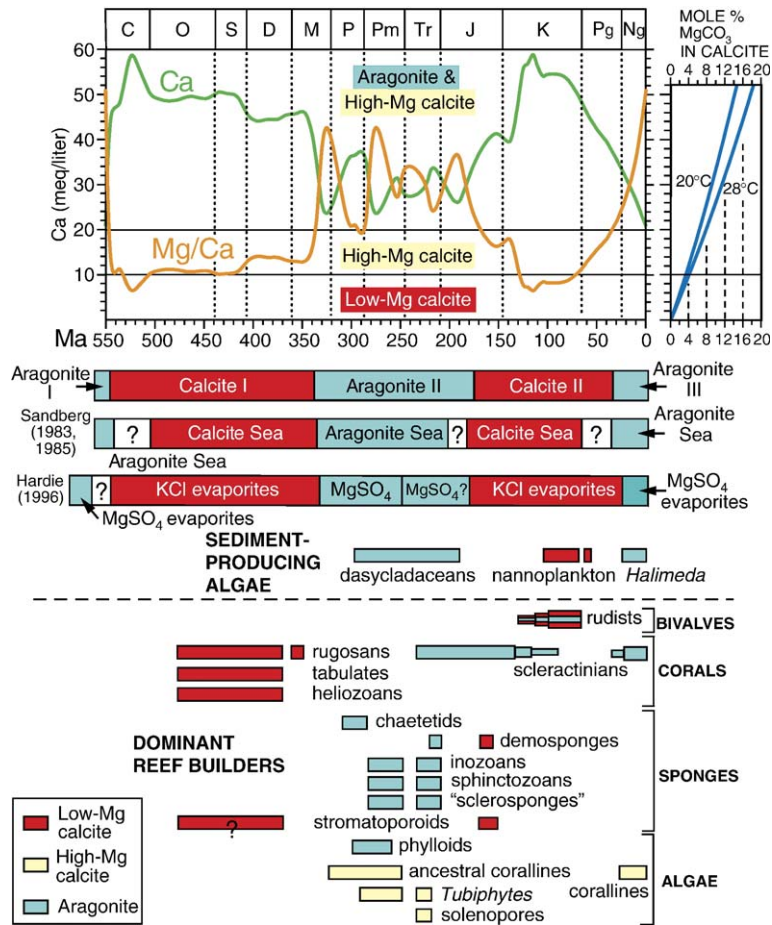
Fig. 1. Comparison of the temporal distribution of mineralogies for important hypercalcifying marine taxa and mineralogies for non-skeletal marine carbonates and evaporites. The large upper diagram shows nucleation fields with respect the Mg/Ca molar ratio of seawater for low-Mg calcite, high-Mg calcite, and aragonite. The graph at the upper right illustrates the incorporation of Mg in nonskeletal calcite as a function of the ambient Mg/Ca ratio at two temperatures (Füchtbauer and Hardie, 1976, 1980). Also shown are the temporal oscillations in the geologic record between calcitic and aragonitic nonskeletal carbonates and the temporal oscillations between KCl and MgSO₄ marine evaporites, which correlate with them. Both oscillations are predicted from estimates of global rates of ocean crust production and the effects of these rates on seawater chemistry (Hardie, 1996). (Modified from Stanley and Hardie, 1998, 1999; Stanley et al., 2002).

activity. Thus, when rates of seafloor formation rise substantially (as in the Cretaceous), the Mg/Ca ratio of seawater declines and the absolute concentration of Ca rises. At such times, sea level rises substantially because igneous activity elevates the seafloor. Conversely, when rates of seafloor formation are low (as at the present), the Mg/Ca ratio of seawater is relatively high and the absolute concentration of Ca is relatively low. At such times, sea level is relatively low. Thus, Hardie (1996) used the first order eustatic sea level curve to calculate the history of the Mg/Ca ratio of seawater (Fig. 1). His calculations precisely predict the observed transitions between aragonite and calcite seas. A revision of the Hardie model incorporating chemical reactions along the flanks of ridges (Demicco et al., 2005) supports the general predictions

of the model. Furthermore, studies of fluid inclusions (Lowenstein et al., 2001) and bromine percentages (Siemann, 2003) in evaporites have confirmed the basic validity of these calculations.

Rowley (2004) challenged the idea that the overall rate of seafloor spreading has varied significantly over time. Even if the mean rate has not varied over hundreds of millions of years, however, the question is whether fluctuations about the mean have been large enough to influence seawater chemistry significantly. Kominz and Scotese (2004) showed that spreading rates during the Cretaceous were, indeed, substantially higher than at any time during the past 50 Ma. Furthermore, it is not simply spreading rates but also rates of production of plateau basalts that influence seawater chemistry and sea level.

For some time, is has seemed likely that changes in some aspect of seawater chemistry have influenced biomineralization (Wilkinson, 1979; Railsbeck and Anderson, 1987; Wood, 1987; Gautret and Cuif, 1989; Railsbeck, 1993; Martin, 1995; Hallock, 1997). It is evident, however, that changes in seawater chemistry have not strongly affected all marine taxa. Mollusks, for example, have secreted both aragonite and calcite—sometimes within single species—prolifically for hundreds of millions of years.

Thus, the fossil record suggests that sophisticated biocalcifiers, including mollusks, have not been powerfully affected by the ambient Mg/Ca ratio. We might, nonetheless, predict that the temporal pattern of nonskeletal carbonate production would be reflected in the history of biologically simple organisms, especially organisms that have performed as hypercalcifiers, i.e. have produced unusually robust skeletons or functioned as major producers of reefs or carbonate sediment (Stanley and Hardie, 1998, 1999). The point is that unsophisticated biomineralizers may be able to survive at times when seawater chemistry does not favor their particular mineralogy, but they may be able to hypercalcify only if seawater chemistry does favor it.

For two reasons, reef builders would be expected generally to conform to the pattern of nonskeletal precipitation (Stanley and Hardie, 1998, 1999). First, successful reef builders must hypercalcify in order to grow rapidly enough to compete for space and overcome agents of reef destruction. Second, most reef builders are biologically simple organisms because the intense competition for space on a reef favors species that reproduce by budding or indeterminate vegetative growth.

We might also expect biologically simple organisms to experience changes in the mineralogy of their skeletons as a result of changes in the chemistry of ambient seawater. It would seem, a priori, that the most likely change of this kind would be a correlation between the Mg/Ca ratio of ambient seawater and the percentage of Mg substituting for Ca in a calcite skeleton (Stanley and Hardie, 1998, 1999); in skeletal formation, this is simply a compositional shift within a solid solution series. Less likely would be a shift from aragonite to calcite or vice versa.

Analysis of the fossil record reveals that the mineralogy of simple organisms, especially ones functioning as hypercalcifiers, has tended to correspond to the mineralogy of nonskeletal precipitates (Stanley and Hardie, 1998, 1999); among these are reef builders. Supporting these paleontological inferences are laboratory experiments showing that changes in Mg/Ca ratio of seawater within the range of compositions that have existed during Phanerozoic time significantly influence (1) the mineralogy of carbonate skeletons, (2) the robustness of carbonate skeletons, and (3) the rate at which calcifying taxa grow or multiply (Stanley et al., 2002, 2005a,b; Ries, 2004). Kiessling (2002) suggested that a different pattern has characterized reef builders, but his data are for taxonomic diversity, rather than volumetric contribution, of various reef builders.

1.2. Siliceous skeletons and seawater chemistry

I will also review evidence that the concentration of silica in seawater has influenced the secretion of siliceous skeletons by marine taxa. Furthermore, because silica is a trace component of seawater, spatial and temporal increases in the abundance of certain silica secretors have constituted an important feedback, depressing the productivity of other silica secretors (Maliva and Knoll, 1989). Here too there is supporting experimental evidence: the ambient concentration of silica governs the robustness of siliceous skeletal elements of at least one sponge species (Maldonado et al., 1999).

2. The paleontological record of biocalcification

Because aragonite is relatively unstable under earth surface conditions and tends readily to dissolve or alter to calcite, it is not always clear whether a fossil that now consists of calcite originally consisted of calcite or aragonite. We can obtain evidence by comparing the quality of preservation for fossils of uncertain primary mineralogy with that for fossils whose primary mineralogy is known. Even so, some comparisons of this type remain controversial. Several additional kinds of evidence have also been invoked:

(1) Remnant aragonite needles or molds of needles, sometimes visible within calcite under a scanning electron microscope, are a telltale sign of original aragonitic mineralogy (Sandberg, 1975; Sorauf and Cuif, 2001).
(2) Dissolution of skeletal aragonite can follow distinctive patterns, as can neomorphic calcite that has replaced aragonite (e.g. James, 1974; Sandberg, 1975, 1984; Sorauf and Cuif, 2001) and, perhaps, low-Mg calcite produced by loss of Mg from high-Mg calcite (Webb and Sorauf, 2002).
(3) The relatively large diameter of the strontium (Sr) atom, prevents it from fitting into the calcite crystal lattice as readily as it lodges in the aragonite crystal lattice. Thus, aragonite contains more Sr than calcite when the two minerals are precip-

itated from waters having the same Sr concentration. When present at an anomalously high concentration in the calcite of a fossil, Sr is often taken to be a chemical remnant from primary aragonite (Lasemi and Sandberg, 2000).

(4) Being of smaller ionic diameter than Ca, Mg tends to leave the lattice of high-Mg calcite during diagenesis. This Mg may remain within the parent fossil as diagenetic dolomite, or it may escape into solution. One can nonetheless estimate the original magnesium content of fossil calcite containing dolomite if there is evidence that the calcite has remained a closed system (Land, 1967; Lohmann and Meyers, 1977; Webb and Sorauf, 2002).

The mineralogy of certain extinct marine taxa can be debated, but when we consider taxa whose skeletal mineralogy is unquestioned, there is a strong temporal correlation between the Mg/Ca ratio of seawater and the mineralogy of simple, hypercalifying organisms (Fig. 1). There is no reason to assume that the relationship between seawater chemistry and biomineralization should have been inviolable, however, because the extent of biological control over biomineralization is likely to have varied among taxa.

In reviewing the Phanerozoic history of carbonate biomineralization, I will herein, as before (Stanley and Hardie, 1998), designate the intervals of aragonite seas as Aragonite I, II, and III and the intervals of calcite seas as Calcite I and II. In the following sections, I will summarize the discussion of this history in Stanley and Hardie (1998) and review some additional evidence.

2.1. Aragonite I (earliest Cambrian)

The aragonite sea of Neoproterozoic time extended into the earliest Cambrian. The only biologically simple hypercalcifiers of earliest Cambrian time were the archaeocyathids, which were reef builders that were likely sponges (Wood, 1990). The excellent preservation that typifies archaeocyathids suggests that they were originally calcitic, but no evidence has yet been adduced as to the original Mg content of their skeletons.

2.2. Calcite I (nearly all of Cambrian to mid-Early Carboniferous)

Paleozoic trepostome and cystoporate bryozoans secreted skeletons that were much more heavily calcified and robust than those of other bryozoan taxa. These hypercalcifying forms served as major rock formers during Ordovician time and, although persisting into the late Paleozoic, were abundant only from Ordovician through Devonian time (Boardman and Cheetham, 1987, p. 517), when the low Mg/Ca ratio of seawater favored their calcitic mineralogy.

Also secreting calcite skeletons during Calcite I were tabulate, heliolitid, and rugose corals, which became the dominant frame builders of tropical reefs during Ordovician time and retained this role until the Late Devonian mass extinction.

There is disagreement about the original mineralogy of Paleozoic stromatoporoid sponges, which performed a cementing function on reefs. Wood (1987) noted that they do not exhibit the same fabrics as those of associated mollusks known to have secreted aragonite. Rush and Chafetz (1991) also argued that stromatoporoids were better preserved than associated aragonitic fossils and probably secreted high-Mg calcite. From a survey of strontium concentrations in fossils, Mallamo and Stearn (1991) concluded that the most primitive stromatoporoids, the labechiids, secreted aragonite but that all post-Ordovician stromatoporoids secreted calcite. Kershaw (2000, p. 157) and Copper (2002) dissented from this view, claiming that all stromatoporoids secreted aragonite.

The typical quality of preservation of non-labecheid stromatoporoids suggests that they secreted calcite. Despite their thin components and high porosity, stromatoporoid skeletons seldom exhibit extensive dissolution or diagenetic obliteration. In this regard, their fossils differ conspicuously from those of chaetetid sponges and scleractinian corals that originally consisted of aragonite. The sugary texture that typifies stromatoporoid skeletal elements probably represents the enlargment of original calcite crystals to a size that reduced surface free energy; this process also accounts for diagenetic increase in the grain size of micritic sediments.

The original mineralogy of receptaculitids, which also contributed to reefs in Calcite I seas, remains controversial (Van Iten et al., 2001).

2.3. Aragonite II (mid-Early Carboniferous to mid-Jurassic)

Reef communities that emerged in late Paleozoic time were conspicuously more aragonitic than the coral-dominated community of earlier Paleozoic time (Railsbeck and Anderson, 1987); there is also evidence that some late Paleozoic reef builders secreted high-Mg calcite, as would be expected given the high Mg/Ca ratio of ambient seawater.

Phylloid algae were major builders of carbonate mounds in late Carboniferous time. The tendency of phylloid algal fossils to experience dissolution during diagenesis has made many subsurface phylloid algal mounds excellent petroleum reservoirs and has long been taken to indicate original aragonitic mineralogy. Exceptional preservation of aragonitic skeletons of phylloid algae in New Mexico has confirmed this inference and demonstrated their close phylogenetic relationship to the codiacean algae *Halimeda* and *Udotea*, which are major producers of aragonite sediments in modern seas (Kirkland et al., 1993). Furthermore, *Halimeda* bioherms of Holocene and Miocene age (Aragonite III) bear a striking resemblance to late Paleozoic phylloid algal mounds (Martín et al., 1997).

Chaetetid sponges were also significant late Paleozoic mound and reef builders, especially in late Carboniferous time. The discovery of Permian chaetetids preserved as original aragonite (Wendt, 1977) supports the inference from the typically poor preservation of chaetetids (West and Clark, 1984) that they secreted aragonite. An atoll system on Honshu Island, Japan provides a continuous record of reef growth over about 45 million years. This record displays a dramatic expansion of the chaetetids during Carboniferous time, while branching rugose corals declined (Ota, 1977). This shift occurred during the Visean Age, at about the time when seawater chemistry shifted from Calcite I to Aragonite II.

During the Permian, sphinctozoan and, to a lesser extent, inozoan sponges emerged as major aragonitic reef builders. Although these forms are characterized by poor skeletal preservation, a few Triassic inozoans and other sponges have been preserved via original aragonite (Veizer and Wendt, 1976).

It has been argued that the microstructure of certain late Paleozoic rugose corals provides evidence that they secreted high-Mg calcite (Webb and Sorauf, 2002). Conversion from low-Mg calcite at the end of Calcite I may explain why colonial branching rugose corals resumed a modest reef-building role late in the Paleozoic (Shen et al., 1998). On the other hand, this group's failure to form massive colonies and attain its earlier reef-building capacity during late Paleozoic time may reflect the fact that incorporation of Mg retards the rate of crystal growth of calcite (Davis et al., 2000).

The aragonitic scleractinian corals began to play a major role in reef-building communities during Late Triassic time and continued to do so throughout the Aragonite II interval (Stanton and Flügel, 1987).

Tubiphytes and solenoporaceans also contributed significantly to Permian and Triassic reefs (Senow-bari-Daryan et al., 1993). *Tubiphytes* has been inferred to have secreted high-Mg calcite (Senowbari-Daryan and Flügel, 1993), and, like related coralline red algae, solenoporaceans probably did as well.

Calcitic frondose bryozoans were important scaffold builders on Permian reefs, but were volumetrically minor (Wood et al., 1996) and the Mg content of their skeletons remains unknown.

Railsbeck (1993) recognized primary calcite in serpulid worm tubes of Mississippian age. From evidence of comparatively poor preservation, relics of aragonite crystals, and high strontium content, he concluded that serpulid tubes of Pennsylvanian age instead consist of calcite replacing original aragonite. Thus, serpulids record the transition from Calcite I to Aragonite II. Their tubes are not body parts, but amount to external shelters of widely varying morphology. It appears that serpulids simply induce precipitation with enough influence over the resulting shape to form a tubular structure. Thus, their skeletal mineralogy corresponds to that of nonskeletal marine carbonates whose precipitation is not biologically induced.

Aragonitic dasycladacean algae were conspicuous producers of packstones and wackestones in the Permian (Malek-Aslani, 1970; Toomey, 1985), and subsequently became such major sediment contributors that they have been viewed as the Triassic equivalents of modern-day *Halimeda* (Elliott, 1984).

2.4. Calcite II (mid-Jurassic through Eocene)

In accord with the lowering of the Mg/Ca ratio that caused the shift to Calcite II, demosponges considered to have secreted calcite emerged as reef-builders in Late Jurassic time, as did calcitic sponges that Wood (1987) has informally termed stromatoporoids (Wendt, 1980; Fagerstrom, 1987, pp. 413–415).

Perhaps the most obvious discrepancy between the fossil record of reef builders and changes in the imputed Mg/Ca ratio of seawater is the persistence of aragonitic scleractinian corals as major reef builders into Late Jurassic and Early Cretaceous time. In part, this discrepancy may reflect the fact that the Mg/Ca ratio of seawater remained close to the boundary between aragonite and calcite seas (Fig. 1). In addition, the scleractinians may have benefited from an absence of effective competitors early in Calcite II.

Furthermore, rudist bivalves replaced corals as the dominant builders of reefs and carbonate banks by late Albian time (Scott, 1984; Kauffman and Johnson, 1988), after the Mg/Ca ratio of seawater declined to about 1.0. The fact that calcite was the primary skeletal

mineral of the principal group of hermatypic rudists, the radiolitids, may have contributed to the rudists' ascendancy (Stanley and Hardie, 1998, 1999; Steuber, 2002). As mollusks, however, rudists were sophisticated biomineralizers upon which seawater chemistry should have exerted a relatively weak effect; more important in the scleractinians' decline may have been their reduced growth rate at the very low ambient Mg/Ca ratio (Stanley and Hardie, 1998, 1999). Unfavorably high temperatures in the central Tethys have also been invoked to explain the restriction of corals to a secondary reef-building role in mid-Cretaceous time (Kauffman and Johnson, 1988).

Significantly, despite the widespread occurrence of warm, shallow seas, scleractinian reefs were sparsely distributed and, for the most part, small during Paleocene and Eocene time, when the Mg/Ca ratio remained in the calcite domain. In fact, coralline algae, played a large role in the construction of many Paleocene reefs (Ghose, 1977; Bryan, 1991; Moussavian and Vecsei, 1995).

It is striking that, during the Cretaceous interval when the Mg/Ca ratio of seawater was very low, a greater volume of chalk accumulated on a global scale than at any earlier or later time. Furthermore, while chalk production subsequently declined as the Mg/Ca ratio of seawater rose, so did the size of individual coccoliths; modal diameter is only about half as large for extant species as for Late Cretaceous species (Young et al., 1994). Later, I will review new experiments in which the productivity of extant coccolithophores rose rapidly as the concentrations of ambient Mg and Ca were shifted to Cretaceous levels.

2.5. Aragonite III (Oligocene to the present)

As the Mg/Ca ratio of seawater rose into the aragonite domain near the beginning of Oligocene time, scleractinian corals began to form large reefs throughout the world for the first time in the Cenozoic Era (Frost, 1977, 1981). This flourishing of reefs is especially striking because global climates had cooled in the Late Eocene (Wolfe, 1978).

Of course, aragonite-secreting scleractinian corals have retained their position as dominant reef builders to the present day. Likewise, the most prolific sediment-producing calcareous algae on shallow tropical seafloors today are aragonitic. *Halimeda*, for example, typically contributes 25–30% of recognizable particulate carbonate particles in perireefal environments (Hillis-Colinvaux, 1980), and *Penicillus* is a major supplier of carbonate mud (Stockman et al., 1967).

3. Experimental evidence of the effects of ambient Mg and Ca concentrations on biocalcification

Pioneers in the study of skeletal growth in seawaters of varying ionic composition include Blackwelder et al. (1976) for coccolithophores, Swart (1980) for corals, and Lorens and Bender (1977, 1980) for the bivalve mollusk *Mytilus*. Although these workers employed ionic compositions outside the range of those estimated for Phanerozoic seawaters (Hardie, 1996; Lowenstein et al., 2001; Siemann, 2003), a review of some of their results is in order.

By varying the Mg/Ca ratio of artificial seawater within its estimated Phanerozoic range, my colleagues and I have conducted a series of laboratory experiments to examine the degree to which this ratio influences skeletal growth rate and mineralogy for the a variety of calcifying organisms (Stanley et al., 2002, 2005a,b; Ries, 2004; 2005). We have grown organisms in several artificial seawaters that were identical in composition (Bidwell and Spotte, 1985) except in having different Mg/Ca molar ratios; the absolute concentration of Mg+Ca has been the same in all these treatments. All experiments have been conducted at 25 °C. Other conditions, such as light intensity and provision of nutrients and food, have also been the same for all treatments.

In some cases, we have also investigated the effect of the absolute concentration of ambient Ca on skeletal growth rate or carbonate production, because an increase in dissolved Ca elevates the degree of supersaturation for both calcite (regardless of its Mg content) and aragonite. To distinguish between the influence of the Mg/Ca ratio and the absolute concentration of Ca, we have conducted experiments in which one of these variables was held constant while the other was varied. In these treatments the total concentration of Mg+Ca has necessarily deviated from that of the other experiments; adjustment of the Na concentration has maintained ionic strength at the same level in these treatments as in others.

The presence of Mg retards step growth of calcite crystals (Davis et al., 2000). We have invoked this process to explain why some taxa grow their calcitic skeletons relatively slowly when the concentration of Mg is increased in ambient seawater, and correspondingly, in their skeletons.

3.1. Changes in skeletal mineralogy with changes in the ambient Mg/Ca ratio

It turns out that the Mg/Ca ratio of ambient seawater strongly influences the mineralogy of skeletal carbonate for many kinds of extant organisms. In particular, it

governs the Mg content of species that secrete high-Mg calcite in modern seawater, and it determines whether the alga *Halimeda* produces skeletal material consisting of nearly pure aragonite or including a large percentage of calcite. Some taxa, however, exert considerable biological control over their skeletal mineralogy. As already noted, mollusks have secreted aragonite and low-Mg calcite simultaneously throughout Phanerozoic time.

Blackwelder et al. (1976) reported that the coccolithophore species *Pleurochrysis carterae* secreted coccoliths consisting of 40% aragonite when it was grown in seawaters with Mg concentrations 2–4 orders of magnitude lower than that of modern seawater (levels never reached in Phanerozoic seas). This puzzling result has apparently never been reexamined. More recent experiments, however, show that changes in the Mg/Ca ratio of seawater influence the mineralogy of many calcareous taxa in ways similar to those observed for mineralogy of nonskeletal carbonates (Stanley et al., 2002, 2005a,b; Ries, 2004).

A wide variety of taxa that secrete high-Mg calcite in modern seas incorporate progressively less Mg into their skeletons as the ambient Mg/Ca ratio is lowered from that of modern seawater (5.2) to that imputed for Late Cretaceous seawater (~0.5–1.0) (Stanley et al., 2002, 2005a,b; Ries, 2004). Fractionation patterns vary among taxa, but some patterns resemble that for nonskeletal precipitation (Fig. 2). All species thus far subjected to experiments of this kind have secreted low-Mg calcite in "Cretaceous" seawater. Although the conventional view is that coccolithophores secrete low-Mg calcite in the modern ocean (Siesser, 1971, 1977), two of three coccolithophore species that we employed in experiments secreted high-Mg calcite in seawater of modern composition (Stanley et al., 2005a,b). Following the typical pattern, these two species incorporated progressively less Mg into their coccoliths as the ambient Mg/Ca ratio was lowered, and they secreted low-Mg calcite in "Cretaceous" seawater (Fig. 2). *Coccolithus neohelis*, was the only one of our three experimental coccolithophore species to secrete low-Mg calcite in seawater of modern composition; it also secreted this mineral in all other seawater treatments.
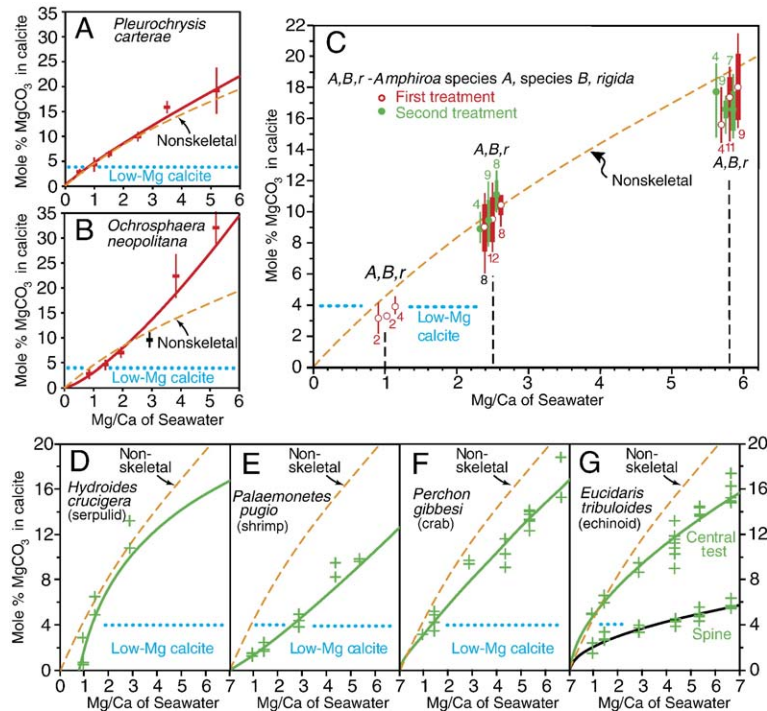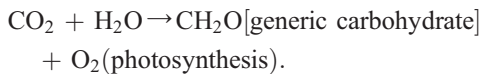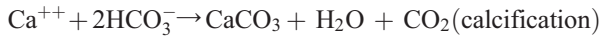

Fig. 2. Decrease in the Mg of skeletal calcite with an increase in the ambient Mg/Ca molar ratio of experimental seawater for a variety of taxa that secrete high-Mg calcite (>4 mol% Mg substituting for Ca) in modern seawater (Mg/Ca=5.2). In "Late Cretaceous" seawater (Mg/Ca=1) all taxa secreted low-Mg calcite (<4 mol% Mg substituting for Ca). Dashed lines illustrate Mg fractionation for nonskeletal calcite. (A, B) Patterns for two species of coccolithophores. Error bars are standard deviations for 5 measurments (from Stanley et al., 2005b). (C) Patterns for three species of coralline red algae of the genus *Amphiroa* (from Stanley et al., 2002). Specimens were switched between seawater treatments with Mg/Ca=2.5 and 5.8. For each treatment, narrow bars show range of measurements and wide bars show standard deviations for the number of measurements indicated. (D–G) Patterns for four animal taxa; the echinoid species (G) incorporated less Mg in spines than in the central test (from Ries, 2004).

3.2. Rates of calcification and growth

The ability to calcify rapidly should be valuable in accelerating skeletal accretion during ontogeny. For photosynthetic organisms, rapid calcification provides an additional benefit: the formation of the biogenic calcium carbonate releases carbon dioxide that radiocarbon tracer studies have shown to fertilize photosynthesis (Borowitzka and Larkum, 1976; Sikes et al., 1980):

$$Ca^{++} + 2HCO_3^- \rightarrow CaCO_3 + H_2O + CO_2 (calcification)$$

$$CO_2 + H_2O \rightarrow CH_2O [generic\ carbohydrate]$$
$$+ O_2 (photosynthesis).$$

Given the importance of CO_2 fertilization via calcification, one can hypothesize that the Mg/Ca ratio and low Ca concentration of seawater should have influenced growth rates of calcareous algae throughout Phanerozoic time. We have tested this idea for both benthic and planktonic calcareous algae.

3.2.1. Coccolithophores: growth rates and chalk production

Late Cretaceous chalks, which consist largely of coccoliths, are far more widespread and voluminous than chalks of any other geologic interval. In fact, chalk gave the Cretaceous Period its name (*creta* being the Latin word for this rock). Late Cretaceous chalk accumulated at depths of ~100–500 m in warm epicontinental seas (Scholle, 1977). We hypothesized that coccolithophores produced chalk so prolifically during the Late Cretaceous because at this time the Mg/Ca molar ratio (≤1) and absolute concentration of Ca (~25–30 mM) in seawater were, respectively, at their lowest and highest Phanerozoic levels (Stanley and Hardie, 1998, 1999). The diversity of coccolithophores remains high today; there are approximately 300 extant species (Winter and Seisser, 1994). Coccolith diversity was also high during Eocene time, and yet massive chalks failed to form, even though warm, shallow seas were widespread.

Today the highest diversity of coccolithophore species is in the nutrient-depleted central regions of subtropical/tropical oceanic gyres (Hulbert, 1967, 1983). Unlike most other kinds of marine phytoplankton, coccolithophore species of these regions are not fertilized by elevation of nitrate, phosphate, or iron above very low levels (Brand, 1994, 1991; Martin et al., 1994; Franck et al., 2000). We hypothesized that this condition exists because the low Mg/Ca ratio of the modern ocean limits population growth for most extant coccolithophore species. A shift in the Mg/Ca ratio of seawater

from that of modern seawater toward that of Cretaceous seawater entails an increase in the absolute concentration of Ca. Because the supersaturation of calcite rises with the absolute concentration of Ca, we must also consider whether the high concentration of ambient Ca, in effect, fertilized Cretaceous coccolithophores.

Experiments have shown the ambient Mg/Ca ratio of seawater to influence both population growth rate and skeletal mineralogy of three coccolithophore species (Stanley et al., 2005b). These species represent a variety of ecological adaptations: *P. carterae* is a nearshore species that blooms in the presence of abundant nutrients (Brand, 1991); *C. neohelis* is a nearshore species that does not bloom; and *Ochrosphaera neopolitana* is an oceanic species confined to oligotrophic environments where it cannot bloom.

C. neohelis secreted low-Mg calcite at all Mg/Ca ratios. Because this mineral is favored by low ratios, one would expect it to calcify and multiply progressively more rapidly as the ambient Mg/Ca ratio is lowered. *Pleurochrysis carterae* and *Ochrosphaeraa neopolitana*, in contrast, secrete calcite with Mg percentages that are compatible with ambient seawater chemistry (Fig. 2A,B). Because incorporation of Mg reduces the rate of step growth in a calcite crystal (Davis et al., 2000), however, one can predict that these two species would also secrete coccoliths more
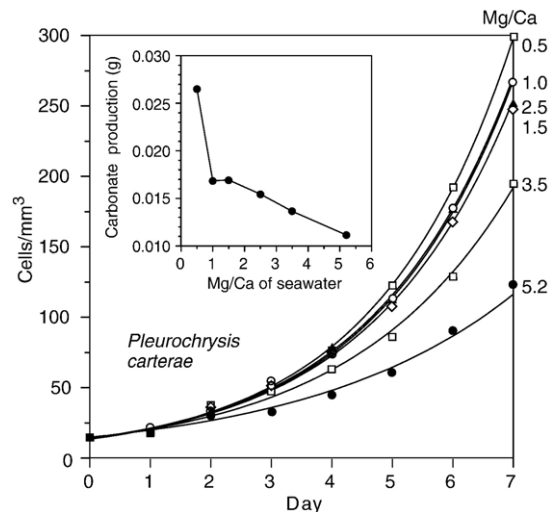

Fig. 3. Increase in rate of exponential population growth and in lime mud production for the coccolithophore *Pleurochrysis carterae* with a reduction of the ambient Mg/Ca molar ratio and associated increase in the Ca concentration of seawater. $R^2 = 0.98$ to 0.99 for exponential fitted curves. Inset displays total lime mud production for each culture of *P. carterae* after 7 days. Spearman rank correlation (rs) = 0.99 for both growth rates and lime mud production (from Stanley et al., 2005b).

effectively and multiply more rapidly with a decrease in the ambient concentration of Mg.

One can also predict that the decline of the absolute concentration of Ca during the shift from Cretaceous to the modern seawater would have retarded population growth for all coccolithophores by reducing the supersaturation of seawater with respect to calcite.

In summary, whether or not a particular coccolithophore taxon incorporated more Mg in its calcite as the Mg/Ca ratio of seawater rose after Cretaceous time and the absolute concentration of Ca declined, it should have calcified and multiplied more slowly.

As predicted, stepwise experimental reduction of the ambient Mg/Ca ratio and concomitant increase in the absolute concentration of Ca from modern seawater values to Cretaceous values (0.5 and 1.0) resulted in progressively higher rates of cell multiplication and lime mud production (Figs. 3, 4). Because the higher growth rates were in unfamiliar media, the results can be considered robust. C. neohelis and O. neopolitana responded more strongly than P. carterae to changes in

seawater chemistry, exhibiting exponential growth rates about three times as high in Cretaceous seawater as in modern seawater (Fig. 4A,B; Fig. 5).

The independent effects of the ambient Mg/Ca ratio and the absolute concentration of Ca on coccolithophore population growth have been tested for P. carterae and C. neohelis, by holding each variable constant while varying the other (Stanley et al., 2005b). Both variables influenced population growth rate in the ways that were predicted (Fig. 6). These experimental results support the hypothesis that both the low Mg/Ca ratio and the high concentration of Ca in Cretaceous seawater were responsible for the high growth rates of coccolithophores that produced the massive Cretaceous chalk deposits (Stanley and Hardie, 1998, 1999).

Estimates of atmospheric pCO_2 for Late Cretaceous time based on stomate densities of conifers range from ~2 to 4 times its present level (Haworth et al., 2005). The calcium carbonate compensation depth in the ocean was shallower during the Cretaceous than it is
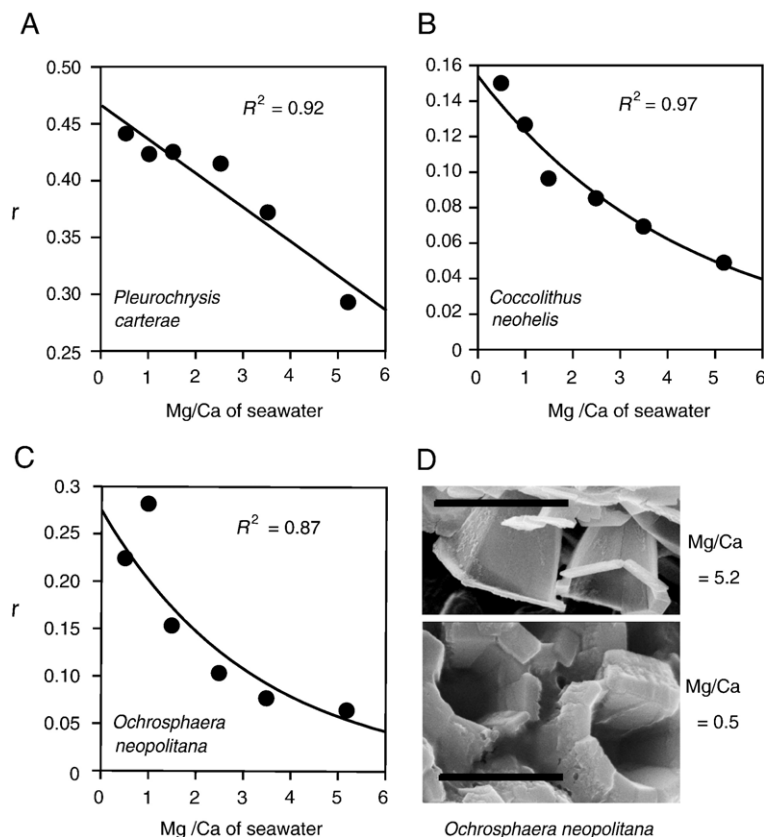

Fig. 4. Increase in growth rate for three coccolithophore species with a reduction of the ambient Mg/Ca molar ratio and associated increase in the Ca concentration of seawater. (A–C) Initial exponential rates of population growth (r) for each species. Fitted curves in (B) and (C) are exponential; that in (A) is linear. For all three sets of data the Sprearman rank correlation=0.99. (D) Increase in the size and robustness of coccoliths of Ochrosphaera neopolitana when grown in seawater of Cretaceous composition (Mg/Ca ratio=0.5) (scale bar=1 μm) (from Stanley et al., 2005b).
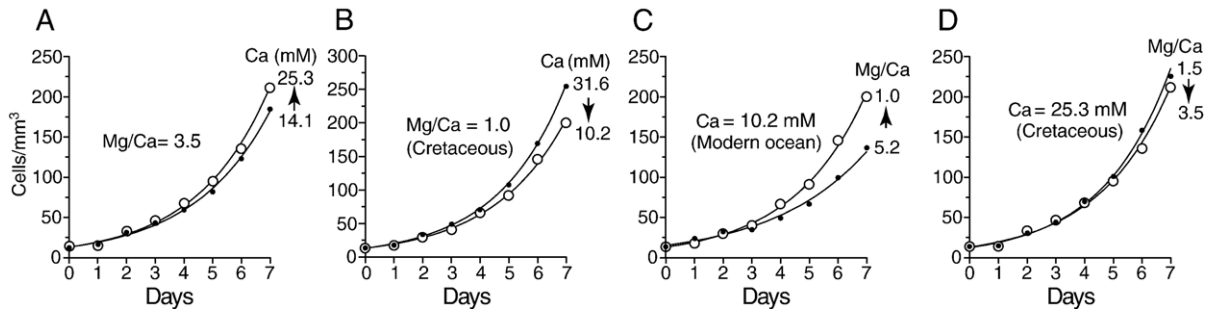
Fig. 5. Effect of both the Mg/Ca ratio and absolute concentration of Ca in ambient seawater on the population growth rate of *Pleurochrysis carterae*. (A) Faster population growth with the Ca concentration elevated from 14.1 to 25.3 mM while the Mg/Ca molar ratio was held constant at 3.5. (B) Slower population growth when the Ca concentration was lowered from a Late Cretaceous level of 31.6 mM to the modern seawater level of 10.2 mM while the Mg/Ca molar ratio held constant at 1.0 (a Late Cretaceous level). (C) Faster population growth when the Mg/Ca molar ratio was reduced from 5.2 (the ratio for modern seawater) to 1.0 (a Late Cretaceous ratio) and the Ca concentration was held constant at 10.2 mM (the concentration in modern seawater). (D) Slower population growth when the Mg/Ca molar level elevated from the Early Cretaceous level of 1.5 to the aragonite sea level of 3.5 while the absolute concentration of Ca was held constant at 25.3 mM (an Early Cretaceous level). Experiments with *C. neohelis* yielded similar results (from Stanley et al., 2005b).

today (Van Andel, 1975); the presence of this condition, despite a warmer deep sea, presumably reflected the high atmospheric concentration of CO_2. Riebesell et al. (2000) grew coccolithophores under conditions that duplicated the oceanic effects of a buildup of atmospheric CO_2 to approximately triple pre-industrial levels. The result was a reduction of the coccolithophores' rate of calcification. Estimates derived from analyses of fluid inclusions in halite indicate that $[Ca^{2+}]$ in Late Cretaceous seawater was ~2.2–2.5

Fig. 6. Percentage of calcite in segments of *Halimeda incrassata* grown in seawaters of three different Mg/Ca ratios: that of modern seas (5.2) and ratios estimated for a portion of Oligocene time (2.5) and Cretaceous time (1.5). Bars indicate standard errors.

times its value in modern seawater (Lowenstein et al., 2001). Our experimental results suggest that, depending on the degree of supersaturation with respect to calcite maintained in Late Cretaceous seas (see Demicco et al., 2003), this high level of $[Ca^{2+}]$ may have more than offset the effects of the relatively high level of atmospheric pCO_2 on coccolithophore calcification.

3.2.2. Calcification and growth of Penicillus

Penicillus is a genus of benthic codiacean green alga sometimes referred to as the shaving brush alga. It contributes large volumes of aragonite needles that accumulate as lime mud in shallow modern seas (Stockman et al., 1967). Because *Penicillus* tends to disintegrate quickly after death, it is seldom recognized in the fossil record. Nonetheless, experiments suggest that it should not have flourished in calcite seas to the extent that it does in today's aragonite sea.

Penicillus offspring bud from rhizoids that grow outward from a parent within the sediment. By comparing the histories of *Penicillus capitatus* offspring from their time of appearance, Ries (2005) was able to compare calcification and primary productivity in different seawater treatments. This species produced skeletons consisting almost entirely of aragonite even in seawater of imputed Cretaceous composition (Mg/Ca mole ratio=1). Thus, it exerts a strong control over its skeletal mineralogy. Nonetheless, seawater chemistry exerts a strong influence over the rate of growth and calcification of *P. capitatus*. Ries (2005) employed specimens of the same size to serve as parents in experiments because codiaceans lack cell walls, which permits the offspring to share products of photosynthe-
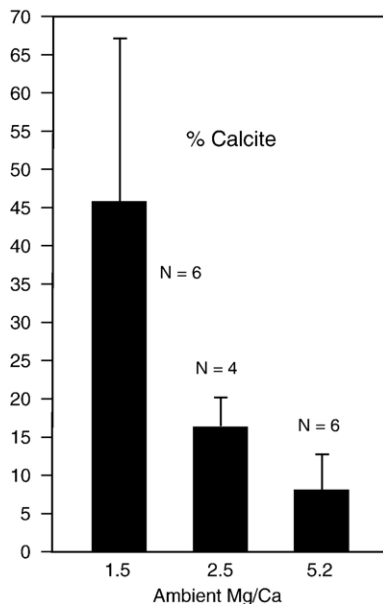
sis of parents to which they remain connected. When the ambient Mg/Ca ratio was lowered from that of the present ocean to the ratio of calcite seas, offspring of *P. capitatus* grew upward more slowly and produced both organic and skeletal material less rapidly.

Heavy mineralization of codiaceans such as *Penicillus* is adaptive in discouraging predators (Littler et al., 1983; Lewis, 1985. In addition, it strengthens the stalk of *Penicillus* against strong currents. Using flume experiments, Ries (2005) showed that increased calcification of *P. capitatus* with an increase of the ambient Mg/Ca ratio stiffened the thallus, producing a steeper slope for a stress–strain curve depicting elastic deformation in unidirectional flow.

Of course, in assessing experiments of the kind just described, it is important to recognize that slower growth in an unfamiliar medium might result, at least in part, from physiological factors unrelated to calcification.

3.2.3. Calcification and growth of Halimeda

We have also conducted laboratory experiments to determine the effect of decreased Mg/Ca ratios on biomineralization by the predominantly aragonitic
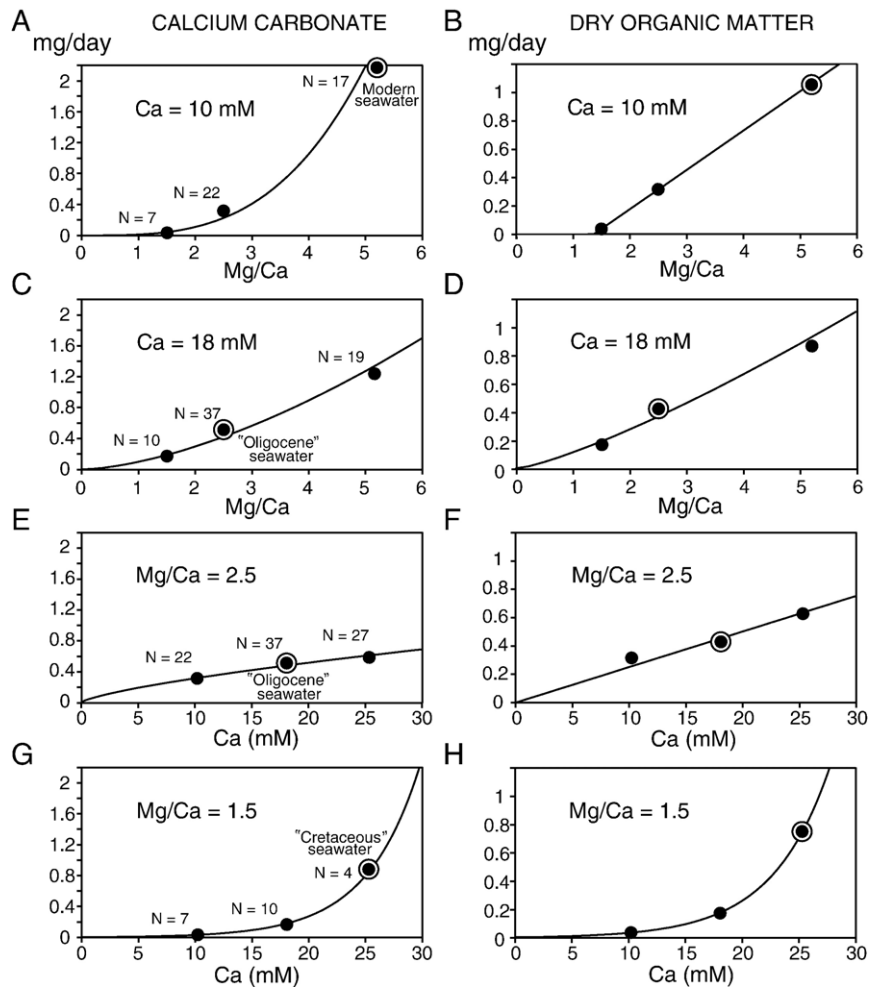

Fig. 7. Rate of calcification and organic matter production by *Halimeda incrassata* as a function of the absolute concentration of Ca and Mg/Ca ratio of seawater. Specimens were transferred to experimental treatments in stages over a 30 day period to avoid physiological shock. Rates were calculated from weights determined for the most recently grown 4–7 segments of actively growing branches. (A–D) Increase in rates of calcification and organic matter production with an increase in the ambient Mg/Ca ratio while the absolute concentration of Ca in seawater was held constant at 10 (A, B) and at 18 mM (C, D). (E–H) Increase in the same rates with an increase in the absolute concentration of Ca while the ambient Mg/Ca ratio was held constant at 2.5 (E, F) and at 1.5 (G, H). Encircled solid circles represent modern seawater (A, B), imputed seawater composition for a segment of the Oligocene (C–F), and imputed seawater composition for a segment of the Cretaceous (G, H). Simple solid circles represent chemical conditions thought never to have existed in the real ocean but having heuristic value. Fitted curves: (A), (C–E), power; (B), (F), linear; (G), (H) exponential. $R^2 > 0.96$ for all plots.

codiacean green alga *Halimeda*, which, as noted above, is a major sediment producer in modern shallow tropical seas (Stanley et al., 2005a). An individual *H. incrassata* consists of small (2–4 mm) plate-like segments that are assembled in tandem. After forming within a single day, a new segment grows and becomes infilled with aragonite over a period of several days.

Growth of specimens of *Halimeda incrassata* in seawaters having Mg/Ca ratios of 5.2, 2.5, and 1.5 yielded remarkable results (Stanley et al., 2005a). Some calcite was produced instead of aragonite in each treatment. Although variability was high, 46% was the mean percentage of calcite for segments grown in the "Cretaceous" treatment (Fig. 6). The formation of so much calcite, in contrast to the biomineralization of *Penicillus*, can perhaps be attributed to the large open spaces between ventricles within the segments of *Halimeda*, where it may be that the alga induces precipitation of $CaCO_3$ out of direct contact with organic materials.

As for other organisms, the calcite produced by *Halimeda* contained Mg in substitution for Ca that increased with the ambient Mg/Ca ratio; in this case, the fractionation pattern was statistically indistinguishable from that of calcite produced by inorganic precipitation.

One can predict that, like other calcareous algae, *Halimeda* should not only calcify at a higher rate when ambient seawater chemistry favors its calcification, but should also grow faster by fertilizing itself more richly with CO_2. Experiments on rates of growth of equal-sized specimens in seawaters of three ambient Mg/Ca ratios confirmed this expectation (Stanley et al., 2005a). Growth and calcification were much faster in seawater having the modern ratio of 5.2 than in seawater having imputed ratios for the Oligocene (2.5) or Cretaceous (1.5) (Fig. 7). The fractional rate of infilling of segments was no more rapid in more favorable seawater treatments, but segments were larger, so that the overall rate of calcification was higher. As happened for coccolithophores, both the Mg/Ca ratio and the absolute concentration of Ca were found to influence growth and calcification. Rate of growth of both organic matter and calcium carbonate increased when the ambient Mg/Ca was elevated while Ca was held constant at 10 mM in one treatment and at 18 mM in another (Fig. 7A–D; similarly, both rates increased when Ca was elevated while the ambient Mg/Ca ratio was held constant at 2.5 in one treatment and at 1.5 in another (Fig. 7E–H). Nonetheless, growth rates were much lower in both of these treatments than in modern seawater.

Interpretations of these growth experiments must be tempered by the observation that the percentage of skeletal calcite increased with the Mg/Ca ratio. This, and nonlinear influences by the ambient Mg/Ca ratio and absolute concentration of Ca, may explain why organic growth and calcification were faster in imputed Cretaceous seawater (Fig. 7C–F) than in imputed Oligocene seawater (Fig. 7G,H).

As noted for *Penicillus*, it remains possible that slower growth of *Halimeda* in an unfamiliar medium resulted, at least in part, from physiological factors unrelated to calcification.

3.3. Robustness of skeletal elements

In laboratory experiments *O. neopolitana* secreted larger and more heavily constructed coccoliths in "Cretaceous" seawater than in modern seawater (Fig. 4D). The more rapid growth and calcification of *Halimeda* with an increase in the ambient Mg/Ca ratio (Fig. 7) can also be viewed as illustrating an increase in the robustness of skeletal elements in that these phenomena entail an increase in the size of calcified segments.

4. Broader consequences of the effects of the ambient concentrations of Mg and Ca on biocalcification

4.1. Implications for biological oceanography

Fertilization experiments in shallow seas have confirmed the hypothesis that iron limits or regulates phytoplankton growth in many regions of the modern ocean (e.g. Martin et al., 1994; Coale, 1996). It has been shown, however, that nearly all oceanic species of coccolithophores fail to respond to fertilization by iron or other nutrients (Brand, 1994, 1991; Franck et al., 2000).

Emiliania huxleyi is exceptional, however, blooming even in seas where low temperatures hinder calcification (Brand, 1994). *E. huxleyi* has been the subject of much more research than any other extant coccolithophore species. It pumps Ca so effectively that it is saturated with this ion at the modern seawater Ca concentration of ~10 mM (Nimer and Merritt, 1996). This species also produces exceptionally large coccoliths at a high rate and sheds about half of those produced (Balch et al., 1992). *Emiliania* is also unusual in having arisen only 268,000 years ago (Thierstein et al., 1977). *Gephyrocapsa oceanica*, an extant species that experiences large blooms in the tropics (Brand, 1994), belongs to the same clade as *Emiliania* and is

also of Pleistocene origin (McIntyre, 1970). Members of this new clade are physiologically distinct from the vast majority of modern coccolithophore species.

Our experiments suggest that the unfavorable (and nearly invariant) concentration of Ca and Mg in modern seawater amount to a universal limiting factor for more typical coccolithophore taxa, preventing them from blooming via fertilization by conventional nutrients. It appears that because most modern coccolithophore species cannot bloom in the presence of abundant nitrate, phosphate, or iron—and thus cannot flourish amidst algae that do bloom—the oligotrophic subtropical/tropical central gyres of modern oceans serve as a refugium for them, and there they exist at relatively low abundance.

4.2. Adjustment of estimates of past levels of pCO_2 based on carbon isotope fractionation

It is well established that the fractionation of carbon isotopes by phytoplankton varies with the ambient concentration of CO_2. In addition, organisms' growth rates influence their fractionation of carbon isotopes (Freeman and Hayes, 1992). Thus, in analyzing carbon isotopes of alkenones produced by coccolithphores and preserved in deep-sea sediments to reconstruct past levels of atmospheric pCO_2, researchers have restricted their samples to low-latitude regions of low productivity; initially, the focus was on late Neogene time (Pagani et al., 1999a,b). Adjustments will be necessary for application of this method to earlier intervals, such as the Eocene (Pagani et al., 2005), when population growth rates for coccolithophore species in oligotrophic regions must have been higher than today because of the more favorable ionic chemistry of seawater.

4.3. Adjustment of temperature estimates based on the Mg/Ca ratio of calcite

Since the seminal work of Chave (1954), it has been understood that the Mg content of skeletal calcite is inversely related to temperature, and in recent years this relationship has been widely employed as a paleothermometer. The discovery that the Mg content of skeletal calcite varies with the Mg/Ca ratio of seawater for a wide variety of organisms (Stanley et al., 2002, 2005a,b; Ries, 2004) indicates that this paleothermometer, as calibrated for living species in modern seawater, will be innaccurate for fossils more than a few million years old.

The relationship between any kind of organism's fractionation and environmental temperature should be established for seawater having the same Mg/Ca ratio as that of the ancient interval being studied. Ries (2004) developed the form of algorithm that must be employed to take into account temporal changes in the Mg/Ca ratio of seawater when estimating temperatures of the geologic past from the Mg content of skeletal calcite. Futhermore, if such studies range back beyond the temporal ranges of extant species, they should include only higher taxa whose extant species all exhibit similar fractionation patterns for skeletal Mg.

4.4. Removal of Mg from seawater by organisms that secrete high-Mg calcite

Incorporation of more Mg in the skeletons of calcite-secreting taxa as the Mg/Ca ratio of seawater increased at any time in earth history must have had an impact on the Mg/Ca ratio of seawater. This phenomenon represents a negative feedback, in that an increase in the rate of addition of Mg to seawater results in an increase in the rate of removal of this ion from seawater. The impact of this biological feedback has not yet been evaluated, but the success of calculations in predicting transitions between aragonite and calcite seas without incorporating it indicates that it has not been of first-order importance.

5. Silica biomineralization and the temporal distribution of siliceous marine sediments and early diagenetic chert

The fact that silica is a minor element in the ocean has an important consequence: variations in the rate at which organisms extract silica from seawater can profoundly alter its abundance in time and space within the ocean.

5.1. Influence of biological secretion on silica in the ocean

The sequential appearance of taxa that secrete siliceous (opaline) skeletons appears to explain the following temporal changes in the environmental distribution of diagenetic cherts derived from biogenic silica (Maliva and Knoll, 1989):

(1) In the absence of silica-secreting organisms, silica was abundant in the ocean during Precambrian time, and early diagenetic cherts formed abundantly in peritidal marine sediments, perhaps as a result of microbial activity.

(2) The demosponges' initial (early Paleozoic) invasion of offshore habitats was apparently inadequate to prevent precipitation of early diagenetic chert in marginal marine environments, but the initial radiation of the Radiolaria apparently did prevent early diagenetic cherts from forming in peritidal environments after Ordovician time. Such cherts continued to form abundantly in subtidal shelf and platform environments from Silurian through Early Cretaceous time.

(3) The final relevant biotic event was the mid-Cretaceous expansion of diatoms, which today extract all but a small fraction of the silica contributed to the ocean by rivers and mid-ocean ridge hydrothermal activity (radiolarians and siliceous sponges extract comparatively little silica). Since the ascendancy of the diatoms, siliceous deposits have been restricted to basinal and deep-sea environments of upwelling.

5.2. Experimental evidence of the influence of the ambient concentration of silica on the phenotypes of siliceous sponges

Organisms do not secrete silica extracellularly but only within their cells. Nonetheless, laboratory experiments have shown that the ambient concentration of silica has a powerful influence on the morphology of siliceous spicules of the sponge species *Crambe crambe*. Maldonado et al. (1999) grew this species in the laboratory in three seawaters differing only in the concentration of $Si(OH)_4$, the form of silica assimilated by organisms. This species inhabits shallow waters in which the concentration of $Si(OH)_4$ is <3 μM, and it normally secretes relatively small, simple spicules (mostly needles). When grown in seawater in which the concentration of $Si(OH)_4$ was an order of magnitude higher than this, *C. crambe* formed spicules that were, on average, more complex; many were large styles or toothed isochelae. A tripling of this already elevated $Si(OH)_4$ concentration produced a larger percentage of complex spicules.

Maldonado et al. (1999) concluded that there is so much flexibility in the morphology of siliceous sponges that only by growing them in seawaters varying greatly in the concentration of $Si(OH)_4$ will taxonomists be able to learn how spicule morphology relates to taxonomy. These authors also suggested that siliceous sponges were able to grow massive skeletons and form reefs during the Jurassic Period because of the relatively high concentration of $Si(OH)_4$ in the ocean prior to the radiation of diatoms.

6. Evolution of skeletal mineralogy in relation to changing seawater chemistry

The discussion thus far has related only to phenotypic effects of changes in seawater chemistry on skeletonized taxa—albeit effects that have often had major ecological consequences. More elusive is unequivocal evidence that shifts in seawater chemistry have driven evolutionary changes in biomineralization.

6.1. The origins of calcification in animals

The earliest influence of seawater chemistry on biocalcification may have been in promoting the evolution of Ca excretion as a means of detoxifying cells in which Ca rose to a harmful level (Simkiss, 1977). It has been suggested that the rise in the absolute concentration of Ca in seawater from Neoproterozoic through Early Cambrian time reached toxic levels that led organisms to evolve mechanisms of Ca excretion. A second step would have been the harnessing of this excretion to form skeletons having useful morphologies (Simkiss, 1977, 1989; Kempe and Kazmierczak, 1994). In fact, it seems unlikely that the absolute concentration of Ca in seawater became toxic to early animals before functional skeletons arose, because it rose from ~11 to ~37 mM during Early Cambrian time (Brennan et al., 2004), but also rose to ~40 mM during Cretaceous time (Hardie, 1996; Demicco et al., 2003, 2005). On the other hand, the dramatic Early Cambrian rise in the absolute concentration of Ca may have facilitated the early evolution of skeletal calcification (Simkiss, 1977, 1989; Kempe and Kazmierczak, 1994; Brennan et al., 2004). Because this increase was associated with a sharp decline of the Mg/Ca ratio of seawater (Hardie, 1996; Demicco et al., 2005) it would soon have favored secretion of calcite.

6.2. Changes in the size and robustness of skeletons

Clearly, some phenotypic changes in the size or robustness of skeletal elements during Phanerozoic time can be attributed to secular changes in seawater chemistry. It appears, however, that some taxa actually evolved larger or thicker skeletons when the chemistry of seawater shifted in favor of their particular mineralogy.

It is striking that the modal size of coccoliths today is 2–6 μm, whereas it was 5–10 μm during Late Cretaceous time (Young et al., 1994), when seawater had a cationic composition that greatly accelerates population growth and coccolith production for mod-

ern coccolithophore species (Stanley et al., 2005b). As already noted, *O. neopolitana*, secretes much larger and more robust coccoliths in seawater of imputed Cretaceous composition than in modern seawater (Fig. 4D). Culturing of many species will be required to evaluate the degree to which phenotypic changes of this kind result from particular changes of seawater chemistry. Possibly a substantial amount of post-Cretaceous size increase for coccolithophores has been evolutionary in nature.

Any long-term trend in the robustness of coccoliths within a clade that entails major changes in morphology almost certainly represents evolutionary change. This kind of trend has long been recognized for *Discoaster*, a highly species-rich coccolithophore genus with a fossil record spanning most of the Cenozoic (Houghton, 1991). Coccoliths of early members of *Discoaster* were boss-like calcitic shields. Later in the Cenozoic, many *Discoaster* species secreted coccoliths with small marginal embayments in their shields. Still later, most species secreted coccoliths with embayments that were wider than the projections in between. Coccoliths of the last surviving members of the genus were characterized by very thin rays radiating from small central disks. This general trend toward reduced calcification probably resulted from the secular increase of the Mg/Ca ratio of seawater and concommitant decrease in the absolute concentration of Ca (Stanley and Hardie, 1998, 1999).

I have already mentioned that trepostome and cystoporate bryozoans, which secreted calcite and were the most heavily calcified bryozoans of the entire Phanerozoic, flourished during Calcite I.

6.3. Origins of new mineralogy within a taxon: evolutionary change in biomineralization or reinvention of the skeleton?

The first appearance in the fossil record of a taxon having a new kind of skeletal mineralogy for a higher taxon that includes both skeletonized and nonskeletonized forms may represent (1) an evolutionary change from pre-existing mineralogy or (2) a reinvention of skeletal secretion by some previously soft-bodied subgroup. In addition, we cannot always be certain that a new taxon having a distinctive mineralogy did not arise earlier than its fossil record suggests.

If it were possible to establish that a large clade characterized by either aragonite or calcite skeletons evolved from naked ancestors in seawater having a chemistry favoring their mineralogy, it would be tempting to attribute that mineralogy to that seawater chem-

istry. Unfortunately, this reasoning is not infallible. Evolution does not always produce optimal adaptations. Furthermore, through biological control, some taxa may be insulated against the effects of seawater chemistry. Thus, at any time in earth history not all skeletonized taxa have secreted minerals favored by seawater chemistry. Finally, some taxa may have evolved skeletons having mineralogies favored by seawater chemistry for reasons unrelated to that chemistry.

All else being equal, at any time there has been a 50% chance that biological control would dictate either aragonitic or calcitic mineralogy for a newly evolving calcium carbonate skeleton. We could potentially resolve this problem with a high degree of probability if it were possible to include many examples of skeletal invention by a single taxon in a statistical test. As the next section will spell out, corals have long posed this kind of problem for paleontologists.

6.3.1. The calcite–aragonite transition in corals

Rugose corals secreted calcite and left a fossil record extending to the uppermost Permian. There follows a hiatus in the fossil record of corals, ended by the appearance of scleractinians in the Middle Triassic. Thus, scleractinians arose during Aragonite II and secreted aragonite skeletons. They may have evolved from rugosans by way of unknown transitional forms, but there is no convincing evidence of this origin (Oliver, 1980). George Stanley (2003) considers it more likely that the scleractinians instead evolved from naked anemone-like ancestors, and he has reviewed molecular evidence that they are polyphyletic. It appears that early scleractinians may have evolved from two clades of naked cnidarians that survived from Paleozoic time; furthermore, skeletons may subsequently have been lost and regained more than once within these clades. Solid evidence for the polyphyletic origin of aragonitic scleractinians during Aragonite II would strongly suggest that the high Mg/Ca ratio of early Mesozoic seawater dictated the mineralogy of the skeletons as they originated.

6.3.2. Oscillations in the mineralogy of carbonate-secreting sponges

It is striking that throughout their evolutionary history carbonate-secreting marine sponges have exhibited skeletal mineralogies that have generally corresponded to that of nonskeletal marine carbonates (Stanley and Hardie, 1998, 1999). Wood (1987) noted aspects of this pattern (as already mentioned, however, there is disagreement about the extent to which Paleozoic stromatoporoids secreted calcite in Calcite I seawater).

Modern calcified demosponges are apparently a poly-phyletic assemblage (Wood, 1987). Thus, calcifying demosponges may have repeatedly reinvented skeletons under the strong influence of ambient seawater chemistry. Evaluation of this proposition will probably require production of molecular phylogenies.

6.3.3. A problematical pattern for Foraminifera

Foraminifera are sophisticated biomineralizers. They exhibit many forms of calcification in modern seas and remodel their tests extensively. In this light, Lowenstam and Weiner (1989, p. 67) referred to them as "veritable 'magicians'". Nonetheless, Martin (1995) suggested that the origins of foraminiferal taxa have tended to entail the evolution of test mineralogies mimicking those of contemporaneous nonskeletal marine carbonates. Distinctions between low- and high-Mg calcite are of little consequence here, however, because as already discussed, the concentration of Mg in skeletal calcite is highly labile in the face of changes in the Mg/Ca ratio of seawater. Two higher taxa of Foraminifera that secrete aragonitic skeletons today, the Lagenina and Involutinina, apparently arose during Aragonite II (Martin, 1995). This is only a sample of two, however, and cannot be considered statistically significant. Foraminifera have constituted major sediment producers in Mesozoic and Cenozoic time, and yet their mineralogy does not show a strong correspondence to that of nonskeletal marine carbonates (Van de Poel and Schlager, 1994).

6.3.4. Bryozoan calcification: strong influence of seawater chemistry on evolution?

Bryozoans are biologically simple organisms for which we might expect seawater chemistry to have influenced biocalcification. In fact, the history of calcification by cheilostomes, the dominant bryozoan group of modern seas, has corresponded strikingly to the history of nonskeletal carbonate precipitation (Stanley and Hardie, 1998, 1999). This group appears to have experienced evolution of skeletal mineralogy strongly influenced by seawater chemistry. It arose in the Cretaceous Period, during Calcite II, and all Cretaceous cheilostomes secreted calcite, with the exception of anascans, which apparently secreted a combination of calcite and aragonite (Boardman and Cheetham, 1987, pp. 548). Aragonitic cheilostomes did not begin to proliferate until Eocene time, however, when the Mg/Ca ratio of seawater was rising nearly to the aragonite realm. The percentage of aragonite-secreting cheilostome taxa increased thereafter, and in modern seas all cheilostomes apparently secrete either aragonite or high-Mg calcite (Rucker and Carver, 1969), the carbonate minerals also produced by nonskeletal precipitation.

6.3.5. Biological control by mollusks

As noted above, mollusks secrete shell material in fluid compartments isolated from seawater. If both calcite and aragonite are secreted, they are formed in separate compartments characterized by different fluid chemistries (Wilbur, 1972); the Mg/Ca ratio of these internal fluids does not always favor the phase of CaCO$_3$ secreted from them. Conventionally, it has been thought that the mineralogy of molluscan skeletons is governed by organic matrices (summary by Lowenstam and Weiner, 1989, pp. 107–109). Nonetheless, the extrapallial fluid of mollusks is probably not sufficiently supersaturated for carbonate minerals to form effectively on organic sheets. Mount et al. (2004) have provided a potential solution to this problem with evidence that hemocytes transport granular calcium carbonate to sites of mineralization in oysters.

Lorens and Bender (1977, 1980) found that elevation of the ambient Mg/Ca from 0.5 to 5.1 (the approximate level of the present ocean) had no effect on the Mg content of skeletal calcite in *Mytilus edulis*; on the other hand, progressive elevation of the ambient Mg/Ca ratio from 5.2 to 13.6 produced an exponential increase in the abundance of Mg in this calcite. The reasonable inference was that *M. edulis*, and presumably other extant mollusks, secrete skeletal calcite in compartmentalized extrapallial fluids from which they exclude enough Mg to form low-Mg calcite; in contrast, at higher Mg/Ca ratios their biological Mg exclusion mechanism becomes saturated, and they can no longer control the level of Mg in their extrapallial fluids.

If, indeed, extant mollusks are at their physiological limit for excluding Mg from extrapallial fluid, this is unlikely to be a matter of chance. Probably, as the concentration of Mg in seawater rose after the Cretaceous, they progressively improved their ability to exclude Mg so as to maintain biological control over their skeletal mineralogy. Natural selection probably favored secretion of low-Mg calcite because its rate of crystal growth is higher than that of high-Mg calcite.

7. Discussion: environmental versus biological control

A central issue in the study of biomineralization has been whether biologically induced or biologically controlled skeletal formation has played a larger role among marine organisms. New research indicates that a compromise is in order. Mollusks exert strong bio-

logical control over their calcification, but for other taxa, to varying degrees, changes in seawater chemistry have significantly influenced biomineralization over the course of geologic time. These environmental changes have caused certain taxa to alter their mineralogy either phenotyically or through evolution. They have also determined whether taxa of unchanging mineralogy have flourished to the degree that they have functioned as major reef builders or sediment producers.

Although evolution often fails to perfect adaptations, it stands to reason that natural selection would tend to favor skeletal mineralogy that is optimal for biological reasons unrelated to seawater chemistry. For example, we might expect that evolution would often have enhanced biological control over biomineralization so as to improve adaptation in some fundamental way or to reduce arbitrary impacts of environmental change.

In the long term, although strong biological control of biomineralization protects a taxon against unfavorable changes of seawater chemistry, it also prevents the taxon from taking advantage of potentially beneficial changes. Ironically, however, a less highly evolved condition, in which skeletal mineralogy remains more at the mercy of seawater chemistry, can be advantageous on geological time scales (Stanley and Hardie, 1999). The ability to shift mineralogy back and forth between aragonite and calcite in response to secular changes in the Mg/Ca ratio of seawater should have allowed some higher taxa to avoid adverse effects of such changes.

On the other hand, elevation of the ambient Mg/Ca ratio would have been deleterious to a taxon that possessed little biological control over production of skeletal calcite in calcite seas but responded to an increase in the Mg/Ca ratio of seawater simply by incorporating more Mg in its skeleton. A taxon that changed in this way would have suffered a reduction in its rate of skeletal growth as a result of the increased abundance of Mg. Sponges and cheilostome bryozoans, which are biologically simple taxa, have undergone polyphyletic evolution of new skeletal mineralogies that have corresponded to those of nonskeletal marine carbonates. Both of these biologically simple groups secrete both aragonite and high-Mg calcite in the modern aragonite sea. If they secreted only aragonite, however, their average rate of skeletal growth would probably be more rapid, at least in warm seas. Perhaps unrelated factors have favored secretion of high-Mg calcite under certain circumstances.

8. Conclusions

(1) The degree to which organisms exercise control over production of mineralized skeletons varies greatly among taxa, but many groups exhibit significant changes in biomineralization in the laboratory when exposed to shifts in the chemistry of ambient seawater mimicking ones that have occurred in the course of Phanerozoic time.

(2) Concentrations of Mg and Ca in seawater that have governed the mineralogy of nonskeletal carbonate precipitates throughout earth history have also strongly influenced which taxa lacking strong control over their biomineralization have flourished as hypercalcifiers: have secreted unusually robust skeletons or produced large volumes of skeletal material. In tropical "calcite seas" (Mg/Ca ratio<2) nonskeletal precipitation has produced low-Mg calcite and marginally high-Mg calcite, whereas in "aragonite seas" (Mg/Ca ratio>2) it has produced aragonite and high-Mg calcite.

(3) The mineralogy of taxa that have functioned as major carbonate reef builders at any time in earth history has tended to correspond to that of nonskeletal precipitates. This is predictable for two reasons. First, because reef-builders must grow rapidly to compete for space, they tend to be simple organisms that expand by asexual budding or vegetative growth. Second, reef builders must hypercalcify in order to offset processes that constantly inflict damage on reefs. Siliceous sponges formed reefs during the Jurassic Period, before diatoms began to extract so much silica from seawater that sponges were no longer able to secrete silica so prolifically.

(4) Laboratory experiments have shown that a wide variety of taxa that secrete high-Mg calcite in the modern ocean incorporate progressively less Mg in their skeletons as the ambient Mg/Ca ratio of seawater is reduced. Fractionation patterns vary among taxa, but all taxa studied thus far secrete low-Mg calcite in ambient seawater with Mg/Ca=1. It follows that all taxa that have secreted high-Mg calcite in aragonite seas would have secreted low-Mg calcite in calcite seas. The rate of skeletal secretion by these species should have decreased with an increase in the ambient Mg/Ca ratio of seawater because Mg reduces the rate of step growth of calcite. Indeed, in laboratory experiments two species of coccolithophores that secrete high-Mg calcite in modern seawater multiplied progressively more rapidly as the ambient Mg/Ca ratio was lowered.

(5) The history of secular changes in the Mg/Ca ratio of seawater will have to be taken into account to accurately employ the Mg content of calcite fossils older than a few million years in paleothermometry.

(6) Changes in the Mg/Ca ratio of experimental seawater can also produce polymorphic shifts in skele-

tal mineralogy. *Halimeda*, which produces a very small percentage of $CaCO_3$ in the form of calcite in modern seawater, has been found to produce skeletons containing almost as much calcite as aragonite when grown in seawater with the imputed Cretaceous Mg/Ca ratio of 1.5. It follows that *Halimeda*, and perhaps other codiacean algae, produced a substantial amount of calcite in Cretaceous seas.

(7) CO_2 liberated by calcification fertilizes photosynthesis. It can therefore be predicted that the rate of growth or multiplication of a calcareous alga that secretes aragonite or low-Mg calcite will increase if the chemistry of ambient seawater shifts to favor secretion of that taxon's skeletal mineral. This relationship can account for the production of large volumes of bioclastic sediment by aragonitic codiacean algae in the modern aragonite sea (Aragonite III) and by aragonitic dasycladacean algae during Triassic time, in the previous aragonite sea. It can also account for the calcite-secreting coccolithophores' production of vast chalk deposits during Late Cretaceous time.

In laboratory experiments, exponential population growth rate for a coccolithophore species that secretes low-Mg calcite rose markedly with stepwise reductions of the ambient Mg/Ca ratio and concomitant increases in the absolute concentration of Ca; controlled experiments showed that both the Mg/Ca ratio and the absolute concentration of Ca influenced growth rates. In complementary fashion, the aragonitic codiacean algae *Penicillus* and *Halimeda* experienced reduced growth rates in experiments when the Mg/Ca ratio was reduced and the absolute concentration of Ca rose concomitantly.

(8) Aragonitic scleractinian corals, which arose in mid-Triassic time (Aragonite II), persisted as major reef builders into Late Jurassic and Early Cretaceous time (Calcite II). Scleractinians relinquished their role to rudist bivalves during Late Cretaceous time, however, as the Mg/Ca ratio of Ca descended to its lowest Phanerozoic level.

(9) Some extant species grow more robust skeletons when seawater chemistry favors their mineralogy. *Halimeda*, for example, produced larger segments under such conditions. Similarly, one extant coccolithophore species, when grown in "Cretaceous" seawater, produced larger and more robust coccoliths than it does in the modern ocean. This kind of phenotypic phenomenon presumably contributed to the general decrease in average size for coccoliths since Cretaceous time, during a pronounced secular elevation of the Mg/Ca ratio and concomitant decline in the absolute concentration of Ca in seawater.

One species of siliceous sponges has also been shown to produce larger, more robust spicules when the ambient concentration of silica is increased in the laboratory.

(10) *E. huxleyi* is an atypical coccolithophore species, being saturated with calcium in the modern low-calcium ocean and blooming prolifically; it also belongs to a very recently evolved clade. Most modern coccolithophores, in contrast, do not respond to fertilization by nitrates, phosphates, or iron. It appears that the low Mg/Ca ratio and low absolute concentration of Ca in the modern ocean limit population growth for typical coccolithophore species, restricting their occurrence to the nutrient-poor subtropical gyres, which serve as a refugium for them.

(11) The use of carbon isotopes in alkenones of fossil coccolithophores to estimate past levels of $p\mathrm{CO}_2$ has been restricted to species that lived in oligotrophic regions of the ocean because fractionation of carbon isotopes is influenced by population growth rate. The new experimental evidence that lower Mg/Ca ratios and higher absolute concentrations of Ca accelerate population growth for oligotrophic coccolithophores will require adjustments in this methodology, via laboratory experiments, to apply this technique to alkenones more than a few million years old.

(12) Biomineralization has influenced seawater chemistry significantly. Whenever the Mg/Ca ratio of seawater has risen during Phanerozoic time, increased incorporation of Mg in the skeletons of some calcite-secreting organisms has served as a negative feedback. Although this phenomenon has not been quantified, it is presumably of second-order importance in the evolution of the Mg concentration of seawater.

Extraction of silica by organisms has had a much stronger impact on ocean chemistry because silica is a minor constituent of seawater. The proliferation of radiolarians early in Paleozoic time reduced the concentration of silica in the ocean. The late Mesozoic proliferation of diatoms further reduced the concentration of silica, preventing siliceous sponges form forming reefs after Jurassic time.

(13) Strong biological control of biomineralization can buffer a taxon against secular changes of seawater chemistry that are unfavorable to its particular skeletal mineralogy. On the other hand, weak biological control of biomineralization permits a taxon to take advantage of secular changes of seawater chemistry through passive changes in skeletal mineralogy.

(14) Secular changes in seawater chemistry have influenced skeletal evolution. Possibly, the rise in the concentration of Ca in the ocean from Neoproterozoic

through Early Cambrian time facilitated the metazoans' initial evolution of calcium carbonate skeletons. One cannot make a statistical case that the origin of a single taxon with a new skeletal mineralogy probably evolved that mineralogy under the influence of seawater chemistry. Polyphyletic patterns are more convincing. Sponges, for example, seem to have invented skeletal secretion several times, generally employing mineralogies favored by ambient seawater chemistry. Scleractinian corals may also have evolved aragonitic skeletons polyphyletically during Aragonite II. Similarly, the polyphyletic origins of aragonite skeletal mineralogy by cheilostome bryozoans as the Mg/Ca ratio rose during the Cenozoic Era suggests influence by seawater chemistry. Also, the rise of the Mg/Ca ratio and decline of the absolute concentration of Ca during the Cenozoic Era was probably responsible for two secular changes in coccolith morphology: the general decline in average coccolith size, which was probably in part evolutionary in nature, and the polyphyletic evolutionary trend within *Discoaster* toward secretion of less robust coccoliths. Mollusks, which exhibit a strong degree of biological control over their skeletal mineralogy, appear to have evolved physiologically so as to limit incorporation of Mg in their skeletons as the Mg/Ca ratio of seawater has risen since Late Cretaceous time. Significantly, there is evidence that modern mollusks cannot maintain this control at higher Mg/Ca ratios than they have experienced during their evolutionary history.

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