

**Effects of Global Seawater Chemistry on Biomineralization:
Past, Present, and Future**

Steven M. Stanley

Department of Geology & Geophysics,
University of Hawaii, 701 POST Building,
1680 East-West Road, Honolulu, HI 96822

Phone: (443) 600-2435

FAX: (808) 956-5512

E-mail: stevenst@hawaii.edu

Contents

1. Introduction
2. Fossil Evidence of Past Skeletal Mineralogies
3. Anatomically Simple Organisms
 - 3.1 Coralline Red Algae: Mg in Calcite
 - 3.2. Coccolithophores: Mineralogy and Carbonate Production
 - 3.3. Calcareous Green Algae: Growth Rates and Mineralogy
 - 3.4. Sponges: Apparent Compatibility with Seawater Chemistry
 - 3.5 Scleractinian Corals: Growth Rates and Mineralogy
 - 3.6. Bryozoans: Apparent Conformity to Seawater Chemistry
4. Higher Animals and the Issue of Biologic Control of Biomineralization
 - 4.1 Serpulid Worms
 - 4.2 Mollusks
 - 4.3 Echinoderms
5. The Mg/Ca Ratio and Evolution
 - 5.1 Evolutionary Changes of Mineralogy in Response to Changes in Seawater Chemistry
 - 5.2 Influence of the Mg/Ca Ratio of Seawater on the Mineralogy of Newly Evolving Skeletons
6. The Importance of CO₂
 - 6.1 Background

6.2. Effects of $p\text{CO}_2$ on Calcification

6.2.1 Coccolithophores

6.2.2 Planktonic Foraminiferans

6.2.3 Corals

6.3 Calcification in the Cretaceous Calcite Sea

6.3.1. Coccolithophores and Chalk Deposits

6.3.2. Reef-building Corals

6.4. Controls and Consequences of Higher Atmospheric $p\text{CO}_2$ in the Future

6.4.1 The Influence of Corals on Atmospheric $p\text{CO}_2$

6.4.2. An Impending Calcification Crisis?

7. References

1. Introduction

There is considerable evidence that changes in seawater chemistry over the course of geologic time have profoundly influenced biomineralization by marine animals. This evidence, some of it based on experiments with living organisms, has revealed that many algae and invertebrates have less control over the chemical composition of their skeletons -- are more at the mercy of seawater chemistry -- than has traditionally been recognized. Nearly all of these organisms produce skeletons that consist largely of CaCO_3 . There is also much evidence that future changes in atmospheric $p\text{CO}_2$ will adversely affect calcifying organisms -- and that feedbacks entailing these organisms will exert a strong influence on the level of atmospheric $p\text{CO}_2$.

Lime sediments, which consist of CaCO_3 with a varying percentage of Mg substituting for Ca, are the precursors of limestone. Abiotic lime sediments form by precipitation in shallow tropical seas, where relatively high temperatures reduce the solubility of CO_2 in seawater. These inorganic precipitates consist largely of three materials: (1) cement that forms in cavities within organic reefs, (2) ooids, which are roughly spherical, sand-sized grains that form by accretion of CaCO_3 around nuclei of skeletal material on wave-agitated shallow sea floors (today these grains form magnificent dunes in the Bahamas), and (3) minute crystals that precipitate from seawater, although certain bacteria also induce the precipitation of such crystals by expelling Ca^{2+} and leaking inorganic carbon from their cells.¹ The mineralogy of these three entities has oscillated over the course of geologic time between aragonite (an orthorhombic polymorph of CaCO_3) and calcite (a hexagonal polymorph of CaCO_3), giving rise to the labels aragonite seas and calcite seas to describe marine conditions that existed over substantial intervals of geologic time.^{2,3} (Actually, as will be explained below, calcite with a high Mg content can form along with aragonite in aragonite seas.) Since the beginning of the Cambrian Period, when for the first time in Earth's history numerous kinds of organisms produced skeletons of CaCO_3 , there have been three intervals of aragonite seas and two of calcite seas (labeled Aragonite I, Aragonite II, etc. in Figure 1).

Because of its crystal structure, calcite tends to incorporate much more Mg (which is of relatively small atomic diameter) than does aragonite. The amount of Mg in abiotically precipitated calcite increases with the ambient Mg/Ca ratio (Figure 1). Calcite has traditionally been classified as high-Mg calcite when the Mg substituting for Ca

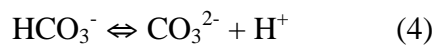
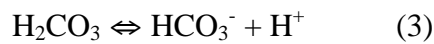
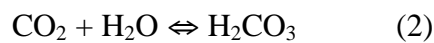
within it exceeds 4 mol% and low-Mg calcite when this percentage is below 4 mol%. Laboratory experiments and observations of carbonate precipitation in lake waters of differing chemistries have shown that the ambient Mg/Ca ratio determines whether calcite alone or calcite with an increased magnesium content and/or aragonite will precipitate inorganically from aqueous fluids.^{4,5} Laboratory experiments have shown that abiotically precipitated CaCO₃ at 25°C consists of low-Mg calcite when the Mg/Ca ratio of a parent aqueous fluid having the salinity of modern seawater is below 1, high-Mg calcite when this ratio is between 1 and 2, and high-Mg calcite and/or aragonite when it is above 2.^{6,7} Thus, high-Mg calcite precipitates along with aragonite in aragonite seas such as those of the present, in which the Mg/Ca ratio is 5.2.

For aragonite or calcite containing little Mg, the saturation state of seawater (Ω) is defined as:

$$\Omega = [\text{Ca}^{2+}][\text{CO}_3^{2-}]/K_{\text{sp}} \quad (1)$$

where K_{sp} is the stoichiometric solubility product for aragonite or calcite.

Furthermore, $[\text{CO}_3^{2-}]$ in seawater is a function of ambient $[\text{CO}_2]$:



Because of the relative values of the equilibrium constants for these reactions, HCO_3^- is much more abundant in seawater than CO_3^{2-} and most calcium carbonate precipitates from this chemical species.

Because mixing rates in the ocean are rapid relative to rates of input and removal of Mg^{2+} and Ca^{2+} , the Mg/Ca ratio is remarkably uniform throughout the ocean at any given

time in Earth's history. There is evidence, however, that this ratio has oscillated markedly since the beginning of the Cambrian Period, when skeletonized animals first became taxonomically diverse and abundant. Part of the evidence for this oscillation comes from calculations based on the observation that when oceanic crust forms along mid-ocean ridges and via the eruption of deep-sea flood basalts, seawater circulates through the newly formed crust and changes its chemical composition before returning to the ocean. During this circulation, minerals formed at high temperatures in Earth's mantle release Ca^{2+} to seawater, while Mg^{2+} is removed from seawater that enters into hydrothermal chemical reactions. Thus, at times when global rates of oceanic crust formation are high, the Mg/Ca ratio of the ocean is low, and at times such as the present when these rates are low, the Mg/Ca ratio is high.⁸ This control of the Mg/Ca ratio of seawater is quite powerful because the causative factors simultaneously shift the numerator and denominator of the ratio in opposite ways.

When global rates of oceanic crust formation increase, the swelling of mid-ocean ridges and/or extrusion of flood basalts push the ocean upward, elevating sea level. In a classic study, Lawrence Hardie used the first-order sea level curve from the beginning of the Cambrian Period to the present to estimate secular changes in the Mg/Ca ratio of seawater.⁸ Hardie's predicted shifts for this ratio across the critical value of 2, which separates precipitation of aragonite from precipitation of low-Mg calcite, matches almost perfectly the observed transitions between aragonite and calcite seas (Figure 1). Hardie's original calculations have been improved on, but with no significant change in the basic pattern.⁹ The steepness of the Mg/Ca curve wherever it crosses the critical value of 2 suggests that the predicted timing of the mineralogical transitions is unlikely to be greatly

in error. Furthermore, Hardie's calculations are in general agreement with a dynamic model of the history of seawater chemistry that employs many more variables,¹⁰ and they have been supported by empirical evidence derived from fluid inclusions in marine evaporates that reflect the composition of ancient seawater.^{11,12,13,14,15,16}

Hardie showed that the compositions of evaporite deposits precipitated at the margin of the ocean in arid climates support his analysis, following temporal oscillations corresponding to those exhibited by CaCO_3 .⁸ Sulfate, like Mg^{2+} , is taken up by deep-sea hydrothermal reactions and, in keeping with Hardie's predictions, magnesium sulfate evaporites have precipitated along the margins of aragonite seas. On the other hand, Earth's mantle releases K^+ to seawater along with Ca^{2+} , and again in conformity with Hardie's predictions, potash evaporates have precipitated along the margins of calcite seas.

Nonetheless, abiotic precipitation of carbonates has accounted for only a small percentage of the lime sediments that have accumulated during more than a half billion years, since skeletonized taxa first became abundant in the ocean. Most lime sediment produced since the beginning of the Cambrian Period, 542 million years ago, has consisted of skeletons and skeletal debris contributed by organisms. It turns out that the mineralogy of these skeletons, like that of abiotically produced CaCO_3 , has been strongly influenced by secular trends in the Mg/Ca ratio of seawater^{17,18} (Figure 1).

The history of the mineralogy of CaCO_3 produced by marine organisms does not correspond perfectly to what would be predicted from calculations of secular changes in the Mg/Ca ratio of seawater, but many organisms are known to exert some degree of control over their mineralogy. Furthermore, the conspicuous departures from the

predicted pattern are for groups such as foraminiferans and mollusks that are recognized to be sophisticated biomineralizers.¹⁹ If one focuses on anatomically simple organisms that are less sophisticated biomineralizers and therefore more likely to have been at the mercy of seawater chemistry (calcareous algae, sponges, corals, and bryozoans), a correspondence to seawater chemistry is quite evident; these forms have tended to flourish at times when the Mg/Ca ratio of seawater has favored their mineralogy.^{17,18} At these times, they have typically been "hypercalcifiers," meaning that have they produced large volumes of sediment or flourished as major builders of organic reefs (Figure 1).

The predicted pattern of calcification is especially evident in tropical regions, where most lime sediments accumulate because high temperatures favor the precipitation of CaCO_3 by reducing the solubility of CO_2 . Biologically simple taxa that are major carbonate producers in the modern tropical ocean match expectations (Figure 1): modern reef-building corals produce skeletons of aragonite, as do the bottom-dwelling green algae that today are the most prolific producers of lime sediment in shallow tropical seas. In addition, coralline red algae, which protect coral reefs by cementing their surfaces, produce high-Mg calcite that closely resembles that precipitated abiotically from modern seawater at similar tropical temperatures. Furthermore, two other anatomically simple animal groups, calcareous sponges and bryozoans, today produce skeletons consisting of aragonite and high-Mg calcite.

There has been considerable controversy among biologists as to the degree to which skeletonized organisms exert biological control over the mineralogy of their skeletons versus the degree to which this mineralogy is governed by environmental conditions.^{19,20,21} Recent experiments reviewed here have demonstrated that while most

organisms exert some degree of control over their skeletal mineralogy, many taxa experience changes in their rate of biomineralization, and even in their skeletal mineralogy, when grown in seawater having different Mg/Ca ratios than that of the present -- but ratios considered to have existed in the geologic past.

Although it is evident that changes in seawater chemistry can induce phenotypic (nongenetic) changes in biomineralization, the question remains, can they induce evolutionary (genetically based) changes in the mineralogy of skeletal material? There are actually two questions here. First, when various soft-bodied taxa first evolved skeletons, did these skeletons tend to have mineralogies favored by seawater chemistry? Second, have skeletonized taxa, once present, evolved new skeletal mineralogies in response to changes in seawater chemistry? I will review evidence suggesting that both of these questions can probably be answered in the affirmative, at least for some taxa.

A second important aspect of the influence of seawater chemistry on biomineralization to be discussed here relates to the impact of changes in atmospheric $p\text{CO}_2$ on biocalcifying taxa, which alter the saturation state of the ocean with respect to calcium carbonate. This issue is attracting a great deal of interest at present because of the elevation of atmospheric $p\text{CO}_2$ that our planet is now experiencing. There is much evidence that many biocalcifying taxa, including reef-building corals, will be adversely affected by rising levels of atmospheric $p\text{CO}_2$. In addition, changes for some of these taxa will provide significant feedbacks for increases of environmental $[\text{CO}_2]$.

2. Fossil Evidence of Past Skeletal Mineralogies

To investigate the history of biomineralization with regard to changes in seawater chemistry over the course of geologic time, it is necessary to identify the original skeletal mineralogy of extinct taxa from fossil evidence. This is usually, but not always, straightforward.

One problem is that in nonmarine settings, under temperatures and pressures found at or near Earth's surface, aragonite readily converts to calcite. Sometimes this alteration occurs *in situ*, and in such cases original skeletal textures may even be preserved. In other cases, especially when exposed to slightly acidic freshwater, aragonite dissolves, and often much of the liberated Ca^{2+} is reprecipitated nearby as low-Mg calcite, the stable polymorph of CaCO_3 . Some of this secondary calcite may fill a mold created by the dissolution of skeletal aragonite, producing a calcite replica of what was originally an aragonite fossil.²²

Observations employing both light and electron microscopy and cathode luminescence can reveal evidence of alteration of aragonite to calcite. In addition, consistently poor preservation for certain taxa is often taken as evidence that aragonite was their original skeletal mineral. The percentage of trace elements in fossil material that is now calcite also provides evidence of original mineralogy; material that is now calcite but was originally aragonite tends to contain less Mg than material that is now, and has always been, calcite because Mg, owing to its small atomic radius, is not readily held within the crystal structure of aragonite. On the other hand, material that was originally aragonite and has been altered to calcite tends to retain more residual Sr than is

normally found in other forms of calcite because, with its large atomic radius, strontium is more readily accommodated in the aragonite crystal structure than in the calcite crystal structure. In addition, remnant needles of aragonite only a few microns long but visible under an electron microscope are sometimes preserved in ancient skeletal material, betraying its original mineralogy.²³ Despite the application of these observations to the reconstruction of original mineralogy, there is still disagreement for a few taxa as to whether their original skeletal material was aragonite or calcite.

Under special circumstances, usually entailing the exclusion of water, fossil aragonite has remained intact for long stretches of geologic time. The most famous example of such ancient aragonite is in the Buckhorn Asphalt of Oklahoma, which though about 310 million years old (of Pennsylvanian age), has protected minute, thin-shelled aragonitic fossils from aqueous solutions that would have dissolved them or altered their mineralogy to calcite.^{24,25}

Establishing the original Mg content of calcite fossils, even to an approximation, is difficult because, over time, Mg escapes from high-Mg calcite under most geologic conditions favorable to the preservation of fossils. Some workers have assumed that a closed system has existed within certain bodies of skeletal calcite, and that all of the Mg liberated from the calcite was incorporated into the secondary mineral dolomite, which consists of $\text{CaMg}(\text{CO}_3)_2$ and is sometimes trapped as small crystals within larger elements of calcite. This assumption was adopted in a study of fossil echinoderms, which secrete high-Mg calcite in the modern ocean.²⁶ It was also assumed that a particular fractionation pattern for Mg applies to all the echinoderm taxa, meaning that it should be possible to estimate the $[\text{Mg}^{2+}]$ for the seawater in which the echinoderms lived. One

source of the scatter of data in this study was that Mg had inevitably been lost from at least some of the material. Another problem is that the fractionation pattern for Mg in the echinoderm skeleton as a function of the Mg/Ca ratio of ambient seawater varies among species – and even within different parts of individual echinoderm animals;²⁷ thus, the fractionation pattern is uncertain for extinct species. Nonetheless, despite considerable scatter, estimations of the original Mg content of the fossil echinoderm skeletons were generally compatible with the established secular pattern for the Mg/Ca ratio of seawater (Figure 1).

It has also been suggested that particular petrographic patterns in tabulate corals preserved in the previously mentioned Buckhorn Asphalt reveal that skeletal material now consisting of low-Mg calcite originally consisted of high-Mg calcite.²⁵ This observation is consistent with seawater chemistry of late Paleozoic time but has not been well tested.

The Mg content of abiotic calcite varies not only with the ambient Mg/Ca ratio, but also with temperature (Figure 1). This is also true for skeletal calcite, even though fractionation patterns as a function of temperature vary greatly among taxa.²⁸ This makes well-preserved calcite a paleothermometer for fossils, but only for very young ones that are very well preserved and that have well known fractionation patterns for Mg as a function of temperature (for the most part, these are extant species whose fractionation pattern can be precisely established). There are three problems with the application of this technique to fossils more than a few million years old. One is that some Mg is likely to have been lost from the calcite being studied. The two other problems are that for any extinct species the exact fractionation pattern for Mg as a function of temperature cannot

be known, and neither can the fractionation pattern as a function of the Mg/Ca ratio of seawater, which has changed through time.

In a more general sense, the problem of assessing changes over time for the Mg content of calcite secreted by marine organisms in tropical climates is alleviated by the results of experiments with living organisms. As will be spelled out below, even though fractionation patterns vary among taxa, these experiments give a strong indication that every kind of marine organism that produces high-Mg calcite today, regardless of its precise fractionation pattern, produced low-Mg calcite in tropical calcite seas.

3. Anatomically Simple Organisms

There are two reasons why one might predict, *a priori*, that seawater chemistry would most strongly influence the biomineralization of organisms that are relatively simple in their overall anatomy.^{17,18} First, such organisms are less likely to calcify in fluid-filled spaces within which chemical conditions differ from those of ambient seawater. Second, these organisms are less likely to influence their biomineralization by means of organic templates that favor aragonite or calcite by specifying that CaO₃ should precipitate with a particular crystal structure.

3.1 Coralline Red Algae: Mg in Calcite

The Mg content of skeletal calcite would seem *a priori* to be the conspicuous biomineralogical variable most likely to be strongly affected by the Mg/Ca ratio of

ambient seawater because it can increase or decrease without a fundamental change of crystal structure. Of the marine organisms that secrete high-Mg calcite in the modern ocean, the coralline algae would seem most likely to adhere to the abiotic pattern of magnesium incorporation in their skeletal calcite as a function of the Mg/Ca ratio of ambient seawater; these algae might be suspected to form their skeletons simply by inducing calcite precipitation by removing CO₂ from internal aqueous fluid for use in photosynthesis, thus having little control over their skeletal mineralogy. It was therefore logical that a group of experiments on the effects of the Mg/Ca ratio of seawater on biocalcification would focus first on coralline red algae.²⁹ Three species of *Amphiroa*, a genus of branching algae belonging to this group, all exhibited essentially the same response to reductions of the Mg/Ca ratio of ambient experimental seawater, incorporating less Mg into their skeletal calcite as the Mg/Ca ratio was reduced; furthermore, their fractionation pattern was very similar to that of modern seawater (Figure 2). Subsequent experiments on crustose coralline algae produced almost identical fractionation patterns.³⁰ These results lend credence to the suggestion that coralline algae simply induce calcite precipitation by extracting CO₂ from the aqueous fluid, which is little-modified seawater, that occupies their thallus.

3.2. Coccolithophores: Mineralogy and Carbonate Production

Coccolithophores are minute, single-celled phytoplankton (photosynthetic floating organisms) that today contribute significantly to the total primary production of organic matter in the upper ocean. They produce shield-like skeletal elements of calcite, termed

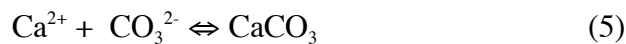
coccoliths, that cover their spherical cells. Coccoliths are produced in the Golgi apparatus of the cell and extruded through the cell wall. They adhere to the outer cell wall by adhesion afforded by mucilage and often by overlapping one another in mutual support.

It was traditionally believed that nearly all coccoliths produced in the modern ocean consist of low-Mg calcite, but a recent analysis of three extant coccolithophore species has revealed that two of them instead secrete high-Mg calcite; furthermore, experiments revealed that the Mg content of coccoliths for both of these species decreased with the Mg/Ca ratio of experimental seawater (Figure 3).³¹ For one of these, *Pleurochrysis carterae*, the fractionation pattern was virtually identical to that of abiotically precipitated calcite. However, coccoliths of a second species, *Ochrosphaera neopolitana*, that was grown in modern seawater contained >30mol% Mg in substitution for calcium at 25°C, a larger percentage than nonskeletal calcite precipitated in seawater of modern composition; this phenomenon remains a puzzle.

Coccolithophores were far more productive in Cretaceous time than they are today (Figure 1). In fact, the Cretaceous Period is named for its widespread chalk deposits, consisting largely of coccoliths that rained down upon the seafloor at moderate depths (100-500m) for several tens of millions of years.³² This chalk, for example, forms the White Cliffs of Dover and the cliffs along the coast of Normandy that Allied forces scaled in World War II.

The Cretaceous was a time when the Mg/Ca ratio of seawater was much lower than it is today (Figure 1). Furthermore, the low Mg/Ca ratio of seawater during most or all of Cretaceous time entailed a level of $[Ca^{2+}]$ more than twice that of the modern ocean

(Figure 1); this condition would have increased the degree of supersaturation of the ocean with respect to calcite, augmenting the effect of the reduced Mg/Ca ratio. Thus, it was hypothesized that coccolithophores flourished to the extent of forming massive chalk deposits during Late Cretaceous time because the low Mg/Ca ratio and high level of $[Ca^{2+}]$ of that interval favored their calcite mineralogy.¹⁷ It has been shown via radiocarbon tracer experiments, that coccolithophores use CO_2 in their photosynthesis that is a byproduct of the second of the following two chemical reactions, which is the one by which they produce most of their calcite:³³



An increase in the rate of calcification by these organisms should therefore result in more frequent cell division, and accelerated growth rates for a population should feed back to yield a still higher total rates of calcite production.

As predicted, for three experimental species of coccolithophores a stepwise reduction of the ambient Mg/Ca ratio and concomitant increase in $[Ca^{2+}]$ from modern seawater values to Cretaceous values resulted in a marked increase in population growth rates³¹ (Figures 4 and 5). *Coccolithus neohelis* and *Ochrosphaera neopolitana* responded more strongly than *Pleurochrysis 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). For these two species, exponential growth rates actually increased exponentially. Because the higher growth rates in these experiments were in unfamiliar

media, the results can be considered robust. Furthermore, *Ochrosphaera neopolitana* secreted much sturdier coccoliths in Cretaceous seawater than in modern seawater (Figure 4D).

The independent effects of the ambient Mg/Ca ratio and $[Ca^{2+}]$ on coccolithophore population growth were tested for *Pleurochrysis carterae* and *Coccolithus neohelis* by holding each variable constant while varying the other; $[Na^+]$ was adjusted to maintain constant salinity in the experiments.³¹ In these experiments, both the Mg/Ca ratio and $[Ca^{2+}]$ influenced population growth rate in the predicted ways (Figure 5). The implication is that both the low Mg/Ca ratio and high $[Ca^{2+}]$ of Cretaceous seas contributed to the coccolithophores' production of widespread chalk deposits.

The experiments on growth rates for coccolithophores have significance for marine biology. Today, there are approximately 300 extant species of coccolithophores,³⁴ and their highest diversity is in the nutrient-depleted central regions of subtropical/tropical oceanic gyres.^{35,36} Unlike most other kinds of marine phytoplankton, coccolithophore species of these regions do not respond in laboratory experiments to fertilization by elevation of nitrate, phosphate, or iron above very low levels.^{37,38,39,40} One such species is *Ochrosphaera neopolitana*, which was included in the experiments on the effect of ambient $[Ca^{2+}]$ and Mg/Ca on coccolithophore population growth rates.³¹ These experiments showed that *Ochrosphaera neopolitana*, like the other two experimental species, were, in effect, "fertilized" by reducing the Mg/Ca ratio and elevating $[Ca^{2+}]$ of its ambient seawater. Thus, it appears that most extant coccolithophore species are unable to respond to rich supplies of nitrates, phosphates, and iron because the high Mg/Ca ratio and low level of $[Ca^{2+}]$ in the modern ocean limit their population growth.

Being unable to compete for nutrients with other types of phytoplankton, they are relegated to regions of the ocean that are poor in conventional nutrients.

C. neohelis secreted low-Mg calcite at all experimental Mg/Ca ratios. Because this mineral is favored by low ratios, one would expect *C. neohelis* to calcify and multiply progressively more rapidly as the ambient Mg/Ca ratio is lowered. *P. carterae* and *O. 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,⁴¹ however, it is not surprising that these two species also secreted coccoliths more effectively and multiplied more rapidly with a decrease in the ambient concentration of Mg²⁺.

Biological oceanographers have focused much research on *Emiliana huxleyi*, a coccolithophore species of the modern ocean that is exceptional in experiencing massive blooms in cool water, which is inherently unfavorable to precipitation of CaCO₃. This species is much more proficient than other coccolithophores at pumping Ca²⁺, and it has been shown to be saturated with this ion at its modern seawater concentration of ~10 mM.⁴² *Gephyrocapsa oceanica* is a species related to *Emiliana huxleyi* that blooms in the tropics. Unlike typical oceanic coccolithophores, these two species respond to nitrate, phosphate, and iron enrichment. *E. huxleyi* appeared only about 268,000 years ago,⁴³ and *G. oceanica* is also of Pleistocene origin.⁴⁴ Apparently these two species possess a novel, recently evolved physiology, and the concentration of so much research on them has given a false impression of the nature of calcification by coccolithophores in general.

3.3. Calcareous Green Algae: Growth Rates and Mineralogy

Calcareous Chlorophyta (green algae) are predominantly aragonitic bottom-dwelling forms that are major producers of lime sediment in shallow tropical regions of the present aragonite sea. Two of the most productive genera of this group, *Penicillus* and *Udotea*, disintegrate upon death to release minute needles of aragonite, which oxygen isotope analyses have shown to be major constituents of carbonate mud in shallow tropical seas.⁴⁵ These two genera, as well as the genus *Halimeda*, a third major producer of lime sediment, belong to the Bryopsidophyceae, a class of calcareous green algae. *Halimeda* forms thalli that consist of branching arrays of platy segments (Figure 6). These segments, typically 2-10 mm in linear dimensions, become conspicuous sedimentary particles when they disaggregate after the death of an alga.

Radiocarbon studies have shown that, like coccolithophores, *Halimeda*, in effect, fertilizes its photosynthesis with CO₂ that is a byproduct of its calcification (equation 2).⁴⁶ Thus, it can be predicted that *Halimeda* and the related genera *Penicillus* and *Udotea*, like coccolithophores,³¹ should experience lower rates of calcification and also lower rates of organic growth when the Mg/Ca ratio of their ambient seawater is lowered experimentally unless this effect is offset by the concomitant increase of [Ca²⁺].⁴⁷ A dominant effect for the Mg/Ca ratio has been demonstrated by experiments on these three genera of calcareous green algae, all of which exhibited lower rates of calcification and organic growth as the ambient Mg/Ca ratio was lowered.⁴⁷⁻⁴⁹ Controlled experiments on *Halimeda incrassata* in which either Mg/Ca or [Ca²⁺] was held constant while the other was varied quantified this comparison: when the ambient Mg/Ca ratio was held at the

modern level of 5.2, elevation of $[\text{Ca}^{2+}]$ from its modern level (10.2 mM) to its Cretaceous level (25.3 mM) resulted in increases in growth and calcification rates by only about 50%, whereas when $[\text{Ca}^{2+}]$ was held at its Cretaceous level of 25.3 mM, elevation of the Mg/Ca ratio from its Cretaceous level of 1.5 to its modern level of 5.2 resulted in increases in these rates by about 300% (Figure 7).

The experiments on the influence of ambient Mg/Ca and $[\text{Ca}^{2+}]$ on coccolithophore population growth and calcification were robust, in the sense that both rates were elevated in an unfamiliar medium. On the other hand, the experiments on the three genera of calcareous green algae might be challenged because they produced reduced growth rates in unfamiliar seawater. The question was whether changes in cation concentrations had negative effects on the experimental algae that were unrelated to calcification. The most likely possibility here would be the occurrence of calcium poisoning.⁵⁰ The controlled experiments on *Halimeda* eliminated this issue, however: for all three ratios of Mg/Ca employed in experiments on this genus, the highest rates of calcification and growth were in treatments with $[\text{Ca}^{2+}]$ levels above that of the modern ocean (Figure 7). Similarly, the experiments showed that neither $[\text{Mg}^{2+}]$ nor $[\text{Na}^+]$ concentrations could have depressed growth rates in unfamiliar seawater.

Penicillus and *Udotea* have poor fossil records because they quickly disintegrate into needles. *Halimeda* and certain other types of calcareous green algae are more readily preserved, yet the fossil record of *Halimeda* has not been well studied. It is clear, however, that the genus diversified and increased its overall productivity markedly early in Miocene time, about 20 million years ago, as the Mg/Ca ratio of seawater was rising rapidly (Figure 1). At this time, *Halimeda* began to form reefs.⁵¹ Another aragonitic

group, known as phylloid algae, flourished late in the aragonite sea of the late Paleozoic to the extent that they formed large reefs. Dasycladaceans, a third group of aragonitic green algae, produced so much lime sediment later in the same aragonite sea that they have been characterized as the *Halimeda* of the Triassic Period.⁵²

Although original mineralogy is not known with certainty for some extinct groups of calcareous green algae, it appears that some members of this group prospered to a degree in calcite seas. Complicating this issue, however, is the observation that, on average, 8% of the CaCO_3 in a species of *Halimeda* grown in modern seawater in the laboratory consisted of calcite, and that this percentage increased to 16% when the Mg/Ca ratio was reduced to 2.5 and to 46% when the ratio was reduced to 1.5 (Figure 8). The Mg content of this calcite adhered almost exactly to the fractionation pattern for abiotic calcite as a function of ambient Mg/Ca. *Penicillus* and *Udotea* produced detectable calcite in the laboratory only when the Mg/Ca ratio was lowered to 1.5, under which conditions they produced CaCO_3 containing 22-25% low-Mg calcite.^{48,49} These experimental results indicated that seawater chemistry can partially override an inherent tendency of modern calcareous green algae to produce aragonite, although seawater chemistry may still dictate the Mg content of any calcite produced instead of aragonite. An additional implication is that the negative impact of the low Mg/Ca ratio of calcite seas on calcareous green algae has probably been partly ameliorated by their production of skeletons containing a substantial proportion of calcite.

3.4. Sponges: Apparent Compatibility with Seawater Chemistry

No laboratory experiments have been conducted to test the effects of the Mg/Ca ratio of seawater on calcification by modern sponges (phylum Porifera), but all calcareous sponges in modern seas secrete aragonite or high-Mg calcite, minerals that are compatible with the chemistry of modern seawater,^{17,18} and as noted by Wood,⁵³ there is evidence that calcareous sponges have always produced skeletal carbonate resembling that of nonskeletal precipitates.

Stromatoporoids, a Paleozoic group of sponges with branching or thickly encrusting calcareous skeletons, were major contributors to reefs in Calcite I seas, playing an important ecological role by cementing the surfaces of coral reefs in the fashion of modern coralline algae. Two workers have argued that all stromatoporoids employed aragonite as their original mineralogy.^{54,55} However, the typically excellent preservation of fine-scale interior architecture of stromatoporoid skeletons suggests that they produced calcite¹⁷. In addition, the relatively high Mg content of the calcite preserved in fossil stromatoporoids indicates that, with the possible exception of the labechiids (the first stromatoporoids to evolve), calcite was the original mineral of stromatoporoid skeletons.⁵⁶

Poor preservation of skeletal materials and rare survival of original aragonite indicate that sponges of the Aragonite I interval, such as the chaetetids, sphinctozoans, and inozoans, secreted aragonite,¹⁷ and rare preservation of original aragonite is even known for some.⁵⁷ In addition, one Triassic genus is considered to have produced high-Mg calcite.⁵⁸

Also following the predicted pattern, calcareous sponges of the Cretaceous segment of Calcite II apparently all produced calcite.⁵⁹ Presumably it was only following the transition to the Aragonite II interval, which occurred about 35 million years ago, that many kinds of calcareous sponges again began to produce aragonite.

Because a variety of organisms that produce high-Mg calcite in the modern aragonite sea have all produced low-Mg calcite in the laboratory when grown in what amounted to calcite sea water (Figure 2), it is reasonable to assume that sponges, given their weak biological control over calcification, have always fractionated magnesium in a generally similar manner when producing calcite. Thus, part way through the Cenozoic Era, their calcitic skeletal material must have shifted from low-Mg to high-Mg calcite.

Sponges that secrete skeletons of silica have also been strongly influenced in this activity by the composition of seawater. Today, the concentration of silica in the ocean is very low because diatoms, highly productive algae that secrete siliceous skeletons, remove most of the silica, which is contributed by two primary sources: (1) river water carrying silica released by weathering of continental materials and (2) hydrothermal activity in the deep sea. Diatoms increased dramatically in both diversity and abundance during the Cretaceous Period, and their flourishing apparently had profound negative consequences for the productivity of siliceous sponges.⁶⁰ During the previous (Jurassic) period, when there was a relatively high concentration of Si(OH)_4 in the ocean, siliceous sponges flourished to the extent that they were able to form siliceous reefs on continental shelves.⁶¹

Maldonado et al. conducted experiments on the siliceous sponge *Crambe crambe* that shed light on the importance of changes in the history silica cycling.⁶¹ This species

inhabits shallow waters of the modern ocean, in which the concentration of Si(OH)_4 is $<3 \mu\text{M}$, and it secretes small, simple spicules, most of which are needles. When grown in seawaters in which Si(OH)_4 was an order of magnitude higher than this, *Crambe crambe* formed spicules that were larger and had more complex morphologies than those that it forms in the ocean today. The conclusion was that the concentration of Si(OH)_4 in seawater has a profound effect on both the productivity of silica by siliceous sponges and on the robustness and morphology of the skeletal elements that these sponges produce.

3.5 Scleractinian Corals: Growth Rates and Mineralogy

Modern corals, formally known as Scleractinia, produce skeletons of aragonite, and as would be expected in the modern aragonite sea, they flourish to the degree that they form massive tropical reefs. To create a large reef, corals must grow rapidly enough to outpace the destruction that storms and scraping and boring organisms inflict on the calcium carbonate framework they produce. This is possible only through the agency of symbiotic algae that inhabit the endoderm of coral polyps, taking in CO_2 for photosynthesis and thus favoring the corals' precipitation of CaCO_3 , while the polyps provide them with nutrients in a symbiotic relationship.

Cuif et al. proposed that organic templates specify the production of aragonite by scleractinian corals, the idea being that these templates capture Ca with a spacing that induces aragonite to form.⁶² However, experiments with three branching species of modern corals showed that organic templates do not totally govern their mineralogy. When grown in the laboratory at an ambient Mg/Ca ratio of 3.5, which is well within the

aragonitic domain (>2), all of these species grew skeletal material consisting of about 10% calcite.⁶³ Furthermore, all three species produced progressively more calcite as the ambient Mg/Ca ratio was lowered further, with the amount averaging about one-third of the skeletal CaCO_3 at an Mg/Ca ratio of 1, which approximates the ratio estimated for much of the Cretaceous Period, when scleractinian corals were diverse and abundant (Figure 1). Following the standard pattern, the three experimental coral species incorporated increasing amounts of Mg into their calcite as the Mg/Ca ratio was elevated, with the average exceeding 20% in modern seawater. Although very small, the percentage of Mg incorporated in aragonite also increased with the ambient Mg/Ca ratio. It is not surprising that corals are strongly influenced by the chemistry of the seawater in which they live because seawater reaches their anatomical region of calcification by diffusing through their porous skeleton and by moving through and between cells.⁶⁴

Recently, one solitary, non-reefbuilding scleractinian coral of Late Cretaceous age has been shown almost certainly to have produced a calcite skeleton.⁶⁵ The evidence is that the fossilized skeletal material of this species consists of very well-preserved calcite, showing no signs of alteration, and it also exhibits a very high Mg/Sr ratio. Before recent observations were made that the Mg/Ca ratio of seawater influences the skeletal mineralogy of many anatomically simple organisms,¹⁷ there was little motivation to search for ancient scleractinian corals that produced calcite in the Calcite II sea. Perhaps further investigations will turn up additional corals of this kind.

Scleractinian corals were the dominant frame builders of carbonate reefs during Jurassic and Early Cretaceous time, but yielded this role to vase-shaped rudist bivalve mollusks during Late Cretaceous time, perhaps because the Mg/Ca ratio of seawater

avored this group's predominantly calcitic mineralogy.^{17,66} The biomineralization of mollusks has not been strongly affected by seawater chemistry during their long history, however. Therefore, it is more likely that the ecological decline of the corals was a more important factor in the ascendance of the rudists than was any benefit that calcite seas conferred upon these bivalves.¹⁷

The rudists died out with the dinosaurs in the terminal Cretaceous mass extinction, but corals did not truly flourish again on a global scale until part way through the Oligocene Epoch, about 35 million years later. It appears that the Mg/Ca ratio of seawater did not rise into the aragonite domain until the Oligocene, and this may explain the delayed ecological expansion of reef-building corals.

It is also possible that the symbiotic algae that Mesozoic scleractinian corals harbored in their cells died out in the terminal Cretaceous mass extinction. In fact, a phylogenetic analysis and application of the molecular clock indicate that *Symbiodinium*, the genus that includes symbionts of scleractinian corals, is monophyletic and belongs to a clade that arose early in Eocene time, between about 56 and 49 million years ago.⁶⁷ Thus, corals probably lacked symbionts during the Paleocene Epoch, which spanned about 10 million years after the Cretaceous mass extinction, and depending on the initial rate of diversification of *Symbiodinium*, they may have benefited only modestly from symbionts for some time after *Symbiodinium* appeared within the next 7 million years.

Another factor in the Oligocene expansion of reef-building corals may have been a marked decline in atmospheric $p\text{CO}_2$ during the Oligocene, which is indicated by the carbon isotope ratios of ancient alkenones, which are produced by coccolithophores and

reflect the ambient CO₂ concentration. The influence of atmospheric pCO₂ on corals and other marine calcifiers will be considered below.

Experiments have also revealed the effects of the Mg/Ca ratio on growth rates of modern corals.⁶³ Rates of calcification for three extant coral species declined between a modern seawater treatment (Mg/Ca = 5.2) and Cretaceous treatments (Mg/Ca = 1.5 and 1.0), but the decrease was nonlinear (Figure 9B). The only clear-cut change occurred when the ratio was lowered from 2.5 to 1.5, which spanned the transition from aragonite to calcite seawater. Complicating the experiments was the progressive increase in the percentage of calcite produced as the Mg/Ca ratio was lowered. In addition, unlike the experiments conducted for coccolithophores and *Halimeda*, the coral experiments did not include treatments showing that changes in cation concentrations (especially an increase in [Ca²⁺] as the Mg/Ca ratio was lowered) did not influence the results. In any event, the results of the experiments are consistent with the hypothesis that the rise in the Mg/Ca ratio of seawater since Cretaceous time has contributed to the flourishing of reef-building scleractinian corals during the past 30 million years or so. These results do not preclude a role for the reduction of CO₂ during Oligocene time or for the post-Paleocene diversification of symbiotic algae.

3.6. Bryozoans: Apparent Conformity to Seawater Chemistry

Bryozoans, all of which are colonial animals, are another group of anatomically simple taxa whose carbonate mineralogy is compatible with seawater chemistry in the present aragonite sea: today they all produce aragonite and/or high-Mg calcite.⁶⁸

It is notable that the cheilostomes, the largest group of extant marine bryozoans, consisted almost entirely of calcite-secreting forms during the Cretaceous Period, when they arose in the middle of the Calcite II Sea interval; only one Cretaceous group, the anascans, may have secreted aragonite in a small portion of their skeletal material that is relatively poorly preserved.⁶⁹ Then, as the Mg/Ca ratio of seawater rose during the Cenozoic Era, many cheilostome taxa began also to produce aragonite. Loss of Mg from fossils makes it impossible to trace the history of the Mg content of bryozoan calcite, except sketchily. Nonetheless, as for sponges, it can be assumed that the percentage of this skeletal Mg has risen since the Cretaceous, in accordance with the general pattern of Mg incorporation exhibited by other taxa (those included in Figure 2 plus the corals) that secrete high-Mg calcite when the ambient Mg/Ca ratio exceeds unity.

During the Paleozoic Era, heavily calcified taxa, informally termed stony bryozoans, flourished from Ordovician through Devonian time in Calcite I seas. These well-preserved forms obviously formed their typically branching, finger-sized colonies of calcite.¹⁷ Later in the Paleozoic, less robust, fan-shaped bryozoans flourished in the Aragonite II sea. Although their skeletons apparently consisted of calcite, following the conventional pattern, this was presumably high-Mg calcite.

4. Higher Animals and the Issue of Biologic Control of Biomineralization

A variety of marine animals that are anatomically more complex than sponges, corals, and bryozoans and that produce high-Mg calcite in the modern ocean have been found to produce low-Mg calcite in seawater of Cretaceous composition.²⁷ These taxa exhibit a

variety of fractionation patterns for Mg as a function of the ambient Mg/Ca ratio. It appears that these and other marine organisms that produce high-Mg calcite today are unable to prevent Mg from entering this calcite effectively, although some can exclude it to some degree. On the other hand, some taxa exclude Mg from their calcite quite effectively and produce low-Mg calcite in the modern aragonite sea. Why might it be advantageous to exclude Mg from skeletal calcite? The most likely reason is that Mg retards the step growth of a calcite crystal.⁴¹ Presumably, then, its presence at the crystal/fluid interface slows skeletal formation, and this is obviously disadvantageous.

Possibly the degree to which some taxa are able to exclude Mg from the calcite they produce is a function of the types of calcium channels present in their cells. The small size of the Mg atom relative to the Ca atom may be the critical factor in this aspect of biological control over skeletal mineralogy. Of course, for anatomically simple taxa such as corals and algae that produce skeletal material from little-modified seawater, the specificity of calcium channels is not an issue.

4.1 Serpulid Worms

There is evidence that at least one anatomically advanced group of animals experienced a shift of skeletal mineralogy from calcite to aragonite during the Calcite I-Aragonite II transition. Tubes of serpulid polychaete worms preserved in Mississippian rocks exhibit primary calcite, and yet relics of aragonite needles, high strontium content, and generally poor preservation indicate that similar tubes of Pennsylvanian age originally consisted of aragonite.⁷⁰ It is possible that serpulids simply induce precipitation of the tube material

by elevating the pH of seawater adjacent to their elongate bodies, rather than actually secreting CaCO_3 ; if this is the case, their skeletal production is equivalent to abiotic precipitation and the resulting mineralogy is beyond their control.

4.2 Mollusks

Mollusks exert considerable biologic control over their calcification. Many mollusk species grow shells that contain both aragonite and low-Mg calcite, which must be secreted in separate compartments. Nonetheless, the Mg/Ca ratio of the extrapallial fluid (fluid between the shell and underlying fleshy mantle) of living marine mollusks, which is in contact with a broad surface of calcification (the mantle), is similar to that of modern seawater; furthermore, it is not highly supersaturated with respect to aragonite or calcite.^{71,72,73} Many researchers have suggested that soluble proteins in particular calcifying spaces combine with the insoluble organic matrix of the molluscan shell to specify nucleation of aragonite or calcite.^{74,75,76,77,78} Mollusk larvae have been found to grow aragonitic shells from a precursor phase consisting of amorphous CaCO_3 .^{79,80} This phenomenon is compatible with a role for proteins and organic matrix in specifying final mineralogy. On the other hand, the extrapallial fluid of mollusks is probably not sufficiently supersaturated with respect to carbonate skeletal minerals for them to form effectively on organic sheets.⁸¹ Furthermore, in oysters amoeboid cells known as granulocytes have been shown to carry minute calcite crystals to sites of shell formation, where they are quickly remodeled; this implies that the original precipitation of calcite

does not occur in the pallial fluid of oysters and that proteins and organic matrix may not be necessary for specification of their predominantly calcitic mineralogy.⁸²

Lorens and Bender 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 the edible mussel, *Mytilus edulis*; on the other hand, progressive elevation of the ambient Mg/Ca ratio from 5.2 to 13.6, a level that has never been reached while skeletonized animals have occupied the ocean, produced an exponential increase in the abundance of Mg in this calcite.^{72,73} Checa et al. similarly showed that, when the Mg/Ca ratio of seawater was elevated to 8.3-9.2, a species of scallop (Pectinidea) and a species of oyster (Ostreidae) secreted aragonite over some regions of the shell where calcite was normally produced.⁸³ Although Lorens and Bender^{72,73} and Checa et al.⁸³ demonstrated the importance of the Mg/Ca of seawater to the calcification of mollusks, they employed levels of Mg/Ca well above those ever known to have existed since mollusks appeared. I will discuss the implications of their results in a subsequent section dealing with the influence of seawater chemistry on the evolution of skeletal mineralogy.

4.3 Echinoderms

Members of the Echinodermata, including sea urchins, produce skeletons of porous calcite crystals that have linear dimensions ranging from about a millimeter to several centimeters. Each spine of a sea urchin consists of one such crystal. Recent studies of sea urchin calcification have revealed that each skeletal crystal grows within its own membranous envelope (syncytium), which is formed of many cells; amorphous CaCO₃

housed within special vesicles is transported into the envelope, where it contributes material to the growth of a large calcite crystal from a small, nucleating crystal or from the broken surface of a pre-existing crystal.^{84,85} The confining shape of the syncytium molds the crystal's growth. These observations appear to answer the age-old question as to what governs the shape of echinoderm crystals.⁸⁶

The percentage of Mg in echinoderm calcite is positively correlated with the Mg/Ca ratio of seawater but as noted above, the fractionation pattern for Mg varies among taxa and even within the skeletons of individual species.²⁷ Presumably the fluid within the syncytium in which an echinoderm crystal grows consists of only slightly modified ambient seawater. It seems likely that the departure of any echinoderm taxon's fractionation of Mg from the pattern for nonskeletal calcite reflects the degree to which the chemistry of its syncytial water differs from that of ambient seawater.

5. The Mg/Ca Ratio and Evolution

As noted earlier, there are two central questions of organic evolution that relate to biomineralization in the ocean. One is, when organisms first evolved skeletons, did their skeletons tend to be of mineralogies favored by ambient seawater? The second is, after particular types of organisms have evolved skeletons, have changes in seawater chemistry induced them to evolve new skeletal mineralogies? I will first take up the second question.

5.1 Evolutionary Changes of Mineralogy in Response to Changes in Seawater Chemistry

We can consider two ways in which seawater chemistry has apparently influenced the evolution of skeletal mineralogy. In the first, evident for anatomically simple animals, evolution has produced biomineralization that is compatible with seawater chemistry. In the second, involving anatomically more advanced animals, evolution appears to have resisted the influence of seawater chemistry so as to favor relatively rapid calcification.

As described above, the cheilostome bryozoans have experienced evolutionary changes in their mineralogy since the Cretaceous that appear to have been dictated by the dramatic rise in the Mg/Ca ratio of seawater. Today all of their species produce aragonite and/or high-Mg calcite, meaning that their skeletal mineralogy is compatible with modern seawater. Calcite was their predominant mineralogy during the Cretaceous, and it can be assumed this was low-Mg calcite because, as already noted, all extant organisms yet studied that today produce high-Mg calcite have produced low-Mg calcite in artificial Cretaceous seawater. Thus, the inferred secular increase in the Mg content of cheilostomes' skeletons was presumably phenotypic, rather than being genetically governed (i.e. it was not a matter of evolution). On the other hand, the cheilostomes' production of aragonite as the Mg/Ca ratio of seawater rose far into the aragonite domain during the Cretaceous is clearly an evolutionary phenomenon. Furthermore, aragonitic skeletons appear to have evolved multiple times among cheilostome taxa during this interval.

Mollusks are anatomically more advanced than bryozoans, and they appear to have evolved in ways that have mitigated effects of changing seawater chemistry that tended to slow their rate of shell growth. The previously mentioned experiments of Lorens and Bender suggest that extant mollusks are at their physiological limit for excluding Mg from their pallial fluid.^{72,73} Similarly, Checa et al. found that scallops and oysters calcified in unconventional ways when grown in seawaters with higher Mg/Ca ratios than mollusks have ever experienced in nature.⁸³ Because the rate of crystal growth of low-Mg calcite is higher than that of high-Mg calcite, natural selection should normally have favored the exclusion of Mg from calcite for all calcitic taxa whose biocalcification is not strongly controlled by ambient seawater chemistry, and mollusks have obviously had sufficient control over their mineralogy to exclude Mg. It appears that, as the concentration of Mg in seawater has risen since Cretaceous time, mollusks have evolved in concert in order to exclude it. Thus, up to the present time in the modern aragonite sea, mollusks have been able to secrete low-Mg calcite in large regions of their shells. It appears that the experiments of Lorens and Bender^{72,73} and Checa et al.⁸³ have quite simply outrun the influence of seawater chemistry on molluscan evolution.

5.2. Influence of the Mg/Ca Ratio of Seawater on the Mineralogy of Newly Evolving Skeletons

Within an anatomically and physiologically advanced group of soft-bodied organisms such as the mollusks, evolution may have the potential to produce a carbonate skeleton that is not favored by seawater chemistry. A carbonate skeleton appearing for the first

time in a taxon of simpler biology is more likely to be compatible with seawater chemistry. There are two problems, however, in trying to assess whether the Mg/Ca ratio of seawater has played a significant role here. One is that evidence of original calcite mineralogy is frequently meaningless, inasmuch as calcite has always been compatible with seawater for many taxa because of its variable Mg content. Thus, the important question becomes whether taxa that have evolved aragonitic skeletons did so in aragonite seas. The issue here is essentially a statistical one. If, as a null hypothesis, seawater chemistry is taken to be immaterial, there is a substantial probability (presumably not differing greatly from fifty percent) that a skeleton consisting of aragonite will originate in calcite seas or that a skeleton consisting of calcite will originate in aragonite seas. As it turns out, although taxa with aragonitic skeletons have existed in calcite seas, there is no unequivocal evidence that an aragonitic skeleton has ever *originated* within a taxon in calcite seas. (It is not clear what the skeletal mineralogy of taxa of bryopsidophycean green algae was when they evolved skeletons, so I exclude them from the following assessment.)

The earliest calcifying animals arose close to the time in the Early Cambrian of the transition from Aragonite I to Calcite I seas. It has been suggested that the rising $[Ca^{2+}]$ of seawater at this time (Figure 1), by favoring precipitation of all forms of $CaCO_3$, triggered the widespread evolution of skeletons at this time;⁸⁷ it is possible, however, that this evolutionary phenomenon was largely a response to the initial appearance and rapid evolutionary size increase of effective multicellular predators. Apart from this issue, there is some evidence that animals that arose in Aragonite I seas secreted aragonite or high-Mg calcite, and those that arose shortly later, in Calcite I seas, secreted calcite.⁸⁸

It is also important to consider to what extent the mineralogy of biocalcifying taxa that arose after the initial Cambrian radiation of marine life was favored by the Mg/Ca ratio of existing seawater. Here too, however, it is important to recognize that the odds will be approximately 50-50 for each such occurrence. Two aragonite-secreting groups of bottom-dwelling foraminiferans (marine amoeba-like forms with skeletons), the Laginina and Involutinina, arose during Aragonite sea II, perhaps having been induced by seawater chemistry to employ this mineralogy.⁸⁹ The modern corals (Scleractinia) evolved in mid-Triassic time (in the Aragonite II sea), apparently from naked anemone ancestors,⁹⁰ and the generally poor state of preservation of their skeletons has been taken to indicate that they consisted primarily of aragonite, like all skeletons of this group today.

It appears that sponges have evolved calcareous skeletons several times in their history, and that these skeletons have generally been compatible with seawater chemistry.⁹¹ As already noted, calcitic stromatoporoids evolved in the Calcite I sea. Certain types of chaetetids, sponges that produced aragonitic skeletons, arose in late Paleozoic time (in the Aragonite II sea), and during the same interval other aragonitic forms, such as sphinctozoans, and to a lesser extent, inozoans, became major reef builders. As already noted, all Cretaceous sponges apparently secreted calcite and aragonitic sponges arose after the transition to Aragonite III.

As also noted above, cheilostome bryozoan taxa evolved skeletons that were entirely aragonitic in Cenozoic time, during or after the shift of seawater chemistry into the aragonite domain (Aragonite III).

In summary, it is quite possible that nearly all known aragonitic marine taxa have evolved in aragonite seas.

6. *The Importance of CO₂*

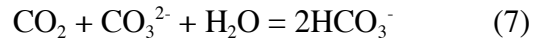
An increase in [CO₂] within seawater, by lowering the pH and [CO₃²⁻], retards calcification by marine organisms (equation 1). Thus, when evaluating rates of calcification by marine life, we must consider the acidity of seawater in addition to its Mg/Ca ratio.

As the concentration of CO₂ in the atmosphere rises today as a result of human activities, the acidity of ocean waters increases, there are the likely to be negative consequences for marine life, including coral reefs.

6.1 Background

It is a simple, but highly significant, fact that the pattern of partitioning of inorganic carbon species in seawater causes $p\text{CO}_2$ to be inversely proportional to [CO₃²⁻].

Calcification results from two reactions (equations 1 and 2). Because only the second reaction releases CO₂, the total amount released by a given amount of calcification depends on the relative amounts of CaCO₃ produced by these two reactions. The amount of CO₂ released by the second reaction is influenced by [CO₂] because of the buffering effect of CO₃²⁻:



At the present level of atmospheric $p\text{CO}_2$, the ratio of CO_2 released by precipitation of carbonate to precipitated carbonate (Ψ) in the ocean is 0.6.⁹² As will be noted below, Ψ increases with the level of atmospheric $p\text{CO}_2$ and thus will increase in the future.

Global carbonate production in the modern ocean happens to be of similar magnitude for the continental shelves and open ocean.⁹³ On continental shelves, reef-building corals, calcareous algae, bottom-dwelling foraminiferans, and a variety of other less productive taxa produce CaCO_3 . In the upper zone of the open ocean, planktonic foraminiferans and a few other unicellular animal-like taxa and animals produce CaCO_3 , but coccolithophores are the most prodigious producers; as noted earlier, *Emiliana huxleyi* accounts for a much larger percentage of planktonic carbonate production than any other species in the modern ocean.

Much of the CaCO_3 released by oceanic plankton dissolves as it descends into waters that become progressively cooler and thus contain increasing concentrations of CO_2 . The lysocline (horizon at which dissolution begins) varies from place to place in the ocean because of the ocean's complex thermal structure. The total amount of CaCO_3 produced by marine organisms exceeds by a factor of two the supply of chemical components of CaCO_3 by submarine hydrothermal vents and rivers.⁹³ The remainder of the CaCO_3 produced by marine organisms is derived from chemical components of CaCO_3 recycled within the ocean, primarily by dissolution of CaCO_3 below the lysocline.

6.2. Effects of $p\text{CO}_2$ on Calcification

As we contemplate future increases in atmospheric $p\text{CO}_2$, we must consider the effects that this change will have on biocalcification, which plays a major role in the global carbon cycle.

6.2.1 *Coccolithophores*

In experiments an increase in ambient CO_2 (and therefore a reduction of pH) has retarded the calcification and/or elevates the production of organic carbon for some species of coccolithophores. *Emiliana huxleyi* and *Gephyrocapsa oceanica* exhibited the pattern that might be expected, displaying a monotonic decline in rate of calcification with an elevation of $p\text{CO}_2$; they simultaneously experienced a less pronounced increase in production of organic carbon through fertilization of their photosynthesis.^{94,95}

Calcidiscus leptoporus also exhibited a decrease in calcification, but this was not accompanied by a change in organic carbon production.⁹⁶ Perhaps the reduction of CO_2 that the calcification supplied to the photosynthesis of these species more-or-less offset the elevation of ambient CO_2 . Reduced calcification in all these species at high CO_2 levels entailed production of deformed and incomplete coccoliths.^{94,95,96} Curiously, another species, *Coccolithus pelagicus*, exhibited no changes in growth rate or calcification over a range of atmospheric CO_2 levels in the laboratory.⁹⁶

Recall that other experiments showed that increased $[Ca^{2+}]$ resulted in higher growth rates for three other species of coccolithophores (Figure 5) and more robust coccoliths in one species (Figure 4).³¹ Here again, the saturation state of seawater had a powerful effect, and the implication is that, as it declines in the future, coccolithophores, as a group, will produce calcite at reduced rates.

Inasmuch as *E. huxleyi* and, to a lesser extent, *G. oceanica* undergo unusually large blooms in the ocean and are major carbonate producers, the effect of pCO_2 on their calcification is especially significant.

6.2.2 Planktonic Foraminiferans

Planktonic foraminiferans are single-celled heterotrophic secretors of calcite. They have been found to produce heavier skeletons when the saturation state of the ambient seawater with respect to calcite is elevated.^{97,98,99} Presumably, when the saturation state of the ocean declines in the future, these organisms will produce lighter skeletons than they do today and, hence, they will produce $CaCO_3$ at a lower global rate; the same change will probably occur for bottom-dwelling foraminiferans. The overall result will have a significant impact on the carbon cycle because both ecological groups of foraminiferans are major producers of carbonate in the ocean.

6.2.3 Corals

Reduction of $[\text{CO}_3^{2+}]$ in aquaria, either directly or via manipulation of atmospheric $p\text{CO}_2$, has also resulted in lower skeletal growth rates for corals.^{100,101,102} In one set of experiments, corals grown under reduced $[\text{CO}_3^{2+}]$ conditions exhibited unusual microcrystalline structures, sometimes entailing diminution of aragonite fibers.¹⁰¹ Coral reef communities assembled in the laboratory have also exhibited reduced total calcification when $[\text{CO}_3^{2+}]$ has been lowered by elevating $p\text{CO}_2$ or employing other means.^{103,104} As noted earlier, three species of reef-building corals experienced lower growth rates when the ambient Mg/Ca ratio and $[\text{Ca}^{2+}]$ were simultaneously lowered.⁶³ Manipulation of $[\text{Ca}^{2+}]$ and $[\text{CO}_3^{2+}]$ in the BIOSPHERE-2 artificial coral reef revealed that the calcification for the entire reef community was a linear function of both of these chemical concentrations, meaning that the saturation state for calcium carbonate was the governing factor; furthermore, organisms failed to acclimate to a lower saturation state over the course of months, and even years.¹⁰³

6.3 Calcification in the Cretaceous Calcite Sea

Evidence from paleobiology provides a perspective as we contemplate future increases in atmospheric $p\text{CO}_2$. The concentration of $[\text{Ca}^{2+}]$ in the ocean was higher during Cretaceous time than it is today, but atmospheric $p\text{CO}_2$ was also higher. Estimates of $[\text{Ca}^{2+}]$ and $[\text{CO}_3^{2-}]$ for the tropical ocean for very late Cretaceous time (~70 million years ago) are about 23 mM and 0.1^{-2} mM, respectively;¹⁰⁵ the corresponding values for the

modern tropical ocean are about 10 mM and 0.25^{-2} mM. Multiplication of each pair of numbers suggests that the saturation state of the ocean with respect to calcite and aragonite near the end of the Cretaceous was virtually the same as that of the modern ocean. Calculations indicate that earlier in the Cretaceous (~ 100-150 million years ago) $[Ca^{2+}]$ was substantially higher in the ocean: 30-40 mM (Figure 1),¹⁰⁵ so that the saturation state of the ocean with respect to calcite and aragonite was probably higher then than it is today.

6.3.1. Coccolithophores and Chalk Deposits

Recall that coccolithophores were so productive during the Cretaceous Period that they generated widespread chalk deposits. Recall that experiments have shown that both the low Mg/Ca ratio and the high ambient $[Ca^{2+}]$ of artificial Cretaceous seawater promote calcification in coccolithophores (Figure 5). As noted above, the high $[Ca^{2+}]$ level of very late Cretaceous seawater more-or-less compensated for the low $[CO_3^{2-}]$ (high atmospheric pCO_2) level. Thus, the high productivity of coccolithophores at that time relative to the present (Figure 1) apparently resulted from the low Mg/Ca ratio of Cretaceous seawater rather than a high saturation state with respect to calcite. The even higher level of $[Ca^{2+}]$ earlier in the Cretaceous may have given the saturation state a larger role in chalk production.

6.3.2. Reef-building Corals

For the history of scleractinian corals, the situation is more complicated. Curiously, these organisms, whose skeletons consist predominantly of aragonite today, flourished as builders of tropical reefs in Calcite II seas of Late Jurassic and Early Cretaceous time before giving way to rudist bivalve mollusks. Although more prolific contributors to Late Cretaceous reefs than corals, the rudists died out with the dinosaurs (Figure 1).

In laboratory experiments, modern scleractinians produced skeletons consisting of about 45 percent calcite in seawater in which the Mg/Ca ratio was 1.5, which is slightly higher than the ratio calculated for Cretaceous seas (Figure 1); the corals also exhibited reduced growth rates under these experimental conditions.⁶³ It is possible that calcium poisoning or some other aspect of the unfamiliar seawater retarded the corals' growth in the experimental aquaria, but the results nonetheless conform to expectations, assuming that the Mg/Ca ratio had a stronger effect than the elevated $[Ca^{2+}]$, as was observed for *Halimeda* (Figure 7). Assuming that corals produced skeletons containing a substantial percentage of aragonite when they flourished as Late Jurassic and Early Cretaceous reef builders, their calcification should have been retarded by the low Mg/Ca ratio of seawater (Figure 1). Furthermore, their calcification should have been retarded by the high level of atmospheric pCO_2 noted above, which is estimated to have produced a level of $[CO_3^{2-}]$ in the tropical ocean during Late Cretaceous time that was only about 40% as high as it is today.¹⁰⁵ Furthermore, the consensus is that atmospheric pCO_2 was even higher in the Late Jurassic and Early Cretaceous than in the Late Cretaceous, with estimates for these earlier intervals ranging from about twice the modern-day level to much high levels.¹⁰⁶

Given that Mesozoic corals were able to prosper under these conditions, it seems likely that they possessed significantly different physiologies than their living descendants.

6.4. Controls and Consequences of Higher Atmospheric $p\text{CO}_2$ in the Future

Two major issues have arisen as to the likely effects of rising atmospheric $p\text{CO}_2$ on the production of skeletal materials in the ocean. One relates to a negative feedback: the rate of CO_2 released to the atmosphere by calcifiers will decline as elevated $p\text{CO}_2$ retards calcification, although Ψ will simultaneously increase so that a larger amount of CO_2 will be released for every molecule of CaCO_3 produced. The second is the potential impairment of biocalcification of marine organisms, including reef-building corals, as the pH of the ocean declines; this effect is anticipated to have highly deleterious consequences for its victims and other forms of life that depend on them.

6.4.1 The Influence of Corals on Atmospheric $p\text{CO}_2$

Coral reefs, through respiration, are net exporters of CO_2 to the atmosphere, but their contribution is estimated to be an order of magnitude less than that from human burning of fossil fuels.⁹² Therefore, a moderate decline of global reef metabolism resulting from future global warming (though not to be desired for other reasons) will do little to offset the impact of the human-induced increase of atmospheric $p\text{CO}_2$.

6.4.1. The Complex Relationship Between Coccolithophores and Atmospheric $p\text{CO}_2$

Largely because of the prodigious productivity of *Emiliania huxleyi*, and to a lesser extent *Gephyrocapsa oceanica*, coccolithophores produce more calcium carbonate in the modern ocean than any other taxon. As a result of the impact of these species, changes in coccolithophore productivity and calcification will affect atmospheric $p\text{CO}_2$ in numerous ways in the future – and the likely result is widely debated. Rather than attempting to anticipate this result, because it is difficult to quantify the relevant factors, the following summary will simply identify those factors that will affect atmospheric $p\text{CO}_2$ on the short time scales relevant to modern civilization (10-10² years), and it will indicate whether these factors will tend to increase (I) or reduce (R) atmospheric $p\text{CO}_2$ or have uncertain consequences (?). The following list includes some factors already discussed.

Increased atmospheric $p\text{CO}_2$ will:

1. Reduce coccolithophores' rate of calcification, a process that releases CO_2 (equation 2). (R)
2. Increase Ψ , so that the production of a given quantity of CaCO_3 will yield a larger amount of CO_2 . (I)
3. Elevate the productivity of coccolithophores and therefore send more organic matter toward the deep sea to be sequestered in sediments. (R)
4. In some way alter the rain of coccoliths sent from the surface toward the deep-sea because the rate of population growth of coccolithophores will increase while at the same time their calcification will be impaired (?).

5. Alter the amount of organic matter being remineralized to CO₂ by microbes in the water column because of a change in the global mass of oceanic coccoliths that is difficult to estimate. The significance of coccoliths here is that, of the total amount organic matter sequestered in deep-sea sediment today, 80-83% has sunk rapidly because of its containment in zooplankton fecal pellets that include calcium carbonate, especially coccoliths, as ballast.¹⁰⁷ (?)
 6. Alter the depth of the lysocline in ways that will vary from place to place as the ocean warms unevenly while [CO₂] rises throughout the ocean; depending on which of these countervailing factors prevails, the percentage of coccoliths that are dissolved before they can be sequestered on the deep-sea floor will change (?).
- On time scales of 10³ years, other factors play a role in coccolithophores' influence on [CO₂],^{108,109,110} but these factors are not relevant to events of the near future.

6.4.2. *An Impending Calcification Crisis*

Feedback by organisms in response to the impending increase in atmospheric $p\text{CO}_2$ is one thing. Survival is another. Little is known about what effects the future lowering of the pH of seawater will have on many aspects of the physiology of marine animals. As noted above, however, research has shown that a negative impact on calcification can be anticipated for many taxa. For reef-building corals, an attendant problem will be bleaching, which is the loss at high temperatures of the symbiotic algae upon which corals rely in order to calcify effectively enough to form reefs in shallow water.^{111,112,113,114,115} To form large reefs, corals must build these structures more rapidly

over many years than storms and bioerosion diminish them. In the future, coral communities that are of reduced diversity and consist of species that calcify more weakly than they do today may lose this battle. Also having a deleterious effect on coral reefs will be reduced calcification for the coralline algae that cement portions of reefs where corals have died, thus girding them against agents of destruction.

More generally, as atmospheric $p\text{CO}_2$ rises, many forms of marine life that depend on skeletons for support or for protection against predators may become naked or so weakly calcified as to be defenseless against predators. This is indeed a gloomy prospect.

A critical factor is that at the present time $[\text{Ca}^{2+}]$ in the ocean happens to be at its lowest level in more than a half billion years (it is estimated to have been about 3-4 times as high, for example, during most of the Cretaceous Period). This circumstance makes the anticipated rise of atmospheric $p\text{CO}_2$ especially problematical because the reduction of $[\text{CO}_3^{2-}]$ in seawater that will result, in combination with the very low level of $[\text{Ca}^{2+}]$, will produce an exceptionally low saturation state for seawater with respect to calcium carbonate.

7. References

- (1) Yates, K. K.; Robbins, L. L. *Geochemica et Cosmochimica Acta* **1999**, *63*, 129.
- (2) Sandberg, P. A. *Nature* **1983**, *305*, 19.
- (3) Sandberg, P. A. *American Geophysical Union Monograph* **1985**, *32*, 585.
- (4) Folk, R. L. *Journal of Sedimentary Petrology* **1974**, *44*, 40.
- (5) Berner, R. A. *Geochemica et Cosmochimica Acta* **1975**, *39*, 489.

- (6) Füchtbauer, H.; Hardie, L. A. *Geological Society of America Abstracts with Programs* **1976**, 8, 877.
- (7) Füchtbauer, H.; Hardie, L. A. *International Association of Sedimentology, Bochum* **1980**, 167.
- (8) Hardie, L. A. *Geology* **1996**, 24, 279.
- (9) Demicco, R. V.; Lowenstein, T. C.; Hardie, L. A.; Spenser, R. J. *Geology* **2005**, 33, 877.
- (10) Arvidson, R. S.; MacKenzie, F. T.; Guidry, M. *American Journal of Science* **2006**, 306, 135.
- (11) Lowenstein, T. K.; Timofeeff, M. N.; Brennan, S. T.; Hardie, L. A.; Demicco, R. V. *Science* **2001**, 294, 1086.
- (12) Brennan, S.; Lowenstein, T. K. *Geochemica et Cosmochimica Acta* **2002**, 66, 2683.
- (13) Horita, J.; Zimmermann, H.; Holland, H. D. *Geochemica et Cosmochimica Acta* **2002**, 66, 3733.
- (14) Lowenstein, T. K.; Hardie, L. A.; Timofeeff, M. N.; Demicco, R. V. *Geology* **2003**, 31, 857.
- (15) Lowenstein, T. K.; Timofeeff, M. N.; Kovalevych, V. M.; Horita, J. *Geochemica et Cosmochimica Acta* **2005**, 69, 1701.
- (16) Timofeeff, M. N.; Lowenstein, T. K.; da Silva, M. A. M.; Harris, N. B. *Geochemica et Cosmochimica Acta* **2006**, 70, 1977.
- (17) Stanley, S. M.; Hardie, L. A. *Palaeogeography, Palaeoclimatology, Palaeoecology* **1998**, 144, 3.

- (18) Stanley, S. M.; Hardie, L. A. *GSA Today* **1999**, 9, 2.
- (19) Lowenstam, H. A.; Weiner, S. *On Biomineralization*; Oxford University Press: New York, 1989, p. 67.
- (20) Mann, S. *Biomineralization: Principles and Concepts in Bioinorganic Materials Chemistry*; Oxford University Press: Oxford, 2001.
- (21) Weiner, S.; Dove, P. M. *Reviews of Mineralogy and Geochemistry* **2003**, 54, 1.
- (22) Bathurst, R. G. C. *Carbonate sediments and their diagenesis*; Elsevier: Amsterdam, 1975.
- (23) Lasemi, Z.; Sandberg, P. A.; Boardman, P. A. *Geology* **1990**, 18, 370.
- (24) Stehli, F. G. *Science* **1956**, 123, 1031.
- (25) Webb, G. E.; Sorauf, J. E. *Geology* **2002**, 30, 415.
- (26) Dickson, J. A. D. *Journal of Sedimentary Research* **2004**, 74, 355.
- (27) Ries, J. B. *Geology* **2004**, 32, 981.
- (28) Chave, K. E. *Journal of Geology* **1954**, 62, 266.
- (29) Stanley, S. M.; Ries, J. B.; Hardie, L. A. *Proceedings of the National Academy of Sciences* **2002**, 99, 15323.
- (30) Ries, J. B. *Geochemica et Cosmochimica Acta* **2006**, 70, 891.
- (31) Stanley, S. M.; Ries, J. B.; Hardie, L. A. *Geology* **2005**, 33, 593.
- (32) Scholle, P. A. *American Association of Petroleum Geologists* **1977**, 61, 982.
- (33) Sikes, C. S.; Roer, R. D.; Wilbur, K. M. *Limnology and Oceanography* **1980**, 25, 248.
- (34) Winter, A.; Seisser, W. G. In *Coccolithophores*; Winter, A., Seisser, W. G., Eds.; Cambridge University Press: Cambridge, 1994.

- (35) Hulbert, E. M. *Deep-Sea Research* **1967**, *14*, 685.
- (36) Hulbert, E. M. *Bulletin of Marine Science* **1983**, *33*, 197.
- (37) Brand, L. E. In *Coccolithophores*; Winter, A., Siesser, W. G., Eds.; Cambridge University Press: Cambridge, 1994.
- (38) Brand, L. E. *Limnology and Oceanography* **1991**, *36*, 1756.
- (39) Martin, J. H.; Coale, K. H.; Johnson, K. S.; Fitzwater, S. E.; Gordon, R. M.; Tanner, S. J.; Hunter, C. N.; Elrod, V. A.; Nowicki, J. L.; Coley, T. L.; Barber, R. T.; Lindley, S.; Watson, A. J.; Van Scoy, K.; Law, C. S.; Liddicoat, M. I.; Ling, R.; Stanton, T.; Stockel, J.; Collins, C.; Anderson, A.; Bidigare, R.; Ondrusek, M.; Latasa, M.; Millero, F. J.; Lee, K.; Yao, W.; Zhang, J. Z.; Friederich, G.; Sakamoto, C.; Chavez, F.; Buck, K.; Kolber, Z.; Greene, R.; Falkowski, P.; Chisolm, S. W.; Hoge, F.; Swift, R.; Yungel, J.; Turner, S.; Nightingale, P.; Hatton, A.; Liss, P.; Tindale, N. W. *Nature* **1994**, *371*, 123.
- (40) Franck, V. M.; Brzezinski, M. A.; Coale, K. H.; Nelson, D. M. *Deep-Sea Research* **2000**, *47*, 3315.
- (41) Davis, K. J.; Dove, P. M.; De Yoreo, J. J. *Science* **2002**, *290*, 1134.
- (42) Nimer, N. A.; Merritt, M. J. *Journal of Phycology* **1996**, *32*, 813.
- (43) Thierstein, H. R.; Geitenhauer, K. R.; Molfino, K. R. *Geology* **1977**, *5*, 400.
- (44) McIntyre, A. *Deep-Sea Research* **1970**, *17*, 187.
- (45) Lowenstam, H. A.; Epstein, S. *Journal of Geology* **1957**, *65*, 364.
- (46) Borowitzka, M. A.; Larkum, A. W. *Journal of Experimental Botany* **1976**, *27*, 879.

- (47) Stanley, S. M. *Palaeogeography, Palaeoclimatology, Palaeoecology* **2006**, 232, 214.
- (48) Ries, J. B. *Journal of Sedimentary Research* **2006**, 76, 515.
- (49) Ries, J. B. *Paleobiology* **2005**, 31, 445.
- (50) White, P. J.; Broadley, M. R. *Annals of Botany* **2003**, 92, 487.
- (51) Mankiewicz, C. *Coral Reefs* **1988**, 6, 271.
- (52) Elliott, G. F. *Palaeogeography, Palaeoclimatology, Palaeoecology* **1984**, 48, 163.
- (53) Wood, R. A. In *The early evolution of Metazoa and the significance of problematic taxa*; Simonetta, A. M., Conway Morris, S., Eds.; Cambridge University Press: Cambridge, 1991.
- (54) Copper, P. *SEPM Special Publication* **2002**, 72, 181.
- (55) Kershaw, S. *Oceanography: An Earth Science Perspective*; Stanley Thornes: Cheltenham, 2000, p.157.
- (56) Mallamo, M. P.; Stearn, C. W. *Geological Society of America Abstracts with Programs* **1991**, 23, 164.
- (57) Veizer, J.; Wendt, J. *Neues Jahrbuch Fur Geologie Und Palaontologie* **1976**, 22, 558.
- (58) Reitner, J. *Geobios* **1987**, 20, 571.
- (59) Hartman, W. D. *Sedimenta* **1980**, VIII, 193.
- (60) Maliva, R. G.; Knoll, A. H.; Siever, R. *Palaios* **1990**, 4, 519.
- (61) Maldonado, M.; Carmona, M. C.; Uriz, M. J.; Cruzado, A. *Nature* **1999**, 401, 785.
- (62) Cuif, J. P.; Dauphin, Y.; Doucet, J.; Gautret, P.; Zibrowius, H. *Geochemica et Cosmochimica Acta* **1999**, 67, 75.

- (63) Ries, J. B.; Stanley, S. M.; Hardie, L. A. *Geology* **2006**, *34*, 525.
- (64) Cohen, A. L.; McConnaughey, T. A. In *Reviews in Mineralogy and Geochemistry*; Dove, P. M., De Yoreo, J. J., Weiner, S., Eds.; Mineralogical Society of America: Washington, D. C., 2003; Vol. 54.
- (65) Stolarski, J.; Meibom, A.; Przeniosło, R.; Mazur, M. *Science* **2007**, *318*, 92.
- (66) Steuber, T. *Geology* **2002**, *30*, 259.
- (67) Pochon, X.; Montoya-Burgos, J. I.; Stadelmann, B.; Pawlowski, J. *Molecular Phylogenetics and Evolution* **2006**, *38*, 20.
- (68) Rucker, J. B.; Carver, R. E. *Journal of Paleontology* **1969**, *43*, 791.
- (69) Boardman, R. S.; Cheetham, A. H. In *Fossil Invertebrates*; Boardman, R. S., Rowell, A. H., Eds.; Blackwell Scientific Publications: Palo Alto, 1987.
- (70) Railsbeck, L. B. *Geology* **1993**, *21*, 703.
- (71) Wilbur, K. M. In *Chemical Zoology*; Florkin, M., Scheer, B. T., Eds.; Academic Press: San Diego, 1972; Vol. 7.
- (72) Lorens, R. B.; Bender, M. L. *Nature* **1977**, *269*, 793.
- (73) Lorens, R. B.; Bender, M. L. *Geochimica et Cosmochimica Acta* **1980**, *44*, 1265.
- (74) Addadi, L.; Moradian, J.; Shay, E.; Maroudas, N. G.; Weiner, S. *Proceedings of the National Academy of Sciences of the United States of America* **1987**, *84*, 2732.
- (75) Belcher, A. M.; Wu, X. H.; Christensen, R. J.; Hansma, P. K.; Stucky, G. D.; Morse, D. E. *Nature* **1996**, *381*, 56.
- (76) Falini, G.; Albeck, S.; Weiner, S.; Addadi, L. *Science* **1996**, *271*, 67.
- (77) Manoli, F.; Koutsopoulos, S.; Dalas, E. *Journal of Crystal Growth* **1997**, *182*, 116.

- (78) Thompson, J. B.; Paloczi, G. T.; Kindt, J. H.; Michenfelder, M.; Smith, B. L.; Stucky, G. D.; Morse, D. E.; Hansma, P. K. *Biophysics Journal* **2000**, *79*, 3307.
- (79) Weiss, I. M.; Tuross, N.; Addadi, L.; Weiner, S. *Journal of Experimental Zoology* **2002**, *293*, 478.
- (80) Marxen, J. C.; Niimtz, M.; Becker, W.; Mann, K. *Journal of Molluscan Studies* **2003**, *69*, 113.
- (81) Crenshaw, M. A. *Biological Bulletin* **1972**, *143*, 506.
- (82) Mount, A. S.; Wheeler, A. P.; Paradkar, R. P.; Snider, D. *Science* **2004**, *304*, 297.
- (83) Checa, A. G.; Jiménez-López, C.; Rodríguez-Navarro, A.; Machado, J. P. *Marine Biology* **2007**, *150*, 819.
- (84) Beniash, E.; Aizenberg, J.; Addadi, L.; Weiner, S. *Proceedings of the Royal Society of London* **1997**, *264*, 461.
- (85) Politi, Y.; Arad, T.; Klein, E.; Weiner, S.; Addadi, L. *Science* **2004**, *306*, 1161.
- (86) Weiner, S.; Sagi, I.; Addadi, L. *Science* **2005**, *309*, 1027.
- (87) Brennan, S.; Lowenstein, T. C.; Horita, J. *Geology* **2004**, *32*, 473.
- (88) Porter, S. M. *Science* **2007**, *316*, 302.
- (89) Martin, R. E. *Global and Planetary Change* **1995**, *11*, 1.
- (90) Stanley, G. D. *Earth Science Reviews* **2003**, *69*, 195.
- (91) Wood, R. A. *Biology and Revised Systematics of Some Late Mesozoic Stromatoporoids*; Palaeontological Association: London, 1987.
- (92) Ware, J. R.; Smith, S. V.; Reakakudla, M. L. *Coral Reefs* **1992**, *11*, 127.
- (93) Milliman, J. D. *Global Biogeochemical Cycles* **1993**, *7*, 927.

- (94) Riebesell, U.; Zondervan, I.; Rost, B.; Tortell, P. D.; Zeebe, R. E.; Morel, F. M. M. *Nature* **2000**, *407*, 364.
- (95) Zondervan, I.; Zeebe, R. E.; Rost, B.; Riebesell, U. *Global Biogeochemical Cycles* **2001**, *15*, 507.
- (96) Langer, G.; Geisen, M.; Baumann, K.-H.; Kläs, J.; Riebesell, U.; Thoms, S.; Young, J. R. *Geochemistry, Geophysics, Geosystems* **2006**, *7*, Q09006.
- (97) Spero, H.; Bijma, J.; Lea, D. W.; Bemis, B. E. *Nature* **1997**, *390*, 497.
- (98) Bijma, J.; Spero, H.; Lea, D. W. In *Uses of proxies in paleoceanography: examples from the South Atlantic*; Fischer, G., Wefer, G., Eds.; Springer, 1999.
- (99) Barker, S.; Elderfield, H. *Science* **2002**, *297*, 833.
- (100) Marubini, F.; Thake, B. *Limnology and Oceanography* **1999**, *44*, 716.
- (101) Marubini, F.; Ferrier-Pages, C.; Cuif, J. P. *Proceedings of the Royal Society of London* **2003**, *270*, 179.
- (102) Renegar, D. A.; Riegl, B. M. *Marine Ecology Progress Series* **2005**, *293*, 69.
- (103) Langdon, C.; Takahashi, T.; Sweeney, C.; Chipman, D.; Goddard, J.; Marubini, F.; Aceves, H.; Barnett, H.; Atkinson, M. J. *Global Biogeochemical Cycles* **2000**, *14*, 639.
- (104) Leclercq, N.; Gattuso, J. P.; Jaubert, J. *Limnology and Oceanography* **2002**, *47*, 558.
- (105) Demicco, R. V.; Lowenstein, T. C.; Hardie, L. A. *Geology* **2003**, *31*.
- (106) Royer, D. L. *Geochimica et Cosmochimica Acta* **2006**, *70*, 5665.
- (107) Klaas, C.; Archer, D. *Global Biogeochemical Cycles* **2002**, *16*, 63.

- (108) Broecker, W. S.; Lynch-Stieglitz, J.; Clark, E.; Hajdas, I.; Bonani, G.
Geochemistry, Geophysics, Geosystems **2001**, 2, 2001GC000177.
- (109) Broecker, W. S.; Peng, T.-H. *Global Biogeochemical Cycles* **1987**, 1, 15.
- (110) Barker, S.; Higgins, J. A.; Elderfield, H. *Philosophical Transactions of the Royal Society of London* **2003**, 361, 1977.
- (111) Glynn, P. W. *Coral Reefs* **1993**, 12, 1.
- (112) Kleypas, J.; Buddemeier, R. W.; Archer, D.; Gattuso, J. P.; Langdon, C.; Opdyke, B. N. *Science* **1999**, 284, 118.
- (113) Ostrander, G. K.; Armstrong, K. M.; Knobbe, E. T.; Gerace, D.; Scully, E. P.
Proceedings of the National Academy of Sciences of the United States of America **2000**, 97, 5297.
- (114) Hughes, T. P.; Baird, A. H.; Bellwood, D. R.; Card, M.; Connolly, S. R.; Folke, C.; Grosberg, R.; Hoegh-Guldberg, O.; Jackson, J. B. C.; Kleypas, J.; Lough, J. M.; Marshall, P.; Nyström, M.; Palumbi, S. R.; Pandolfi, J. M.; Rosen, B.; Roughgarden, J. *Science* **2003**, 301, 929.
- (115) Feely, R. A.; Sabine, C. L.; Lee, K.; Berelson, W.; Kleypas, J.; Fabry, V. J.; Millero, F. J. *Science* **2004**, 305, 362.

Figure captions

Figure 1. Comparison of the temporal distribution of mineralogies for non-skeletal marine carbonates and evaporates and of biologically simple carbonate-producing taxa that have functioned as important reef-builders and producers of marine sediment.^{17,18}

The large upper diagram shows nonskeletal precipitation of low-Mg calcite, high-Mg calcite, and aragonite as a function of the Mg/Ca molar ratio of seawater.^{8,9} The graph at the upper right illustrates incorporation of Mg in nonskeletal calcite as a function of the ambient Mg/Ca ratio at two temperatures.^{6,7} The uppermost two broad horizontal bars show intervals of aragonite and calcite seas, as indicated by two assessments of the geologic record of nonskeletal carbonate precipitation.^{2,3} The lowermost broad horizontal bar shows temporal oscillations observed in the geologic record between calcitic and aragonitic nonskeletal carbonates and between KCl and MgSO₄ marine evaporates.⁸ Shown below are temporal distributions of the carbonate-producing taxa.^{17,18,47}

Figure 2. Increase in the Mg of skeletal calcite with an increase in the ambient Mg/Ca molar ratio of experimental seawater at 25°C for three species of coralline red algae of the genus *Amphiroa*.²⁹ All specimens were switched between seawater treatments with Mg/Ca = 2.5 and 5.8. For each treatment, narrow bars show the range of measurements and wide bars show standard deviations for the number of measurements indicated. The fractionation pattern resembles that for nonskeletal calcite. In seawater of Cretaceous composition (Mg/Ca = 1) all taxa secreted low-Mg calcite (< 4 mole % Mg substituting for Ca). Salinity and total [Mg²⁺]+[Ca²⁺] were held constant.

Figure 3. Increase in the Mg of skeletal calcite with an increase in the ambient Mg/Ca molar ratio of experimental seawater for three species of coccolithophores at 25°C.³¹ Error bars are standard deviations for 5 measurements. A. A species that produces skeletons that consist of marginally low-Mg calcite in modern seawater (Mg/Ca = 5.2). B

and C. Two species that secrete high-Mg calcite in modern seawater. All taxa secreted low-Mg calcite in seawater of Cretaceous composition ($\text{Mg}/\text{Ca} \leq 1$). Dashed lines illustrate Mg fractionation for nonskeletal calcite. Salinity and total $[\text{Mg}^{2+}] + [\text{Ca}^{2+}]$ were held constant.

Figure 4. Increase in growth rate and calcification at 25°C for three coccolithophore species with a reduction of the ambient Mg/Ca molar ratio and associated increase in $[\text{Ca}^{2+}]$ of experimental seawater.³¹ Salinity and total $[\text{Mg}^{2+}] + [\text{Ca}^{2+}]$ were held constant. (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. Spearman rank correlation = 0.99 for all three species. (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 bars = 1 μm).

Figure 5. Effect of both the Mg/Ca ratio and $[\text{Ca}^{2+}]$ of experimental seawater on the population growth rate of the coccolithophore *Pleurochrysis carterae* at 25°C.³¹ A. Increase of population growth rate when $[\text{Ca}^{2+}]$ was elevated from 14.1 mM to 25.3 mM while the Mg/Ca molar ratio was held constant at 3.5 (an aragonite sea level). (B) Reduction of population growth rate when $[\text{Ca}^{2+}]$ was lowered from a Cretaceous level of 31.6 mM to the modern seawater level of 10.2 mM while the Mg/Ca molar ratio was held constant at 1.0 (a Cretaceous level). (C) Increase of population growth rate when the Mg/Ca molar ratio was reduced from 5.2 (modern seawater ratio) to 1.0 (a Cretaceous ratio) and $[\text{Ca}^{2+}]$ was held constant at 10.2 mM (modern seawater concentration). (D)

Reduction of population growth rate when the Mg/Ca molar level was elevated from the Cretaceous level of 1.5 to the aragonite sea level of 3.5 while $[\text{Ca}^{2+}]$ was held constant at 25.3 mM (a Cretaceous level). Salinity was held constant by adjusting $[\text{Na}^{+}]$.

Experiments with *C. neohelis* yielded similar results.

Figure 6. *Halimeda incrassata*, a geographically widespread species of segmented calcareous green algae that has been employed in calcification experiments (scale in millimeters). When *Halimeda* dies, it disaggregates and its aragonitic segments turn white; they constitute major components of lime sediments in the modern ocean. Scale in millimeters (©The Cooks Islands National Heritage Trust.)

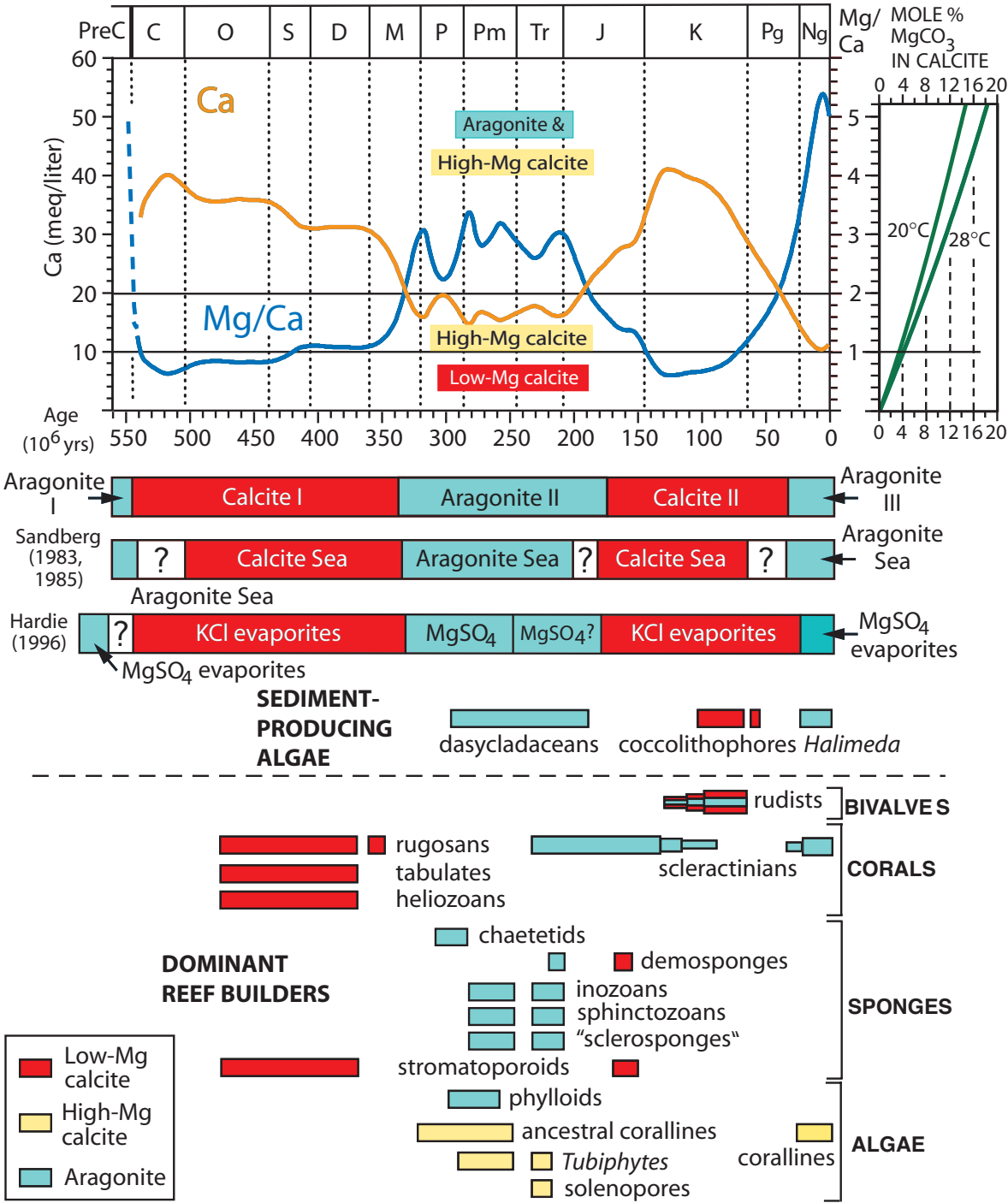
Figure 7. Rates of calcification (A), primary production (B), and linear growth (C) for *Halimeda incrassata* grown in nine experimental seawaters at 25°C. All rates increased significantly ($p < 0.05$) for both natural and non-natural seawaters both with an increase in ambient Mg/Ca ($[\text{Ca}^{2+}]$ fixed) and an increase in ambient $[\text{Ca}^{2+}]$ (Mg/Ca fixed). Salinity was held constant by adjusting $[\text{Na}^{+}]$. Numbers in parentheses to the left of data points in A are sample sizes (numbers of thalli); standard deviations are shown to the right of points.

Figure 8. Percentage of calcium carbonate precipitated as calcite instead of aragonite within skeletons of *H. incrassata* in three experimental seawaters at 25°C (Mg/Ca = 1.5, $[\text{Ca}^{2+}] = 25.3$ mM; Mg/Ca = 2.5, $[\text{Ca}^{2+}] = 18.1$ mM; Mg/Ca = 5.2, $[\text{Ca}^{2+}] = 10.2$ mM).⁴⁷ Percentages were determined by powder x-ray diffraction. Numbers of

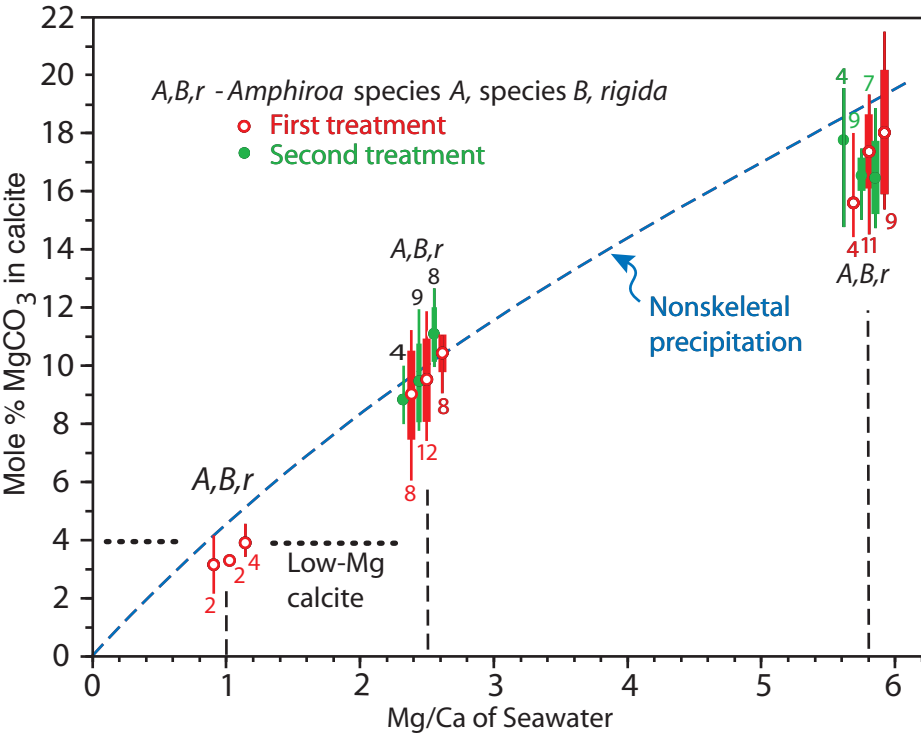
measurements are shown in parentheses. Standard deviations (error bars) represent instrument error and variation among specimens.

Figure 9. Mineralogy and calcification rates of the corals *Acropora cervicornis*, *Montipora digitata*, and *Porites cylindrica* grown in artificial seawater treatments at 25°C.⁶³ A. Molar % calcite in skeletons versus the Mg/Ca ratio of artificial seawater (n = 15 for all species). B. Calcification rate versus the Mg/Ca ratio of artificial seawater (n = 50 for all species). Standard deviations (error bars) represent instrument error and variation among specimens.

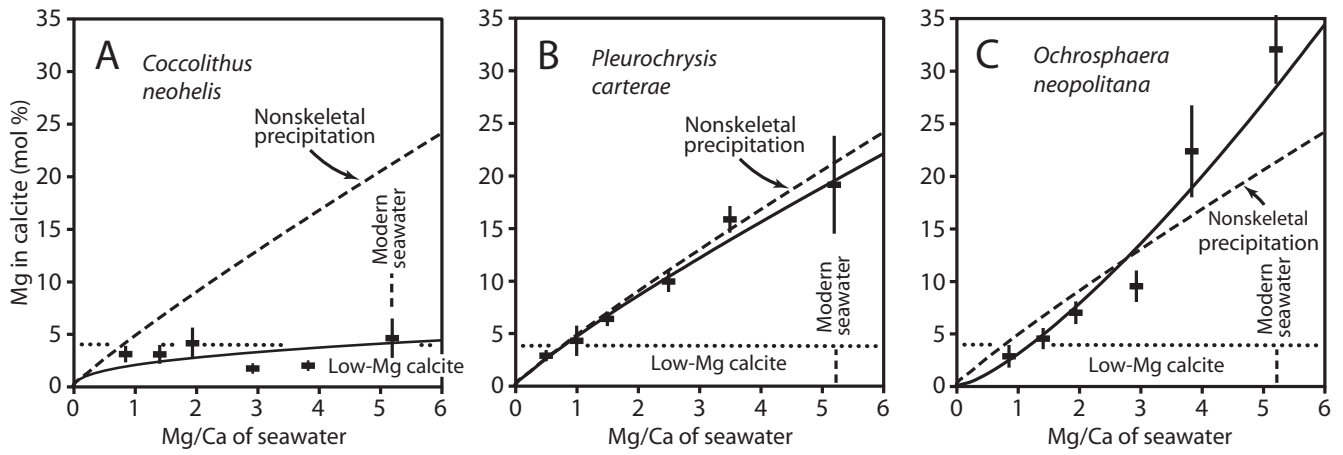
Stanley -- Figure 1



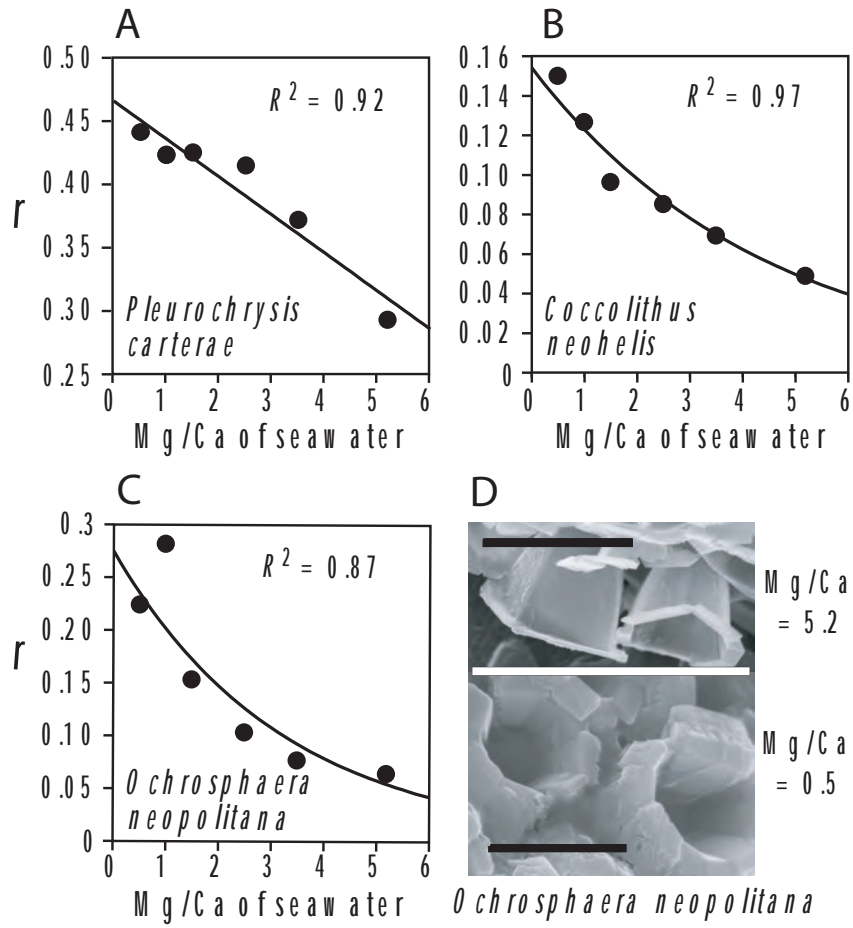
Stanley - Figure 2



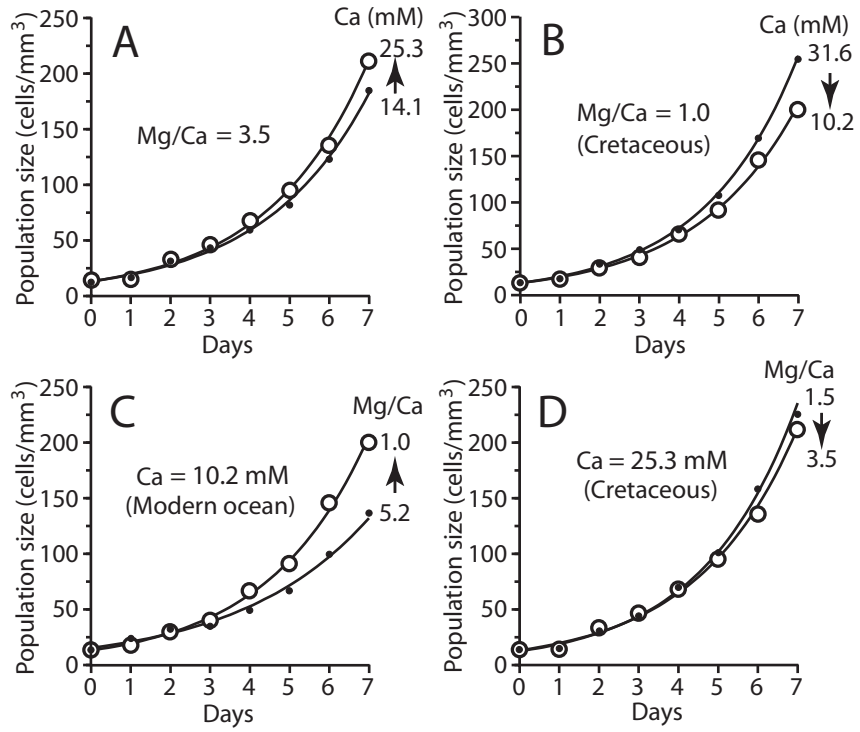
Stanley - Figure 3



Stanley -- Figure 4



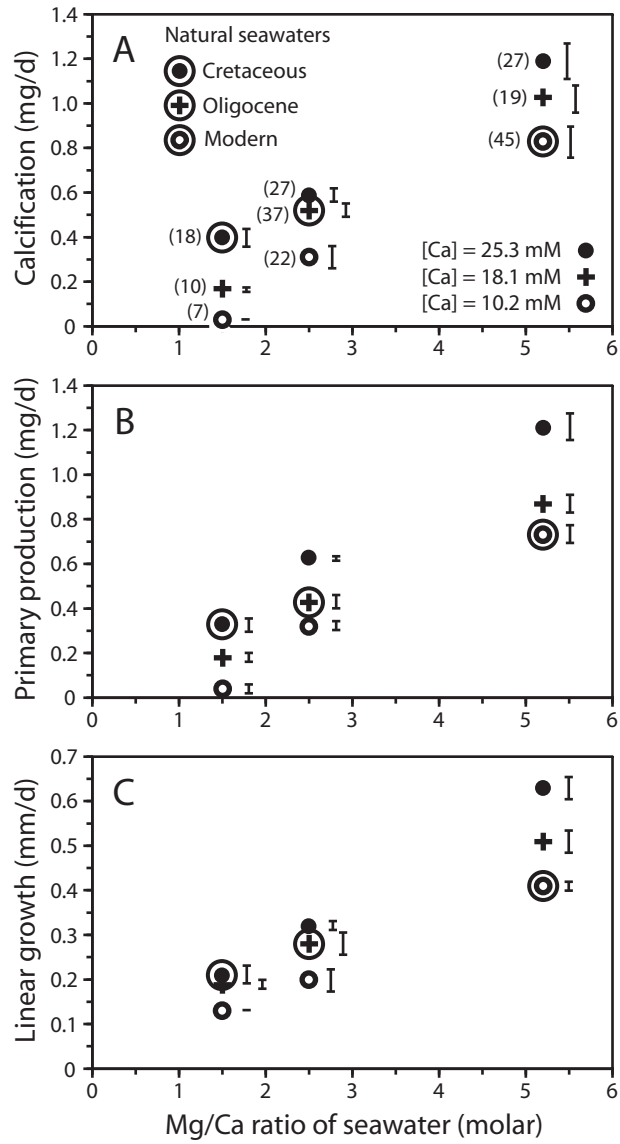
Stanley - Figure 5



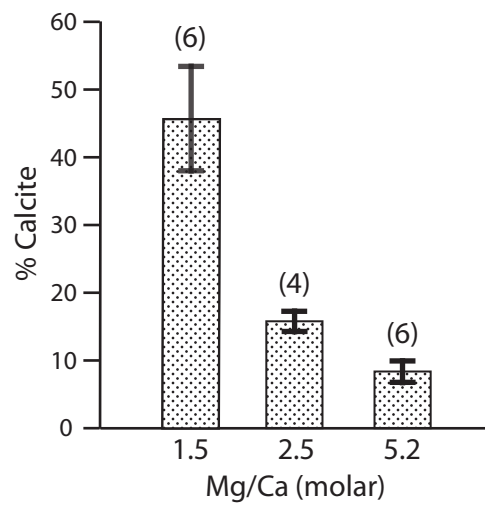
Stanley -- Figure 6



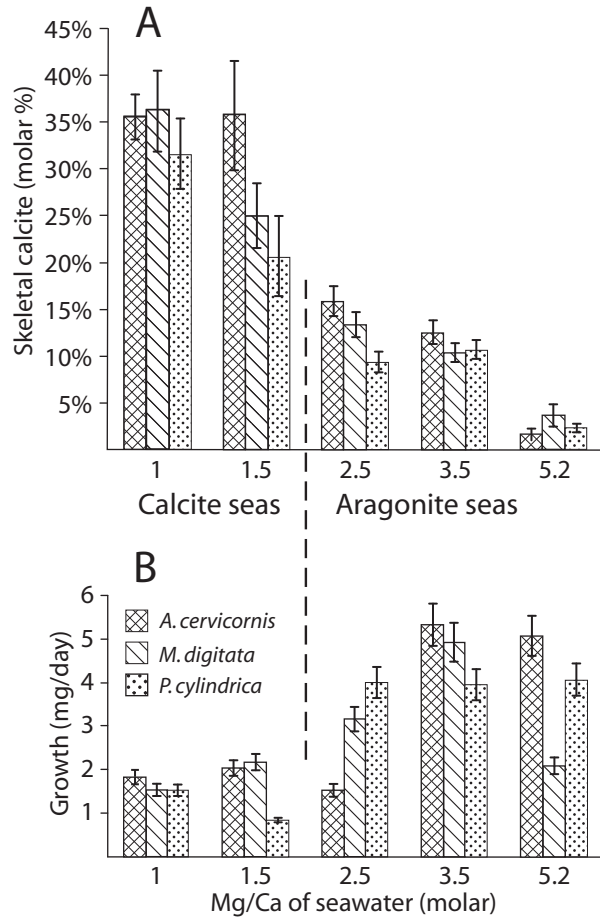
Stanley -- Figure 7



Stanley -- Figure 8



Stanley -- Figure 9



Biography

Steven Stanley grew up in a village several miles east of Cleveland, Ohio. He received his bachelor's degree from Princeton University (1963) and his Ph.D. from Yale University (1968). After two years as an assistant professor at the University of Rochester, he moved to Johns Hopkins University, where he was promoted to full professor in 1974 and remained until 2005, when he became a research professor at the University of Hawaii at Manoa. Much of his work has concerned rates, trends, and patterns of macroevolution, and for more than twenty years it has focused on the history of life in the context of past environmental change. He has served as president of the Paleontological Society and American Geological Institute and was elected to the National Academy of Sciences in 1994. His most recent awards have been the National Academy's Mary Clark Thomson Medal, the Paleontological Society Medal, and the Twenhofel Medal of the Society for Sedimentary Geology (SEPM).

