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Secular oscillations in the carbonate mineralogy of reef-building and sediment-producing organisms driven by tectonically forced shifts in seawater chemistry

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Abstract

The primary mineralogy of oolites and early marine carbonate cements led Sandberg [Nature 305 (1983), 19–22] to divide the Phanerozoic Eon into three intervals of ‘aragonite seas’ and two intervals of ‘calcite seas’. Hardie [Geology 24 (1996), 279–283] has shown that these oscillations, together with synchronous oscillations in the mineralogy of marine potash evaporites, can be explained by secular shifts in the Mg/Ca ratio of seawater driven by changes in spreading rates along mid-ocean ridges. The Hardie model also predicts that high-Mg calcite should precipitate along with aragonite, as it does in today’s aragonite sea. We have uncovered oscillations in the carbonate mineralogy of hypercalcifying organisms (ones that have produced massive skeletons, large reefs, or voluminous bodies of sediment) that correspond to Sandberg’s aragonite seas and calcite seas and that are predicted by the Hardie model. Particular groups of corals, sponges, and algae appear to have been dominant reef builders only when favored by an appropriate Mg/Ca ratio in seawater. In early and middle Paleozoic calcite seas (Calcite I), reefs were dominated by calcitic tabulate, heliolitid, and rugose corals and calcitic stromatoporoids. In contrast, during the period of late Paleozoic–early Mesozoic aragonite seas (Aragonite II), aragonitic groups of sponges, scleractinian corals, and phylloid algae, as well as high-Mg calcitic red algae, were principal reef builders. During Late Cretaceous time, at the acme of Calcite II, massive rudists displaced aragonitic hermatypic corals. In today’s aragonite sea (Aragonite III) scleractinian corals are again dominant reef builders, along with high-Mg calcitic coralline algae. Major sediment-producing algae exhibit temporal patterns similar to those of reef builders. Calcitic receptaculitids flourished during Calcite I, whereas aragonitic dasycladaceans did not become dominant rock formers until Aragonite II. During Calcite II, calcitic nannoplankton formed massive coccolith chalks in warm shallow seas of the Late Cretaceous, after the Mg/Ca ratio of seawater had reached a very low value and calcium concentration, a very high value. As the Mg/Ca ratio of seawater rose and calcium concentration fell during the Cenozoic Era, individual coccoliths, on average, became less massive and encrusted cells less thickly. By Pliocene time, during Aragonite III, the prominent genus *Discoaster* secreted only narrow-rayed coccoliths that covered less than 25% of the cell surface. Also during Aragonite III, the aragonitic green alga *Halimeda* emerged as the dominant skeletal sediment producer in reef tracts. The influence of seawater chemistry on skeletal secretion appears to have been especially strong for morphologically simple taxa that exert relatively weak control over their own calcification. Such groups include algae, sponges, corals, and bryozoans. Morphological simplicity also permits these groups to adopt vegetative or colonial modes of growth that confer success in competition for space on reefs. This linkage, in addition to the basic chemical demands of hypercalcification, has given

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the Mg/Ca ratio of seawater strong control over the success of individual reef-building taxa. More generally, this ratio appears to have strongly influenced evolutionary changes in the skeletal mineralogy of sponges and cheilostome bryozoans throughout their history. We conclude that throughout Phanerozoic time a chain of causation has extended from mid-ocean ridge processes, via seawater chemistry, to the mineralogical and biological composition of reef communities and bioclastic carbonate deposits. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Sandberg (1983) divided the Phanerozoic Eon into three intervals when the primary mineralogy of ooids and early marine cements has been aragonitic and two intervals when it has been calcitic. In the present paper, expanding on earlier brief contributions (Hardie and Stanley, 1997; Stanley, 1997), we present evidence that the primary carbonate mineralogy of important reef-building and sediment-producing marine organisms correlates with these Phanerozoic oscillations for non-skeletal carbonates. In accordance with a model that Hardie (1996) applied to non-skeletal carbonates and marine evaporites, we interpret these oscillations in biomineralization as responses to secular variation in the Mg/Ca ratio and Ca^{2+} concentration of seawater driven by changes in sea-floor spreading rates. In this model high-Mg calcite precipitates inorganically along with aragonite when the Mg/Ca ratio is unusually high, as it is today (high-Mg calcite contains more than, and low-Mg calcite less than, 4 mole% MgCO_3 ; we will refer to low-Mg calcite simply as calcite). Being favored by the high Mg/Ca ratio of modern seawater, aragonite and high-Mg calcite both precipitate today, with aragonite being favored over high-Mg calcite at relatively high temperatures (Füchtbauer and Hardie, 1976, 1980; Morse et al., 1997).

In the 1970s it was suggested that during the Phanerozoic Eon a single transition from 'calcite seas' to 'aragonite seas' occurred, either in the Cenozoic Era (Sandberg, 1975) or Carboniferous Period (Milliken and Pigott, 1977). Wilkinson (1979) argued for a corresponding one-time shift in the prevailing mineralogy of carbonate-secreting marine organisms, based on the relative diversities and biomasses of various taxa. His data were highly generalized and incomplete, however, and some were in error. For example, he failed to include data for

sponges or pre-Jurassic dasycladacean algae. Also, contrary to his assessments, many modern bryozoans secrete aragonite rather than high-Mg calcite (Rucker and Carver, 1969); tetracorals secreted calcite (Sorauf, 1978), not high-Mg calcite; and many mollusk shells are not entirely, or even mostly, aragonitic (Carter, 1980). Furthermore, in analyzing mineralogical data, Wilkinson did not consistently distinguish between calcitic and Mg-calcitic taxa. To subsequent workers, post-Cambrian skeletal trends have not seemed readily apparent, in part because various members of some large taxa, such as the Mollusca, have secreted aragonite, calcite, or both of these minerals since early in the Paleozoic (Lowenstam and Weiner, 1989, p. 237).

In our study we have adopted two strategies to search for trends. First, we have focused on taxa that exemplify *hypercalcification*, which we define as (1) production of exceptionally massive skeletons by certain species of a higher taxon, or (2) rampant skeletal productivity by entire populations, such as ones contributing to massive reef growth or voluminous sediment production. The rationale here is that organisms capable of secreting skeletons that are not in thermodynamic equilibrium with seawater may nonetheless require favorable seawater chemistry in order to hypercalcify. Modern hermatypic corals illustrate this point with respect to CO_2 . They can survive outside the tropics, and they can survive in the tropics without symbiotic algae in their tissues. In order to produce massive reefs, however, they require tropical temperatures and symbiotic algae, both of which reduce concentrations of CO_2 . Thus, we have hypothesized that aragonitic corals also require a high Mg/Ca ratio in seawater in order to form massive reefs.

As a second strategy, we have focused on taxa that exert only weak control over their calcification. Many of these taxa exhibit low levels of biologi-

cal organization. An extreme example would be an organism that simply induces precipitation by removing CO₂ from neighboring seawater. The importance of biological complexity is seen in the effect of temperature on the Mg content of skeletal calcite in today's oceans. In many taxa Mg content increases with temperature, as it does for inorganically precipitated calcite (Füchtbauer and Hardie, 1976, 1980; Morse et al., 1997), but partition coefficients vary among taxa, and the effect of temperature is strongest for biologically simple organisms (Chave, 1954). Because competition for space is especially severe on reefs (Fagerstrom, 1987, pp. 113–116), rapid growth is at a premium; this condition favors simple taxa, such as sponges, corals, and algae, which can spread rapidly by means of colonial budding or indeterminate vegetative growth. This rationale strengthens the likelihood that reef communities might exhibit mineralogical trends corresponding to those of non-skeletal carbonates.

We have not attempted in this paper to explore how changes in seawater chemistry might have triggered the initial, Cambrian evolution of phosphatic (Cook and Shergold, 1984) or calcitic (Kazmierczak and Degens, 1986; Kempe and Kazmierczak, 1994) invertebrate skeletons or might have influenced secular changes in the overall rate of carbonate productivity by marine organisms (Kazmierczak et al., 1985; Riding, 1992, 1993). Neither have we attempted to relate seawater chemistry to sudden extinction, as Masse (1989) did in invoking sudden changes in dissolved CO₂, dissolved O₂, and the Mg/Ca ratio of seawater to explain an abrupt disappearance of many species of aragonitic foraminifera, calcareous algae, and rudists from the Mediterranean region in mid-Aptian time. In this regard, the Hardie model predicts that major changes in seawater chemistry occur over time periods on the order of 10 million years, making it unlikely that a change in the Mg/Ca ratio of seawater could have contributed to a sudden event that was confined to the middle of a single stratigraphic age. Before employing the strategies described above to analyze mineralogical changes in biological calcification during the Phanerozoic, we will review models that have been advanced to explain the mineralogy of non-skeletal carbonates.

2. Factors controlling the mineralogy of non-skeletal carbonates

When Sandberg (1975) originally proposed that the mineralogy of ancient oolites underwent a single shift from calcite to aragonite during the Phanerozoic Eon, he suggested that this shift was caused by an increase in the Mg/Ca ratio of seawater during the Mesozoic that resulted from the rise of calcareous nannoplankton and planktonic foraminifera, which by secreting calcitic skeletons caused selective removal of calcium ions from the oceans (see also Folk, 1974, p. 47).

On the basis of more extensive data on ancient marine oolites and early marine cements, Sandberg (1983) later abandoned the idea of a single shift in the mineralogy of these non-skeletal carbonates. He showed that the Phanerozoic Eon could instead be divided into two aragonite-inhibiting episodes or 'calcite seas' (Cambrian to Late Mississippian and Late Triassic/Early Jurassic to Early/Middle Cenozoic) and three aragonite-facilitating episodes or 'aragonite seas' (Late Precambrian to at least Early Cambrian, Late Mississippian to Late Triassic/Early Jurassic, and early/middle Cenozoic to the present). On the basis of this oscillating pattern (Fig. 1) Sandberg ruled out plankton-driven changes in the Mg/Ca ratio of seawater as a control. Instead, following Mackenzie and Pigott (1981), he speculated that the observed mineralogical oscillations were mainly the result of tectonically induced changes in atmospheric *p*CO₂. The rationale for this explanation was that first-order sea level changes driven by sea-floor spreading correlate with Sandberg's calcite sea–aragonite sea oscillations and with the 'icehouse–greenhouse' cycles of Fischer (1981, 1982): when MOR activity was high, global sea level and atmospheric *p*CO₂ would have been high, and 'greenhouse' conditions would have prevailed. This mechanism has remained the favored explanation for calcite sea–aragonite sea oscillations (see, for example, Sandberg, 1985; Wilkinson and Algeo, 1989; Mackenzie and Morse, 1992; Hallock, 1997).

One problem with the CO₂ model is that the rate of ocean crust production does not appear to be of first-order importance in the control of atmospheric *p*CO₂ (Bernier, 1994). There are also more fundamental problems with this model, as outlined below.

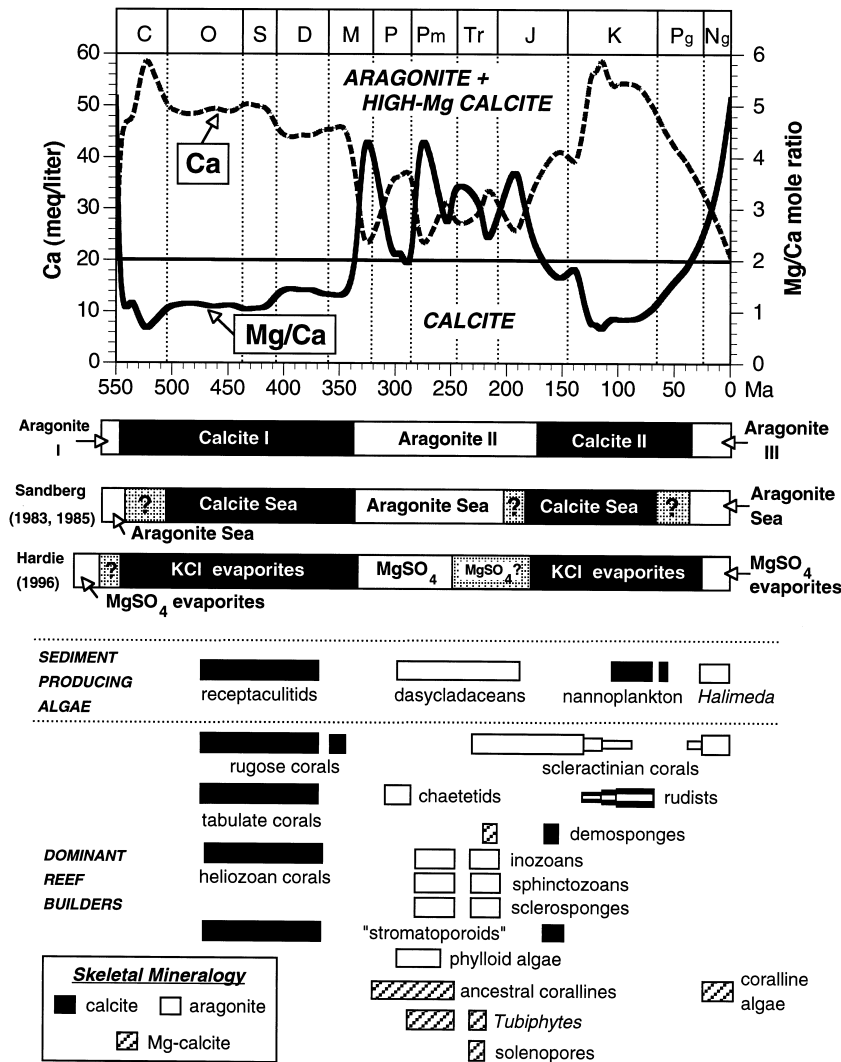


Fig. 1. Comparison of the temporal distribution of taxa in roles as major reef builders and sediment producers (this study) with the temporal distributions of non-skeletal carbonates (Sandberg, 1983) and of periods when seawater should have precipitated calcite or aragonite + high-Mg calcite (Calcite I through Aragonite III) according to the Hardie model for the secular variation in the Mg/Ca ratio and Ca concentration in seawater at 25°C (updated version of Hardie, 1996, see text). The boundary between the nucleation fields of low-Mg calcite and aragonite + high-Mg calcite is shown in the plot as a horizontal line at Mg/Ca = 2 (see Fig. 1B). Also shown are the temporal distributions of KCl and MgSO₄ marine evaporites in the geologic record, which correlate, respectively, with those of calcitic and aragonitic non-skeletal carbonates; oscillations in these types of evaporites closely match those predicted from estimates of spreading rates and the effects of these rates on seawater chemistry (Hardie, 1996).

2.1. Inadequacies of the CO₂ model

Sandberg (1983, p. 589) suggested that "elevated $p\text{CO}_2$ would not only lower the CO_3^{2-} concentration but could perhaps also produce a marine system below aragonite saturation, but still supersaturated

with respect to calcite." Using the computer program PHRQPITZ (Plummer et al., 1988) to calculate the equilibrium solubilities of low-Mg calcite and aragonite in modern seawater as a function of $p\text{CO}_2$ at Earth surface temperatures, we confirm that Sandberg's suggested scenario is theoretically possible,

but only for an extremely narrow range of carbon dioxide partial pressures that are an order of magnitude greater than today's value. Specifically, modern seawater at 25°C should become undersaturated with respect to aragonite but supersaturated with respect to low-Mg calcite only within the range of $p\text{CO}_2$ between $10^{-2.53}$ and $10^{-2.73}$ atm (for comparison, the present level is $10^{-3.5}$ atm; see also Morse et al., 1997, p. 87). At CO_2 pressures below this range seawater would be supersaturated with respect to both aragonite and low-Mg calcite (as it is today), and above this range seawater would be undersaturated with respect to both minerals (a situation that obviously has not occurred during the Phanerozoic). Three basic problems with the CO_2 model emerge from this analysis and related considerations.

(1) For changes in atmospheric CO_2 to be the principal factor that determines when low-Mg calcite would be favored in seawater with today's chemical composition, the values of atmospheric $p\text{CO}_2$ not only would have to fit into a very small window but they would have to be an order of magnitude higher than today's value. However, estimates both from computer modeling (Berner, 1997) and from isotopic evidence from marine biomarkers (Freeman and Hayes, 1992) and pedogenic carbonates (Ehrlinger and Cerling, 1995) point to levels of atmospheric $p\text{CO}_2$ at most twice that of the present for Late Cretaceous and early Cenozoic time, a period characterized by calcite seas.

(2) To produce calcite seas, levels of $p\text{CO}_2$ would have had to be so high that aragonitic skeletons, such as those of ammonites and gastropods, would have undergone rapid postmortem dissolution. Even for live animals, external shell surfaces unprotected by periostracum would have begun to dissolve immediately after forming. Clearly this did not happen in the calcite seas of Late Cretaceous and early Cenozoic time.

(3) The $p\text{CO}_2$ -driven model for aragonite–calcite oscillations is not supported by experimental work on nucleation of calcitic phases from natural seawater (Mg/Ca mole ratio = 5.17) under elevated CO_2 partial pressures. For example, Burton and Walter (1991, table 1) have shown that high-Mg calcite rather than calcite nucleates at CO_2 partial pressures as high as $10^{-1.0}$ atm. The effect of an increase in $p\text{CO}_2$ from $10^{-4.5}$ to $10^{-1.0}$ atm at 25°C is only to

lower the MgCO_3 content of the nucleated high-Mg calcite from 12 to 7 mole% MgCO_3 . These experimental data indicate that high-Mg calcite and not calcite should be precipitated from warm shallow calcite seas under the conditions imposed by the $p\text{CO}_2$ -driven model, a prediction not consistent with the calcite mineralogy of ancient oolites and early cements that characterize Sandberg's episodes of calcite seas.

2.2. Empirical evidence that the Mg/Ca ratio controls carbonate mineralogy

It has long been recognized from experimental studies that elevated concentrations of Mg^{2+} in aqueous solutions cause aragonite and/or high-Mg calcite rather than calcite to precipitate (Berner, 1975). Following proposals by earlier workers such as Lippman (1960), Folk (1974) suggested that if the Mg/Ca ratio of an aqueous solution is greater than 2 by weight, then aragonite will precipitate instead of low-Mg calcite (and vice versa if the ratio is <2), with the exact value varying with unspecified "temperature and other conditions." In support of this suggestion, Folk pointed to the findings of Müller et al. (1972) on the formation of alkaline earth carbonates in modern saline lakes. Müller et al. (1972) proposed that for surface lake waters with an Mg/Ca wt. ratio <2 (mole ratio <3.3) only low-Mg calcite would precipitate, but for lake waters with Mg/Ca wt. ratio >2 either a mixture of aragonite + high-Mg calcite (Mg/Ca wt. ratio $>2 <12$) or aragonite (Mg/Ca wt. ratio >12) would form (Fig. 2A).

In a series of laboratory experiments on the system $\text{MgCl}_2\text{--CaCl}_2\text{--Na}_2\text{CO}_3\text{--H}_2\text{O}$, Füchtbauer and Hardie (1976, 1980) showed that the kind and composition of alkaline earth mineral that nucleated and grew from supersaturated solutions depended on (1) the Mg/Ca ratio of the solution, (2) the ionic strength of the solution, and (3) the temperature (Fig. 2B). Comparison of Fig. 2A and 2B demonstrates an excellent agreement between the experimentally determined mineral synthesis fields in Mg/Ca–salinity space and those of Müller et al. (1972) based on data from natural saline lakes. In the important region of the calcite–aragonite + high-Mg calcite boundary at the salinity of seawater, the natural data cited by Müller et al. (1972) are sparse and lack tempera-

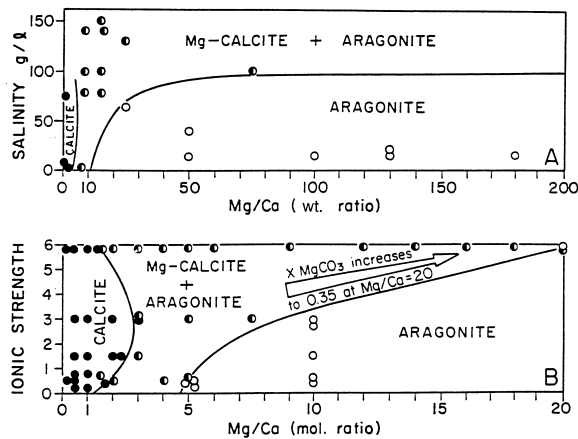


Fig. 2. Comparison of natural and laboratory data for the nucleation fields of aragonite, high-Mg calcite, and calcite at typical surface temperatures and pressure (from Hardie, 1987, fig. 3). (A) Salinity–Mg/Ca ratio relations in modern natural lake waters precipitating aragonite, Mg-calcite and calcite (data from Müller et al., 1972). (B) Ionic strength–Mg/Ca ratio relations in $\text{MgCl}_2\text{--CaCl}_2\text{--Na}_2\text{CO}_3\text{--H}_2\text{O}$ solutions precipitating aragonite, high-Mg calcite, and calcite under laboratory conditions at 28°C, 1 atm total pressure and atmospheric $p\text{CO}_2$ (based on unpublished data of Füchtbauer and Hardie, 1976). This diagram yields a value of Mg/Ca mole ratio ~ 2 (± 0.5) for the boundary between the calcite and the aragonite + high-Mg calcite nucleation fields for chloride solutions with the ionic strength of modern seawater ($I = 0.7$).

ture measurements. Therefore, in the present study we have used the value of Mg/Ca mole ratio = 2 for the calcite–aragonite + high-Mg calcite boundary derived from the more extensive experimental results of Füchtbauer and Hardie at seawater ionic strengths and 28°C (Fig. 2B; see also Rushdi et al., 1992, p. 577, who found that “low-magnesium calcite is favored at $\text{Mg} : \text{Ca} < 2$ ”). From their experimental results, Füchtbauer and Hardie (1976, 1980) also calculated the homogeneous coefficients for distribution of Mg and Ca between modern seawater and Mg-calcites at temperatures from 4° to 50°C. These coefficients indicated that high-Mg calcite cements precipitated from modern seawater should have about 12 mole% MgCO_3 at 25°C and 4 mole% MgCO_3 at 6°C, in close agreement with natural cements in warm shallow shelves and cool deep sea floors, respectively (Demico and Hardie, 1994, fig. 136).

Although the Füchtbauer–Hardie experiments involved kinetically driven and not reversible equilib-

rium reactions, their ability to duplicate the behavior of both saline lake precipitates and marine cements lends powerful support to the conclusion that at a given temperature Mg/Ca ratio is the major control over which alkaline earth carbonate minerals will precipitate. A recent study supports this conclusion: using a different experimental approach from that of Füchtbauer and Hardie, Morse et al. (1997) have shown that for any given temperature in the range 6° to 35°C, the Mg/Ca ratio of the solution determines whether aragonite or low-Mg calcite will precipitate, with high Mg/Ca ratios and high temperatures favoring aragonite and vice versa for calcite. Rather than assigning atmospheric $p\text{CO}_2$ the major role in determining the mineralogy of non-skeletal carbonates during the Phanerozoic (Mackenzie and Morse, 1992), Morse et al. (1997, p. 87) have concluded that “the results of this, and other recent studies, support the hypothesis that the chemistry of seawater varied substantially during the Phanerozoic.”

3. A model for secular variation in seawater chemistry

Hardie (1996) showed that Sandberg’s oscillating episodes of aragonite and calcite seas coincide with secular changes in the mineralogy of marine potash evaporite deposits during the Phanerozoic Eon (Fig. 1). Furthermore, the explanation for the coupled mineralogical oscillations must be sought in changes in the major ion chemistry of seawater rather than changes in atmospheric $p\text{CO}_2$ because, quite apart from the deficiencies of the CO_2 model described above, $p\text{CO}_2$ does not influence the essential mineralogy of marine evaporites.

Spencer and Hardie (1990) showed that the composition of modern seawater can be accounted for by steady-state mixing of the two major contributors to ocean chemistry, river water (RW) and hydrothermal brines of mid-ocean ridges (MOR), coupled with precipitation of solid CaCO_3 and SiO_2 phases. They presented a simple quantitative model for calculation of the chemistry of ancient seawater based on the MOR/RW flux ratio. The most significant prediction of the model is that relatively small changes in the MOR flux can lead to changes in the Mg/Ca, Na/K, and Cl/ SO_4 mole ratios of seawater that

would drastically alter the primary mineralogy of marine evaporites and limestones.

Hardie (1996) further proposed that secular changes in seawater chemistry have occurred as a result of secular variation in the flux of mid-ocean ridge (MOR) hydrothermal brines driven by secular variation in the rate of ocean crust production. Mid-ocean ridges operate as huge ion exchange systems where conversion of basalt to greenstone releases Ca^{2+} to seawater and removes Mg^{2+} . Increases in the rate of ocean crust production therefore lowers the Mg/Ca of seawater, while at the same time increasing the concentration of Ca^{2+} .

Based on the experimental work of Füchtbauer and Hardie (1976, 1980) (see Fig. 2B), Hardie (1996) predicted that in seawater at 25°C when the Mg/Ca mole ratio is greater than about 2, aragonite + high-Mg calcite would precipitate and when Mg/Ca is <2, low-Mg calcite would precipitate. Thus, during periods when rates of ocean crust production were high (as during the Mid-Cambrian through mid-Mississippian and Mid-Jurassic through early Paleogene intervals; Hardie, 1996, fig. 2), the Mg/Ca ratio would have been low and low-Mg calcite, rather than aragonite, would have been the non-skeletal carbonate precipitate. Conversely, when the rates of ocean crust production were low (as during the mid-Mississippian through Mid-Jurassic and late Paleogene to the present), Mg/Ca ratio would have been high and aragonite + high-Mg calcite would have precipitated (with the MgCO_3 content of the high-Mg calcite controlled by the Mg/Ca ratio of seawater; see Füchtbauer and Hardie, 1976). As shown in Fig. 1, this quantitative model predicts temporal oscillations in calcite seas and aragonite seas that closely match Sandberg's (1983) two aragonite-inhibiting episodes (calcite seas) and three aragonite-facilitating episodes (aragonite seas) during the Phanerozoic Eon. The Mg/Ca and Ca^{2+} curves shown in Fig. 1 are based on a new set of calculations by L.A. Hardie (in prep.) using an improved method for predicting ancient seawater compositions by mixing MOR hydrothermal brine and river water; the Mg/Ca and Ca^{2+} values shown in Fig. 1 supersede the values given originally in Hardie (1996). Note, however, that the aragonite sea–calcite sea episodes predicted by these new calculations (Fig. 1) are little changed from those of Hardie (1996, fig. 4).

Phanerozoic potash evaporite deposits, like non-skeletal limestones, show well-defined secular variation in their mineralogies (Hardie, 1996), oscillating between intervals when the characteristic minerals of the late stages of evaporation are MgSO_4 minerals (such as kieserite, $\text{MgSO}_4 \cdot \text{H}_2\text{O}$, and polyhalite, $2\text{CaSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 2\text{H}_2\text{O}$) and intervals when instead the characteristic minerals are KCl salts (such as sylvite, KCl). It is of special significance that the secular oscillations in potash evaporite mineralogy occur *in phase* with the oscillations for non-skeletal carbonate mineralogy: periods of aragonite seas are synchronized with MgSO_4 evaporites, while periods of 'calcite seas' are synchronized with KCl evaporites, as illustrated in Fig. 1. This synchronicity is predicted by the Hardie model (see Hardie, 1996). For example, increased rates of ocean crust production, such as occurred during the Cretaceous, leads to an increase in MOR/RW flux ratio, which in turn increases the global seawater concentration of K along with that of Ca, while lowering the concentration of SO_4 along with that of Mg. These chemical changes simultaneously favor KCl evaporites over MgSO_4 evaporites and calcite over aragonite + Mg-calcite (Mg/Ca and SO_4/Ca ratios low). The reverse is true for periods, such as the present, when the overall rate of ocean crust production is low; then Mg/Ca and SO_4/Ca ratios are high and MgSO_4 evaporites are favored over KCl evaporites, while aragonite + Mg-calcite is favored over calcite. The ability of the model to predict the synchronous secular changes in the mineralogies of both non-skeletal limestones and marine potash evaporites suggests that the basic tenets of the hypothesis are correct.

In the present paper we show that oscillations in the carbonate mineralogy of hypercalcifying organisms, like the oscillations in non-skeletal carbonates, correlate with the secular changes in the Mg/Ca ratio of seawater predicted by the Hardie (1996) model. We refer to the three intervals of aragonite seas as Aragonite I, II, and III and the two intervening intervals of calcite seas as Calcite I and II (Fig. 1).

4. Caveats for analysis of hypercalcification

Because temperature influences mineralogy in alkaline earth carbonate precipitation (Füchtbauer and

Hardie, 1976, 1980; Morse et al., 1997) and because hypercalcification is primarily a phenomenon of warm seas, our analysis is restricted to warm-adapted taxa. In addition, we adopt the following premises.

(1) Mineralogical patterns for hypercalcifying taxa may correlate with those for non-skeletal carbonates but need not have shifted precisely in concert with them: organically precipitated carbonates need not be in equilibrium with seawater.

(2) Biogenic precipitation of aragonite and high-Mg calcite in calcite seas should be less difficult than biogenic secretion of calcite in aragonite seas because the high absolute concentration of Ca^{2+} in calcite seas (Fig. 1) enhances supersaturation with respect to all three minerals.

(3) Skeletal aragonite offers stronger evidence of secular trends in hypercalcification than high-Mg calcite, for the following two reasons. First, by expelling Mg diagenetically without obvious evidence of recrystallization, high-Mg calcite can masquerade as primary calcite with a low Mg content. Second, taxa that today secrete high-Mg calcite may have incorporated less Mg into their skeletons at times when the Mg/Ca ratio was lower than it is today, just as they do in modern seas at relatively low temperatures (Chave, 1954); as a result of such flexibility, reductions in the Mg/Ca ratio of seawater may have affected rates of calcification less strongly in these taxa than in aragonitic taxa.

(4) The model used to determine the Mg/Ca curve for seawater shown in Fig. 1 is based on several simplifying assumptions (Spencer and Hardie, 1990; Hardie, 1996). Uncertainties introduced by these assumptions, together with the uncertainties in Füchtbauer and Hardie's experimental data (Fig. 2B), could lead to errors in the prediction of mineralogy during those times when the calculated Mg/Ca value is close to 2 (Fig. 1).

5. Sediment production

Van de Poel and Schlager (1994, p. 45), having assessed likely primary mineralogies for a large sample of skeletal limestones, detected a "not dramatic, yet clearly recognizable" mineralogical correspondence between skeletal and non-skeletal carbonates for the

Mesozoic–Cenozoic interval. They were, however, unable to decide whether their results pointed to a major Mesozoic excursion toward calcite secretion or depicted a second-order shift imbedded in a general Phanerozoic trend for prevailing skeletal mineralogy from calcite to aragonite (Wilkinson, 1979). We suggest that Van de Poel and Schlager uncovered a relatively weak pattern because their study included skeletal remains of taxa, such as foraminifera and mollusks, for which calcification is not strongly linked to seawater chemistry. Our data for hypercalcifying taxa, including calcareous nannoplankton, a group not included in the study of Van de Poel and Schlager, do not show a persistent Phanerozoic shift from calcitic to aragonitic skeletal mineralogy. Instead, the mineralogy of hypercalcifying carbonate sediment producers has oscillated along with the mineralogy of non-skeletal carbonates since at least the Ordovician Period.

5.1. Chalk deposition

The widespread occurrence of thick chalk deposits in the Upper Cretaceous has long seemed problematic. More than 40 genera of calcareous nannoplankton existed during Early Cretaceous time (Tappan, 1980, p. 773), but widespread deposition of massive chalk did not begin until early in the Late Cretaceous. This occurrence cannot be attributed simply to the presence of broad shallow seas, because such seas also existed in Early Cretaceous time. Maximum productivity for modern coccolithophores occurs where supersaturation with respect to calcium carbonate is greatest (Tappan, 1980, p. 223). This pattern suggests an important role for seawater chemistry in the biomineralization of coccolithophores, a conclusion supported by evidence that in laboratory cultures an increase in the concentration of dissolved calcium enhances calcification by this group (Blackwelder et al., 1976). Significantly, widespread deposition of massive coccolith chalk occurred in the Cretaceous only after the absolute concentration of Ca^{2+} in seawater had reached a very high level and the Mg/Ca ratio, a very low level (Fig. 1). Three additional facts support the idea that the shift in seawater chemistry permitted chalk deposition.

(1) Although the terminal Cretaceous extinction severely reduced the productivity of calcareous

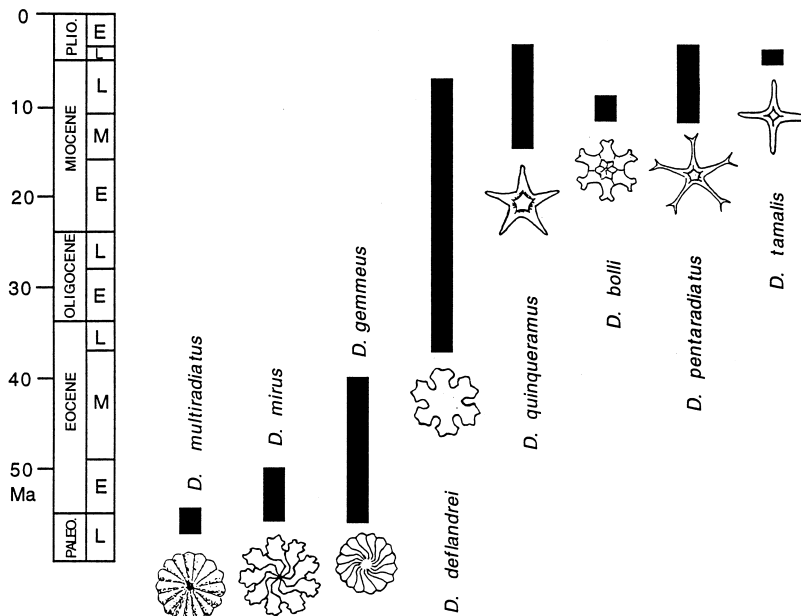


Fig. 3. Coccoliths of *Discoaster* species for various Cenozoic intervals illustrating the general trend toward less robust morphologies (not to scale). After Houghton (1991, fig. 10 a–p) with stratigraphic ranges partly from Martini and Müller (1986).

nannoplankton (Percival and Fischer, 1977), chalk deposition resumed early in the Paleocene, when the Mg/Ca ratio of seawater remained low and Ca^{2+} concentration high late in the Calcite II episode (Fig. 1).

(2) After the Early Paleocene there was a global decline in chalk production despite global climatic warming during the Early Eocene (Wolfe, 1978) and marked evolutionary diversification of calcareous nannoplankton (Tappan, 1980, p. 772). This decline coincides with a progressive rise in the Mg/Ca ratio of seawater and a concomitant fall in the Ca^{2+} concentration (Fig. 1). While it is true that bathyal chalks accumulated off New Jersey during Early Eocene time (Aubry et al., 1996), these local deposits do not appear to be typical of overall chalk production during the Eocene. Significantly, massive chalk deposits have not accumulated during the Oligocene–Holocene interval, when seawater Mg/Ca ratio has been very high and Ca^{2+} concentration very low — conditions that strongly favor aragonite + high-Mg calcite over calcite (Fig. 1).

(3) the Cenozoic has been marked by a polyphyletic trend toward reduced shell volume for individual coccoliths (Houghton, 1991). During the Pale-

ocene and Eocene, for example, the genus *Discoaster* included species whose coccoliths were thick-rayed and often bore large central knobs, but by the Late Pliocene *Discoaster* secreted only narrow-rayed coccoliths that covered less than 25% of spheroidal cell surfaces (Bukry, 1971; Houghton, 1991) (Fig. 3). More generally, coccoliths underwent a pronounced polyphyletic decline in average size during the Cenozoic, leaving cells of Neogene species thinly encrusted (Bukry, 1971; Houghton, 1991). We suggest that the pervasive Cenozoic trend for nannoplankton toward reduced calcification resulted from the dramatic rise of the Mg/Ca ratio and decrease in the absolute concentration of Ca^{2+} that occurred between Paleocene time and the present (Fig. 1). The correlation of decreasing Ca^{2+} concentration and reduction in the areal coverage and thickness of coccoliths on cell surfaces is consistent with results of laboratory experiments on in vivo coccolithophore cultures. Blackwelder et al. (1976) found that at low Ca^{2+} concentrations (10^{-3} – 10^{-4} M) decalcified live cells failed to develop skeletons, but when the Ca^{2+} concentration was raised to 10^{-2} M over 75% of the cells grew coccoliths within 24 h and almost 100% were recalcified in 2 days or less.

Secretion of massive individual coccoliths in the Cretaceous and Paleocene can be viewed as hypercalcification on a unicellular scale dictated by the Mg/Ca ratio and the Ca^{2+} concentration of seawater. Secretion of low-volume coccoliths later in the Cenozoic is an evolutionary analog of osteoporosis in vertebrate animals.

5.2. Green algae

Because calcareous green algae only weakly control their mineralization or simply induce it by modifying the chemistry of neighboring seawater (Lowenstam and Weiner, 1984, p. 27), we might expect their productivity to have been strongly affected by secular changes in seawater chemistry. Indeed, aragonitic codiaceans have been conspicuous rock formers only during Aragonite III. Outstanding examples are *Halimeda*, which contributes, on average, 25–30% of the recognizable skeletal grains in Neogene reefal lagoons (Hillis-Colinvaux, 1980), and *Penicillus*, a major producer of aragonite needle mud in present-day shallow subtidal environments.

Aragonitic dasycladaceans are sporadically abundant in rock units ranging back to the Ordovician (Johnson and Sheehan, 1985), but they became major rock formers through contribution of recognizable grains only late in the Paleozoic (early in Aragonite II) (Flügel, 1977; Madi et al., 1996). The highest productivity of dasycladaceans was early in the Mesozoic; in fact, they are viewed as the rock-forming equivalents of *Halimeda* for the Triassic (Elliott, 1984). Dasycladaceans remained moderately abundant during the Jurassic and Early Cretaceous but were less common during the Late Cretaceous (Mu, 1993), when the Mg/Ca ratio of seawater was at its lowest Phanerozoic level (Fig. 1).

Receptaculitids, which are generally regarded as green algae (Rietschel, 1977), secreted massive skeletons that are very well preserved, a textural characteristic that points strongly to an original calcite mineralogy. Receptaculitids were restricted to the Ordovician–Devonian interval and, in contrast to the aragonitic dasycladaceans, flourished in reef and near-reef settings throughout this Calcite I interval (Byrnes, 1968; Alberstadt and Walker, 1976).

5.3. Paleozoic bryozoans

Paleozoic trepostome and cystoporate bryozoans appear to illustrate the hypercalcification of individual colonial skeletons in response to a favorable Mg/Ca ratio in seawater, followed by a decline in productivity when the Mg/Ca ratio became unfavorable. Heavily calcitic ('stony') trepostome and cystoporate bryozoans abounded only from Ordovician to Devonian time (Calcite I). They were major rock formers during the Ordovician Period, and their robust colonies are the most abundant megafossils in some Ordovician strata (Boardman and Cheetham, 1987, p. 517). These taxa persisted into Aragonite II but were relatively inconspicuous, while the fenestrates and cryptostomates became the most prominent bryozoans of warm shallow shelves. These latter groups were much less heavily calcified calcitic groups, typically forming delicate dendroid, bifoliate, reticulate, or pinnate colonies (Boardman and Cheetham, 1987, pp. 517–518).

6. Reef building

There is a striking correspondence between the mineralogy of productive reef builders and that of non-skeletal carbonates throughout the last 450 million years (Fig. 1). Elements of this pattern have been noted by Van de Poel and Schlager (1994), Hallock (1997), Hardie and Stanley (1997), and Stanley (1997).

6.1. Calcite I

Because taxa of uncertain taxonomic affinities and mineralogical composition (e.g. archaeocyathids, *Renalcis*, *Epiphyton*, etc.) played major roles in early Paleozoic reef building (Fagerstrom, 1987, pp. 325–542), we will begin our analysis with reefs of Late Ordovician age. From this time until the mid-Mississippian, the dominant reef builders of Calcite I were all calcitic: tabulate, heliolitid, and rugose corals (Oliver and Coates, 1987) and stromatoporoid sponges. It has been suggested that stromatoporoids secreted aragonite (Stearn, 1966), but their skeletal microarchitecture is typically much better preserved than that of co-occurring taxa known originally to have been

aragonitic. This pattern points to an originally calcitic mineralogy (Wood, 1987), as does the fact that Paleozoic stromatoporoids are seldom preserved as molds.

No frame-building reef community emerged immediately after the Late Devonian mass extinction. However, colonial rugosans resumed their reef-building role in the Visean (Fagerstrom, 1994), during the final Paleozoic pulse of conspicuous calcitic reef construction. Soon thereafter, seawater chemistry shifted far into the aragonite regime (Fig. 1).

6.2. Aragonite II

Ancestral coralline algae, presumed to have secreted high-Mg calcite like that of modern corallines, expanded ecologically at about the time of the Late Mississippian shift to aragonite seas. This group and related forms became important reef builders and rock formers, constituting up to 50% by volume of many Pennsylvanian facies (Wray, 1977). Aragonitic phylloid algae also became major elements in large reefs (Wray, 1977; Flügel, 1977). Playing a lesser role were chaetetid sponges. The typically poor microstructural preservation of these forms (West and Clark, 1984) points to an original aragonitic composition, and, in fact, Permian chaetetid colonies have been found preserved as primary aragonite (Wendt, 1977). A brief dip of the Mg/Ca ratio of seawater during the latter half of the Pennsylvanian Period produced no obvious biotic response (Fig. 1), probably because (1) the ratio remained near the limit for aragonite seas, and (2) as noted earlier, high absolute levels of Ca^{2+} in calcite seas may have weakened the negative impact of the low Mg/Ca ratio on precipitation of aragonite and high-Mg calcite.

During Permian time, sphinctozoan and, to a lesser extent, inozoan sponges became significant aragonitic reef builders throughout the Tethyan region (Flügel and Reinhardt, 1989; Toomey, 1991). Joining them was *Tubiphytes*, an alga inferred to have secreted high-Mg calcite (Senowbari-Daryan and Flügel, 1991). Although calcitic frondose bryozoans were important scaffold builders in Late Permian reefs, they were volumetrically minor (Wood et al., 1996). Significantly, although various colonial rugose corals also occupied Late Permian reefs, these calcitic forms were minor frame builders (Weidlich and Flügel, 1995).

As a result of the terminal Permian mass extinction, reefs are unknown from Lower Triassic rocks. When reef building resumed in Middle Triassic time, aragonitic sphinctozoan and inozoan sponges again played a prominent role (Flügel and Stanley, 1984); inozoans and other Triassic reef builders thought to have been sclerosponges have been preserved as original aragonite (Veizer and Wendt, 1976). In addition, the Late Triassic hermatypic demosponge *Cassiathalamia* exhibits a microstructure that seems to reflect original high-Mg calcite mineralogy (Reitner, 1987). Also contributing to Triassic reefs were calcitic bryozoans of unknown magnesium content and *Tubiphytes* and solenoporacean red algae (Senowbari-Daryan et al., 1993), both considered to have secreted high-Mg calcite. This predominantly aragonitic and high-Mg calcitic reef community persisted into the Late Triassic, when it was progressively augmented by aragonitic scleractinian corals (Stanton and Flügel, 1987; Bernecker, 1996). The terminal Triassic mass extinction interrupted reef growth, and scleractinian corals then dominated the earliest (Sinemurian) reef known from the Jurassic (Stanley and McRoberts, 1993).

6.3. Calcite II

Significantly, hermatypic demosponges that apparently secreted calcite appeared in the marginally calcitic seas of the Late Jurassic early in Calcite II (Gautret and Cuif, 1989). In addition, calcitic sponges that are loosely termed stromatoporoids (Wood, 1987) suddenly emerged as major reef builders in Late Jurassic time (Wendt, 1980; Fagerstrom, 1987, pp. 413–415). Nonetheless, aragonitic coral reefs remained widespread on shallow shelves after the Mid-Jurassic shift to calcite seas (siliceous sponges were dominant reef builders in deeper habitats) (Leinfelder et al., 1994). Several factors may explain the persistence of aragonitic reefs: (1) until Cretaceous time, the Mg/Ca ratio remained near the minimum level for aragonite seas (Fig. 1); (2) the elevated concentration of Ca^{2+} in seawater may have reduced inhibition of aragonite secretion; (3) unusually warm Late Jurassic climates, which permitted reefs to develop even in northern Scotland (Leinfelder et al., 1994), should have favored all kinds of carbonate reef growth; (4) there may have been

no calcitic reef builders that could compete with corals.

During the Cretaceous Period, when the Mg/Ca ratio of seawater plunged to a very low level, rudists that were predominantly calcitic progressively displaced aragonitic corals as dominant reef builders. Rudists dominated some reefs by Hauterivian time (130 Ma) and attained general supremacy by the late Albian (100 Ma) (Scott, 1984; Kauffman and Johnson, 1988). As mollusks, which secrete skeletal material from pallial fluid, rudists were probably not strongly influenced by the Mg/Ca ratio of seawater. Thus, although the radiolitids, which were the dominant reef-building rudists during the final 30 million years of the Cretaceous (Kauffman and Johnson, 1988), were predominantly calcitic, their ascendancy was probably not a direct consequence of the mid-Cretaceous shift from aragonite to calcite seas. We suggest that the pivotal factor was a decline of the aragonitic corals resulting from the decrease in the Mg/Ca ratio of seawater; this opened the way for the rudists in the highly competitive reef environment. Supporting this idea is the fact that reef-building corals failed to recover until long after the Maastrichtian extinction of the rudists (Hallock, 1997; Hardie and Stanley, 1997; Stanley, 1997).

Coral reefs remained small and uncommon until Oligocene time, (S.F. Frost, pers. commun., 1997) despite the exceptional climatic warmth of the Early and Middle Eocene (Wolfe, 1978) and the existence of numerous hermatypic coral genera (Fagerstrom, 1987, p. 165). Interestingly, calcitic foraminifera with an encrusting growth habit built large Early Eocene reefs in the region of the modern Pyrenees (Plaziat and Perrin, 1992). Hallock (1997) suggested that high levels of atmospheric CO₂ promoted this development, but the dominance of calcitic reef builders is consistent with our Mg/Ca model.

6.4. Aragonite III

Paradoxically, luxuriant reefs emerged on a global scale during the Oligocene Epoch (Frost, 1977, 1981). Even after global climates had cooled markedly (Wolfe, 1978), Early Oligocene reefs flourished as far north as northern Italy (Bosellini and Russo, 1988). We suggest that, although the Mg/Ca ratio of seawater rose too high early in the Paleogene

for continued chalk deposition, it did not rise high enough to permit aragonitic reefs to flourish until early in Oligocene time.

During the Oligocene, coralline algae also began to form algal ridges along reef fronts and generally flourished as never before. These algae had begun to expand late in the Cretaceous and were relatively more successful than hermatypic corals during the Paleocene and Eocene (Ghose, 1977; Moussavian and Vecsei, 1995), perhaps because they incorporated less magnesium into their Mg-calcite skeletons than they do today.

7. Influence of seawater chemistry on evolution and extinction

It appears that changes in the Mg/Ca ratio of seawater not only influence hypercalcification by existing species but also guide patterns of evolution and extinction. It is possible that calcite seas promoted the initial evolution of calcite skeletons in tetracorals and tabulate corals and that aragonite seas later promoted the evolution of scleractinian corals. A single event of origination that fits the Mg/Ca model may represent mere coincidence, however. More compelling are polyphyletic changes in calcification for calcareous nannoplankton, sponges, and bryozoans, as outlined below.

7.1. Calcareous nannoplankton

The rising Mg/Ca ratio and declining absolute concentration of Ca²⁺ during the Cenozoic appear to have influenced both the evolution and extinction of calcareous nannoplankton. We suggest that this chemical change favored the evolutionary reduction of calcification by individual cells that is seen in two Cenozoic trends we have described: the progressive diminution of coccoliths, which reduced the total volume of calcite secreted by individual cells, and the general evolutionary transition in *Discoaster* from robust, circular coccoliths to star-shaped coccoliths with slender rays (Fig. 3). When *Discoaster* disappeared during the Pliocene, its composite external skeleton had been reduced from solid armor to a coarse mesh, which left more than 75% of the total surface area of the cell exposed to micropredators. This pattern of

change raises the possibility that increased predation pressure contributed to the demise of the genus.

7.2. Sponges

Sponge taxonomy and phylogeny are currently in a state of flux, and many traditionally recognized higher taxa appear to include clades in which skeletons of a particular kind arose polyphyletically (Wood, 1991). When new clades have appeared, however, their skeletons, whether inherited or newly evolved, have nearly always been of a mineralogy favored by the Mg/Ca ratio of seawater.

Noting that the mineralogy of demosponges appears to match that of non-skeletal carbonates for the Mesozoic–Cenozoic interval, Gautret and Cuif (1989) suggested that secular changes in seawater chemistry may have strongly influenced non-spicular calcification in this group. Additionally, Wood (1991) noted that the weak biological control that calcisponges exert over their skeletal secretion has likely given seawater chemistry a strong influence over their mineralization. She further noted the lability of calcisponges' mineralogy through time and, in particular, the emergence of aragonitic forms during Aragonite II. We concur with these authors' inferences and, in fact, conclude that throughout Phanerozoic time sponges have been at the mercy of the Mg/Ca ratio of seawater when evolving new kinds of carbonate skeletons. We have already noted the prominence of calcitic stromatoporoids during Calcite I before the ascendancy of several groups of aragonitic reef-building sponges during Aragonite II. Remarkably, hermatypic demosponges appear to have secreted high-Mg calcite during Aragonite II (Late Triassic; Reitner, 1987), whereas new taxa secreted calcite early in Calcite II (Late Jurassic; Gautret and Cuif, 1989). Furthermore, all known Cretaceous (Calcite II) sponges appear to have been calcitic, whereas in present-day aragonite seas all calcareous sponges — both calcisponges and demosponges — secrete aragonite, high-Mg calcite, or both of these minerals (Hartman, 1980).

7.3. Bryozoans

The dominant modern group of bryozoans, the cheilostomes, appeared during the Cretaceous Pe-

riod (Calcite II). All Cretaceous cheilostomes secreted calcite, with unknown quantities of magnesium; only a few anascans secreted a combination of calcite and aragonite (Boardman and Cheetham, 1987). Aragonitic cheilostomes did not proliferate until the Eocene (A.H. Cheetham, pers. commun., 1997), when the Mg/Ca ratio of seawater was rising toward the minimum level for aragonite seas. Today, when high-Mg calcite and aragonite are strongly favored by the high Mg/Ca ratio of seawater, most cheilostome species secrete high-Mg calcite, but in accordance with the temperature pattern for non-skeletal precipitation (Morse et al., 1997), many tropical species secrete aragonite. No modern marine bryozoan species is known to secrete calcite (Rucker and Carver, 1969). This striking pattern in modern seas supports the notion that changes in the Mg/Ca ratio of seawater have guided the evolution of skeletal mineralogy in cheilostomes.

8. Discussion and conclusions

The proposition that the Mg/Ca ratio and Ca^{2+} concentration of seawater have strongly influenced patterns of hypercalcification in many marine organisms gains strength from the fact that it connects many otherwise puzzling phenomena with a single explanation. These phenomena include:

- (1) the restriction of major reef building by calcitic taxa to Calcite I and Calcite II seas;
- (2) the comparable restriction of aragonitic reef-builders to Aragonite II and Aragonite III seas, or to calcite seas in which the Mg/Ca ratio approached that of aragonite seas and the concentration of Ca^{2+} was higher than in modern seawater;
- (3) the restriction of extensive rock forming by aragonitic green algae to Aragonite II (dasycladaceans) and Aragonite III (*Halimeda*), whereas calcitic receptaculitids flourished during Calcite I;
- (4) widespread deposition of massive chalk deposits during Late Cretaceous time, when the Mg/Ca ratio and concentration of Ca^{2+} in seawater were, respectively, at very low and very high levels;
- (5) the decline of aragonitic corals as reef builders during this same Late Cretaceous interval, and the simultaneous ascendancy in the highly competitive reef ecosystem of the rudists, which, as mollusks,

should not have been strongly influenced by the Mg/Ca ratio of seawater;

(6) following the Cretaceous mass extinction, the resumption of conspicuous chalk deposition early in the Paleocene, when the Mg/Ca ratio of seawater remained low;

(7) the failure of calcareous nannoplankton to produce widespread, massive chalk deposits during the Eocene Epoch, when climates were exceptionally warm and these algae were diversifying markedly; significantly, at this time the Mg/Ca ratio of seawater was rising and the Ca^{2+} concentration was falling;

(8) the general trend from the Paleocene to the present for calcareous nannoplankton toward production of low-volume coccoliths that have encrusted cells thinly or covered only a small fraction of cell surfaces — a trend that parallels the rise of the Mg/Ca ratio and the fall of the Ca^{2+} concentration in Cenozoic seawater;

(9) following the rudists' extinction, the failure of aragonitic reef corals to flourish until Oligocene time, when, although the global climate was cooler than during the Eocene, the Mg/Ca ratio of seawater rose substantially above its Eocene level;

(10) Phanerozoic oscillations in the mineralogy of sponge skeletons that correspond to the oscillations for non-skeletal carbonates;

(11) the abundance of calcitic stony bryozoans during Calcite I and their sparse representation during Aragonite II;

(12) the appearance of many aragonitic species of cheilostome bryozoans as the Mg/Ca ratio of seawater rose during the Cenozoic.

All of the taxa for which we have suggested linkage between biomineralization and seawater chemistry appear to have lacked the ability to remodel their skeletons through resorption. It would appear that these taxa have had only limited ability to regulate the chemical milieu in which their skeletons have formed. Though otherwise simple organisms, foraminifera are able to remodel their skeletons, and as Lowenstam and Weiner (1989, p. 670 noted, "their diversity in terms of basic modes of mineralization . . . is almost unparalleled". Two possible exceptions to the resorption rule, however, may be the reef-building *Solenomeris* foraminiferans of the Early Eocene (Plaziat and Perrin, 1992) and the huge, rock-forming nummulitid foraminiferans of

the same age. These were calcitic groups in calcite seas (Hallock, 1997).

Biological simplicity has endowed successful reef builders with the advantages that vegetative and colonial growth provide in competition for living space. This simplicity has also made these groups strongly dependent on seawater chemistry for their success. They can dominate reefs through hypercalcification when the Mg/Ca ratio is favorable, but they also suffer when the ratio is unfavorable: their productivity is unstable on long time scales. Taxa that engage in more sophisticated biomineralization cannot take full advantage of beneficial seawater chemistry in the same way, but all else being equal, the carbonate productivity of these groups, such as the Mollusca, has been more stable throughout the Phanerozoic.

For some taxa, trends in the Mg/Ca ratio of seawater appear to have controlled not only productivity but also evolution of biomineralization. Among sponges, for example, these trends seem to have favored the evolution of calcitic skeletons during some Phanerozoic intervals and aragonitic or high-Mg calcitic skeletons during others. In addition, a rising Mg/Ca ratio during the Cenozoic Era appears to have promoted the polyphyletic origins of aragonitic cheilostome bryozoan taxa and of progressively less robust calcitic coccoliths among calcareous nannoplankton.

Extinction has also contributed to the patterns we have described, but episodes of hypercalcification interrupted by mass extinction have resumed whenever seawater chemistry has not shifted significantly after the crisis and some hypercalcifying taxa have survived. This happened at the end of the Permian, for example. Clearly, taxonomic diversity has not been of first order importance in the biogenic carbonate productivity of particular groups of organisms.

We conclude that a chain of causation, leading from variable spreading rates at mid-ocean ridges through the chemistry of seawater to biocalcification, has profoundly influenced marine carbonate sedimentation and reef growth throughout Phanerozoic time.

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