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Hypercalcification: Paleontology Links Plate Tectonics and Geochemistry to Sedimentology

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ABSTRACT

During the Phanerozoic Eon, the mineralogies of nonskeletal marine cements and oolites have oscillated on a 100–200 m.y. scale between aragonite ± high-Mg calcite (aragonite seas) and low-Mg calcite (calcite seas). Oscillations in the carbonate mineralogy of dominant reef-building and sediment-producing organisms are in harmony with the oscillations for nonskeletal carbonates. These oscillations, together with synchronous oscillations in the mineralogy of marine potash evaporites, can be explained by secular variation in the Mg/Ca ratio of seawater driven by changes in the spreading rates along midocean ridges. The temporal patterns for biocalcification have come to light through a focus on (1) simple taxa that exert relatively weak control over the milieu in which they secrete their skeletons, and (2) taxa that hypercalcify—i.e., secrete massive skeletons or are exceptionally productive, for example, in forming voluminous chalk deposits. Most major reef-building and sediment-producing taxa belong to both of these categories. It appears that the Mg/Ca ratio of seawater has not only controlled Phanerozoic oscillations in hypercalcification by simple taxa, such as calcareous nannoplankton, sponges, and bryozoans, but has strongly influenced their skeletal evolution.

INTRODUCTION

Following an era of specialization in the earth sciences, many conceptual advances are now emerging through interdisciplinary research. The flow of earth materials through chemical cycles, for example, links diverse scientific fields, as do sequences of causal relationships that connect noncyclical physical, chemical, and biological phenomena. We have concluded that Phanerozoic oscillations in the



An aragonitic brain coral, *Diploria strigosa*, of late Pleistocene age, from the Cockburn Town fossil coral reef, San Salvador Island, Bahamas. This reef formed during the most recent interval of aragonite seas. Photo by Al Curran, Smith College.

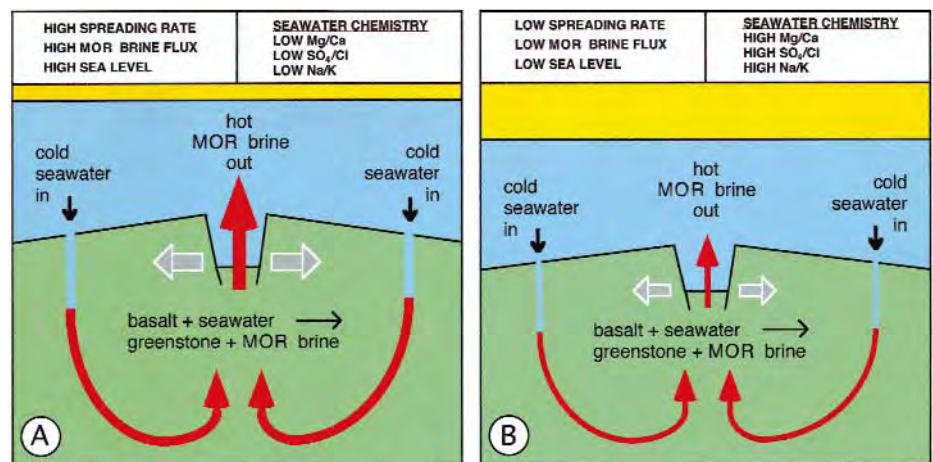


Figure 1. Effect of changes in the rate of seafloor spreading (ocean crust production) on global sea level, the flux of MOR hydrothermal brine, and the chemistry of seawater as predicted by Spencer and Hardie (1990) and Hardie (1996). A—high-spreading-rate conditions; B—low-spreading-rate conditions. Red arrows—MOR brine paths (thicknesses of the arrows are proportional to the brine flux but not to scale). Gray arrows proportional to spreading rates (not to scale).

mineralogy of dominant reef-building and sediment-producing organisms can be linked to shifts in seawater chemistry controlled by changes in global spreading rates along mid-ocean ridges (Fig. 1).

In a seminal study of oolites and early marine cements, Sandberg (1983) showed that nonskeletal carbonate precipitation

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In Memoriam

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 Boulder, Colorado
 January 2, 1999

Tylor R. Kittredge
 Panama
 October 1998

Harold W. Scott
 Urbana, Illinois
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 Lakewood, Colorado
 September 25, 1998

John F. Wosinski
 Corning, New York

Hypercalcification *continued from p. 1*

in Phanerozoic seas has oscillated between aragonite and calcite (Fig. 2). It has been widely held that relatively low levels of atmospheric pCO₂ have produced "aragonite seas," while relatively high levels have produced "calcite seas" (Wilkinson and Algeo, 1989; Mackenzie and Morse, 1992). Calculations using the computer program PHRQPITZ (Plummer et al., 1988) show, however, that pCO₂ is not a viable control (Stanley and Hardie, 1998). Seawater of modern composition would be supersaturated with respect to calcite and undersaturated with respect to aragonite only for a narrow range of pCO₂, within which all values are more than an order of magnitude greater than that of the present—a level almost certainly not attained during the Cretaceous interval of calcite seas (Berner, 1994). In fact, such high levels of pCO₂ would cause aragonitic shells of organisms to begin dissolving immediately after their secretion. Furthermore, experiments show that for present-day seawater at 25 °C (Mg/Ca mole ratio = 5.17), raising pCO₂ from 10^{-4.5} to 10^{-1.0} atm simply lowers the MgCO₃ content of precipitated calcite from 12 to 7 mol% (Burton and Walter, 1991); it does not cause

low-magnesium calcite to precipitate instead of aragonite.

It has long been recognized that changes in the Mg/Ca ratio of seawater can dictate whether calcite or aragonite precipitates from seawater. Experiments demonstrating this relationship (Füchtbauer and Hardie, 1976, 1980), which are in accord with data for natural saline lakes (Müller et al., 1972), indicate that, at 25 °C and present seawater ionic strength and atmospheric pCO₂, a ratio for Mg/Ca of ~2 separates a regime of calcite precipitation from a regime of aragonite ± high-Mg calcite precipitation (Fig. 3).

Spencer and Hardie (1990) introduced a quantitative model for calculating the chemistry of ancient seawater based on the premise that the composition of modern seawater results primarily from the mixing of average riverwater (a Ca-HCO₃ water) and mid-ocean ridge (MOR) hydrothermal brines (Na-Ca-Cl waters). This model predicts that relatively minor changes in the flux of MOR hydrothermal brines would change the Mg/Ca, Na/K, and Cl/SO₄ ratios in seawater enough to drastically alter the primary mineralogy of nonskeletal marine carbonates and evaporites.

CALL FOR NOMINATIONS

History of Geology Award

The History of Geology Award is presented annually to an individual who has made contributions of fundamental importance to our understanding of the history of the geological sciences. Outstanding contributions might include publication of papers or books of distinction that contribute new and profound insight into the history of geology (based either on original research or on a synthesis of existing knowledge); discovery of and making available to scholars of rare resource materials; providing comprehensive bibliographic surveys; editing a thematically integrated collection of articles; organizing meetings and symposia that generate interest in the history of geology; innovative research into original sources; creative interpretations of data; translations of key materials; and exceptional services to the GSA History of Geology Division.

To nominate a deserving individual, send a letter of nomination that describes the contributions that warrant the award, along with supporting materials, including the candidate's curriculum vitae to the chair of the award committee, Gerard V. Middleton, Dept. of Geology, McMaster University, 1280 West Main, Hamilton, ON L8S 4M1, Canada (middleto@mcmaster.ca; fax 905-522-3141). All nominations are valid for three years.

Nomination deadline: April 1, 1999.

Mid-ocean ridges act as huge rock-fluid ion exchange systems for Ca^{2+} and Mg^{2+} , Ca^{2+} being released to the fluid and Mg^{2+} being consumed by the rock in the conversion of oceanic basalts to greenstones and amphibolites by interaction with hot seawater (Fig. 1). Low spreading rates (= low hydrothermal brine fluxes; Baker et al., 1995) should lead to elevated Mg/Ca mole ratios in seawater of the open oceans; if this ratio rose above ~ 2 for warm surface seawater, then aragonite \pm high-Mg calcite would precipitate instead of low-Mg calcite (Fig. 2), as occurs in today's oceans. Conversely, high spreading rates (= high hydrothermal brine fluxes; Baker et al., 1995) should lower the Mg/Ca mole ratio in seawater; if this ratio dropped below ~ 2 , then low-Mg calcite would precipitate instead of aragonite \pm high-Mg calcite (as predicted, for example, for the Cretaceous Period; Fig. 2). Using

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The deadline for applications or nominations is March 15, 1999.

first-order sea-level curves as a proxy for the record of ocean crust production during the Phanerozoic Eon, Hardie (1996) employed the Spencer-Hardie model to predict the mineralogies of nonskeletal marine carbonate ooids and cements as a function of secular changes in the Mg/Ca ratio of seawater. The results are in close agreement with Sandberg's (1983) periods of aragonite seas and calcite seas, as shown in Figure 2 (see also Hardie, 1996, Fig. 5).

Potash evaporites in the geological record fall into two main chemical groups: (1) KCl evaporites characterized by potassium chloride salts such as sylvite (KCl) and an absence of magnesium sulfate salts, and (2) MgSO_4 evaporites characterized by magnesium sulfate salts such as kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$) (Hardie, 1996). These two evaporite types precipitate from two very different parent brines, Na-Ca-Mg-K-Cl brines ("calcium chloride" brines) and

Na-Mg-K-Cl- SO_4 brines, respectively, which lie on either side of a fundamental chemical divide, the " CaSO_4 divide" (Hardie and Eugster, 1970). Because both Mg^{2+} and SO_4^{2-} are extracted from seawater at mid-ocean ridges, whereas Ca^{2+} and K^+ are released, MOR hydrothermal brines are of the calcium chloride type. Therefore, during periods of high spreading rates, the elevated fluxes of MOR brine will drive seawater toward a calcium chloride composition that on evaporative concentration would produce KCl evaporites. On the other hand, low spreading rates would push seawater toward MgSO_4 -enriched composition and precipitation of MgSO_4 -type evaporites. Calculations based on the Spencer-Hardie model predict that KCl evaporites should have precipitated from calcite seas and MgSO_4

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evaporites from aragonite seas. The rock record confirms this correspondence (Fig. 2; see also Hardie, 1996, Fig. 5). The fact that the Spencer-Hardie and Hardie models successfully predict the Phanerozoic history of two different families of nonskeletal minerals precipitated from seawater—carbonates and potash evaporites—makes a strong case that both models are fundamentally valid.

STRATEGIES FOR UNCOVERING TRENDS IN BIOMINERALIZATION

From sparse data, Wilkinson (1979) proposed a unidirectional Phanerozoic trend from calcite to aragonite for the

dominant mineralogy of marine biocalcifiers. Although such a trend has not been apparent to more recent workers (Lowenstam and Weiner, 1989, p. 237), Wilkinson's data led Mackenzie and Agegian (1989, p. 20) to conclude that "the oscillatory trend seen in non-skeletal carbonate components ... is not clearly apparent in the mineralogy of fossil organisms." Wilkinson's data also dissuaded Van de Poel and Schlager (1994) from claiming such a correspondence, although their survey of bioclasts in Mesozoic and Cenozoic carbonate rocks indicated maxima for aragonitic components in Triassic and late Cenozoic strata.

Rather than conducting a general survey, we adopted a double strategy to inves-

tigate the effects of seawater chemistry on biocalcification (Stanley and Hardie, 1998). First, we focused on what we call hypercalcifying tropical taxa. Forming one subset of this group are species that have secreted unusually massive skeletons for the higher taxa to which they belong; stony bryozoans of the Paleozoic are an example. A second, overlapping subset of hypercalcifiers includes species whose populations engage in rampant carbonate production. Reef builders and major sediment producers fall within this category.

As a second strategy, we hypothesized that relatively unsophisticated carbonate secretors—ones that exert weak control over the chemical milieu in which they secrete their skeletons—are strongly influenced by the Mg/Ca ratio and temperature of seawater. Significant here is the observation that magnesium increases with temperature in the skeletons of modern marine organisms, as in nonskeletal marine carbonates, but partition coefficients vary among taxa and the effect of temperature is inversely related to biological complexity (Chave, 1954).

Employing these two strategies, we uncovered a strong correspondence between the mineralogy of biologically simple hypercalcifying taxa and that of nonskeletal carbonates from Ordovician time to the present (Fig. 2). We conclude that although these taxa, including reef builders, need not have secreted skeletons that were in thermodynamic equilibrium with seawater, their skeletal productivity has been strongly influenced by the ambient Mg/Ca ratio. The taxa that yield this pattern share one deficiency: they are unable to remodel their skeletons through resorption during their ontogeny. It appears that the inability to remodel is linked to unsophisticated modes of biocalcification that also result in reliance on favorable seawater chemistry. Foraminifera, though otherwise simple organisms, are sophisticated skeletal secretors, which employ an "almost unparalleled" variety of basic modes of mineralization (Lowenstam and Weiner, 1989, p. 670) and also have the ability to remodel their tests; there is no apparent overall temporal relationship between their predominant mineralogy and the Mg/Ca ratio of seawater. Reef builders are probably heavily influenced by the ambient Mg/Ca ratio for two reasons. First, they must meet the basic demands of hypercalcification. Second, nearly all organisms able to flourish in the severe competitive battle for space within reef-building communities have succeeded through vegetative or colonial growth. Thus, these organisms have characteristically been simple forms, such as algae, sponges, and corals, which are unsophisticated carbonate secretors.

As described below, application of our strategies to the geologic record provides explanations for many previously puzzling

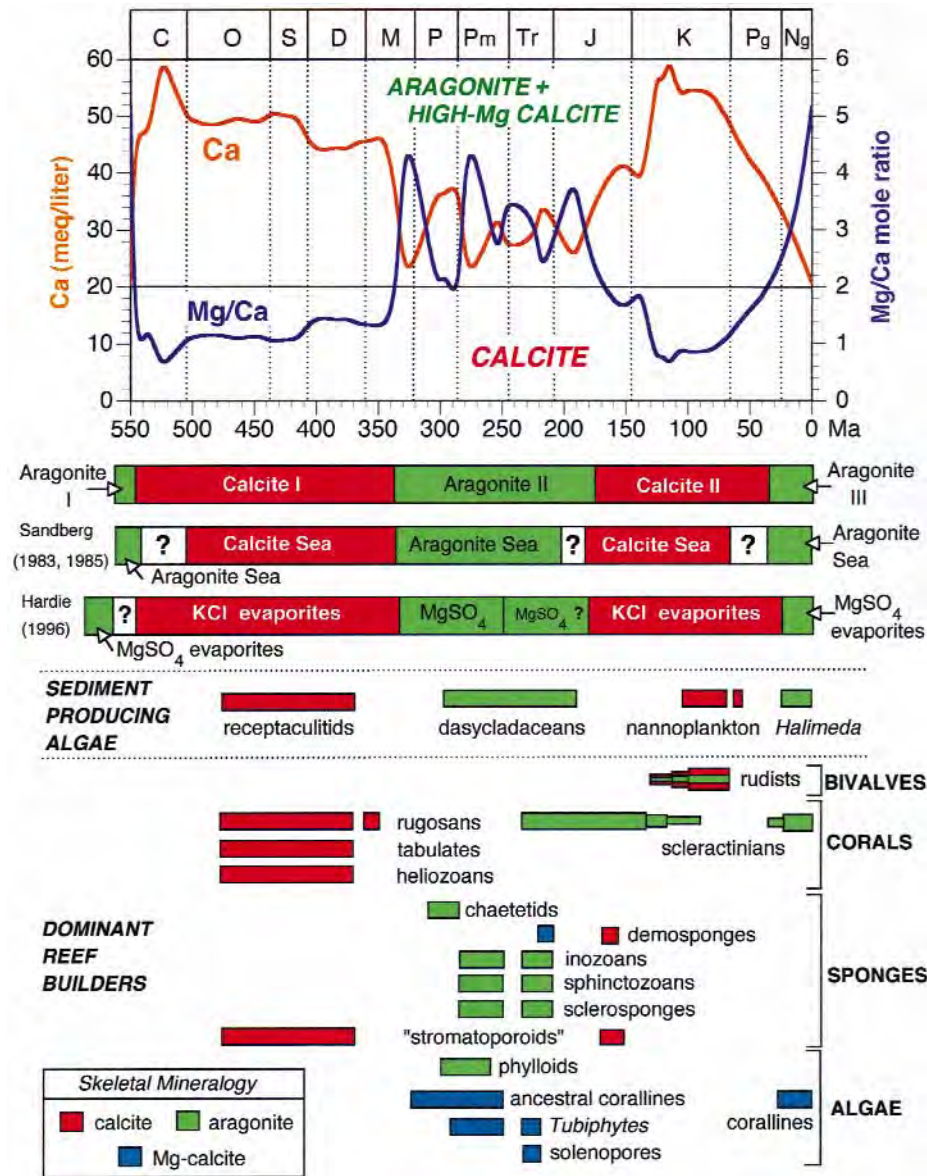


Figure 2. Correspondence between secular oscillations for the carbonate mineralogy of dominant hypercalcifying marine taxa, the mineralogy of marine evaporites and nonskeletal carbonates, and the Mg/Ca ratio and absolute concentration of calcium (Ca) in seawater as calculated by Hardie (1996). The boundary separating the nonskeletal nucleation fields of low-magnesium calcite (< 4 mol% MgCO₃), which we will term calcite, and high-Mg calcite (> 4 mol% MgCO₃) and aragonite is shown as a horizontal line at Mg/Ca = 2 (after Stanley and Hardie, 1998).

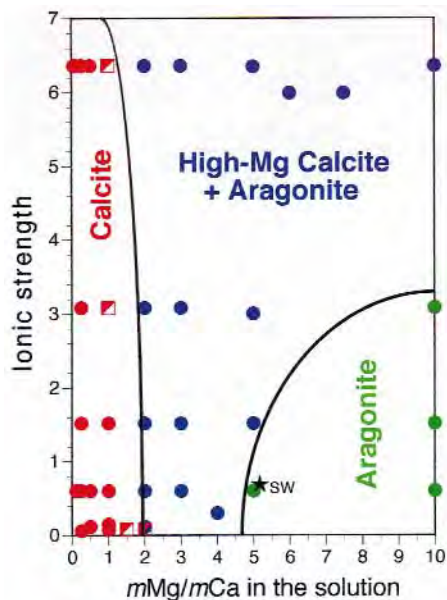


Figure 3. Experimentally determined nucleation fields of low-Mg calcite (red), high-Mg calcite + aragonite (blue), and aragonite (green) in $MgCl_2$ - $CaCl_2$ - Na_2CO_3 - H_2O solutions at 28 °C, atmospheric pCO_2 and 1 atm total pressure (1976 unpublished data of Füchtbauer and Hardie). Red symbol—calcite with $MgCO_3$ content up to 4 mol%; half-solid red square—calcite with $MgCO_3$ content >4, <6 mol%. $MgCO_3$ content of high-Mg calcite in the blue symbol field increases systematically with increase in the Mg/Ca ratio in the aqueous solution (see Füchtbauer and Hardie, 1976, 1980). Black star—modern seawater (SW).

phenomena in the history of reef building and sediment production and in the evolution of calcareous taxa.

DOMINANT REEF BUILDERS

Before Late Ordovician time, reefs were built by taxonomically problematical taxa of uncertain mineralogy. For this reason, we began our analysis of the mineralogy of reef builders with the reef community that flourished from Late Ordovician to Late Devonian time in the calcite sea designated Calcite I (Fig. 2). In accordance with our hypothesis, this community was dominated by calcitic taxa: stromatoporous sponges and several groups of calcitic corals (Oliver and Coates, 1987).

The Late Devonian mass extinction decimated the calcitic reef community. Late in the Mississippian Period, the Mg/Ca ratio of seawater shifted far into the aragonitic regime (Aragonite II), and new reef-building communities of aragonite and high-Mg calcitic algae and sponges emerged (Fig. 2). Members of these communities formed the enormous Horseshoe Atoll of central Texas and the Permian reef complex of west Texas. Aragonitic members of the same and similar taxa emerged as the reef-building community of the Middle Triassic, and in Late Triassic time aragonitic corals of the mod-

ern type (scleractinians) joined them as dominant reef builders (Stanley, 1988).

The only discrepancy between the mineralogy of dominant reef builders and that of nonskeletal carbonates is for Late Jurassic and Early Cretaceous time, when scleractinian corals persisted as major reef builders. The continued success of this aragonitic group probably resulted from two circumstances. First, the Mg/Ca ratio remained near the calcite-aragonite boundary during this interval. Second, the high absolute concentration of Ca^{2+} during this interval may have promoted nonequilibrium precipitation of all forms of calcium carbonate. In mid-Cretaceous time, when the Mg/Ca ratio descended to its lowest Phanerozoic level according to the calculations of Hardie (1996), corals relinquished to rudists their role as dominant reef builders (Scott, 1984). As bivalve mollusks, rudists were probably not strongly influenced by seawater chemistry. Thus, although shells of radiolites, the most successful reef-building rudists of the Late Cretaceous, contained more calcite than aragonite (Kauffman and Johnson, 1988), it is most reasonable to view the rudists as beneficiaries of the decline of aragonitic reef-building corals that occurred when the Mg/Ca ratio dropped. Support for this interpretation comes from the previously unexplained failure of corals to build large reefs for more than 30 m.y. after the disappearance of the rudists at the end of the Cretaceous Period. Scleractinian corals existed in considerable diversity early in the Cenozoic Era, but produced only small, inconspicuous bioherms, even during the extremely warm Eocene interval. Not until early in the Oligocene did corals begin to produce massive reefs throughout the world (Frost, 1977), despite the fact that warm seas had contracted toward the equator (Zachos et al., 1994). At this time, the Mg/Ca ratio of seawater was rising far into the aragonitic regime (Fig. 2).

We have provided elsewhere a more detailed picture of the correspondence between the mineralogy of major reef builders and nonskeletal marine carbonates (Stanley and Hardie, 1998). Aspects of the pattern we have described were noted by Van de Poel and Schlager (1994) and Hallock (1997).

DOMINANT SEDIMENT PRODUCERS

The widespread deposition of massive chalk during Late Cretaceous time is another phenomenon of hypercalcification that has long defied explanation but can be accounted for by a change in seawater chemistry: it coincided with the interval during which the Mg/Ca ratio was at its lowest level during the past 500 m.y. (Fig. 2). Calcareous nannoplankton—potential chalk producers—had attained

high taxonomic diversity during Early Cretaceous time but had failed to form massive chalk deposits. Following the setback of calcareous nannoplankton by the terminal Cretaceous extinction, massive chalk deposition resumed in early Paleocene time. Then, as the Mg/Ca ratio of seawater rose toward the aragonitic domain, widespread deposition of massive chalk ceased, and it failed to resume even during the exceptionally warm Eocene interval, when epicontinental seas were widespread.

The attribution of extensive chalk deposition to changes in seawater chemistry gains support from the observation that an increase in the concentration of dissolved Ca^{2+} enhances calcification by calcareous nannoplankton in the laboratory (Blackwelder et al., 1976). Additional support comes from two puzzling temporal patterns for coccoliths (Houghton, 1991). One of these is a polyphyletic decline in the mean size of coccoliths during the Cenozoic Era. The result was thinner calcitic encrustation of cells. The second pattern pertains to the genus *Discoaster*. Coccoliths of this genus were solid, circular shields early in the Cenozoic, but as the era progressed, they became increasingly diminished in volume by marginal embayments. By the time *Discoaster* became extinct in the Pliocene, all of its members secreted spindly, star-shaped coccoliths that covered only a small fraction of the cell surface (Fig. 4). These trends for coccoliths can be viewed as amounting to evolutionary osteoporosis, caused by an increase in the Mg/Ca ratio of seawater that was accompanied by a decline in the concentration of Ca^{2+} (Fig. 2).

The Mg/Ca model also provides an explanation for patterns of hypercalcification for green algae. Aragonitic codiaceans (especially *Halimeda*) produce vast quantities of carbonate sediment today, and dasycladaceans were so productive during Aragonite II that they have been regarded as the *Halimeda* of the Triassic (Elliott, 1984). On the other hand, the massive, calcitic receptaculitids were significant sediment producers throughout Calcite I.

EVOLUTIONARY TRENDS

The Cenozoic evolutionary trend toward weakly calcified nannoplankton species appears to reflect the influence of seawater chemistry (Fig. 4). Among cheilostome bryozoans, changes in the Mg/Ca ratio appear to have influenced the evolution of skeletal mineralogy. The cheilostomes originated as a calcitic group during the Cretaceous Period (Calcite II), although a few species of one subgroup secreted a combination of calcite and aragonite (Boardman and Cheetham, 1987). Fully aragonitic species did not arise until

Hypercalcification continued on p. 6

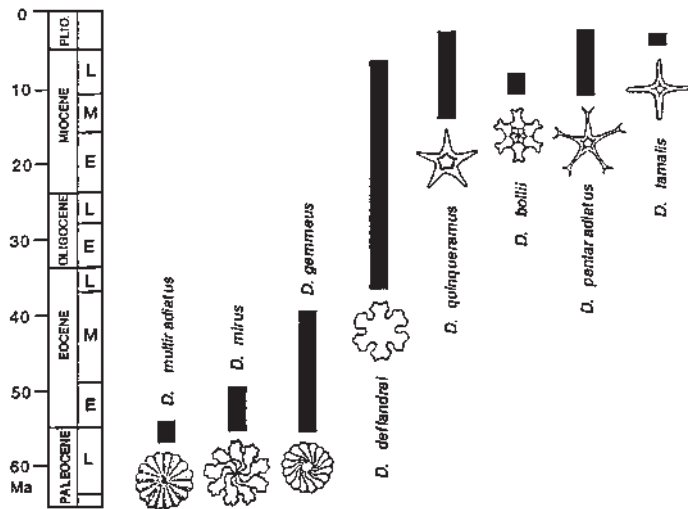


Figure 4. Stratigraphic ranges of typical species of *Discoaster*, a genus of calcareous nannoplankton whose calcitic skeletal elements underwent a striking net evolutionary trend during the sharp Cenozoic rise in the Mg/Ca ratio of seawater. Species with heavy, shield-shaped coccoliths gave way to species with delicate, star-shaped coccoliths. (Modified from Houghton, 1991.)

Hypercalcification *continued from p. 5*

the Eocene Epoch, when the Mg/Ca ratio of seawater had risen markedly. Today most cheilostome species secrete high-Mg calcite, but many tropical species secrete aragonite (Rucker and Carver, 1969); this distribution corresponds to the temperature pattern for nonskeletal precipitation of carbonates in laboratory experiments (Morse et al., 1997).

Several workers have noted that the mineralogy of calcareous sponges has frequently coincided with that of nonskeletal carbonates during the Phanerozoic (Reitner, 1987; Gautret and Cuif, 1989; Wood, 1991). Our survey suggests that calcareous sponges have in fact been at the mercy of seawater chemistry throughout their history (Fig. 2). During the Cretaceous, for example, all of them appear to have been calcitic, but all present-day representatives secrete aragonite, high-Mg calcite, or a combination of these minerals (Hartman, 1980).

Martin (1995) has noted that some suborders of foraminifera originated with skeletal mineralogies corresponding to those of nonskeletal carbonates, although, as we have already noted, there does not appear to be a strong temporal correlation between the Mg/Ca ratio of seawater and the mineralogy of highly productive foraminifera.

DISCUSSION

The fact that we have been able to connect many previously problematical phenomena with a single causal explanation gives credence to the Mg/Ca model. The results have additional biologic and geologic implications, some of which suggest promising avenues for future research.

For many taxa, degree of ecologic stability exhibited over tens or hundreds of millions of years seems to reflect the degree to which seawater chemistry has influenced skeletal mineralogy. Sophisticated carbonate secretors have the poten-

tial to optimize their skeletal structures without inhibition by the Mg/Ca ratio of seawater. Ammonoids, which secreted thin shells within which the gas pressure was about 1 atm, must have been served well by the relatively great bending strength of their nacreous aragonite. Ammonoids should therefore have benefited from their ability to secrete aragonite readily even in calcite seas. Thus, although being relatively independent of the ambient Mg/Ca ratio leaves a taxon such as the Ammonoidea unable to benefit from a favorable ratio, all else being equal, this independence confers long-term ecologic stability. Conversely, although unsophisticated carbonate secretors, such as algae, sponges, and corals, automatically benefit from the presence of a favorable Mg/Ca ratio, these forms also suffer severe declines when the ratio shifts to an unfavorable domain; they tend to follow a "boom-or-bust" pattern of productivity—and perhaps also taxonomic diversity—in the course of geologic time.

We think it likely that the Mg concentration in skeletons of taxa that secrete high-Mg calcite has been positively correlated with the Mg/Ca ratio of seawater back through Phanerozoic time, just as today the Mg concentration in calcite skeletons increases with increasing ocean temperature (Chave, 1954). Experimental growth of modern species under varying ambient Mg and Ca concentrations could shed light on this possibility by demonstrating lability in skeletal mineralogy for individual organisms. Study of the abundance of exsolved microdolomite and of trace elements in fossils may also expand our knowledge of skeletal Mg concentrations for extinct taxa.

Changes in carbonate productivity resulting from shifts in the Mg/Ca ratio of seawater must have affected the carbon cycle significantly in the course of geologic time. Today, a large proportion of carbonate and bicarbonate ions entering the ocean are incorporated into organic

reefs. If, long after forming, reef carbonate becomes metamorphosed during orogenesis, it will release CO₂ to the atmosphere (Berner, 1994). The flux of oxidized carbon to reef carbonate reservoirs would have been reduced at times, such as the early Cenozoic, when an unfavorable Mg/Ca ratio suppressed reef building. Carbonate storage in reefs increased dramatically early in Oligocene time, following the shift from calcite to aragonite seas. At about the same time, through reduced productivity during the dramatic rise in the Mg/Ca ratio of seawater, nannoplankton began contributing progressively less carbonate to the deep sea for possible future subduction and release of CO₂. Thus, during the past 30 m.y. or so, the increasing Mg/Ca ratio of seawater has influenced the relative proportions of total carbonate that have accumulated in the deep sea and in shallow-water reefs, where the mean residence time for oxidized carbon is much longer.

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