# 11   Biomineralization and Evolutionary History

Andrew H. Knoll

Department of Organismic and Evolutionary Biology
Harvard University
Cambridge, Massachusetts, 02138 U.S.A.

INTRODUCTION

The Dutch ethologist Niko Tinbergen famously distinguished between proximal and ultimate explanations in biology. Proximally, biologists seek a mechanistic understanding of how organisms function; most of this volume addresses the molecular and physiological bases of biomineralization. But while much of biology might be viewed as a particularly interesting form of chemistry, it is more than that. Biology is chemistry with a history, requiring that proximal explanations be grounded in ultimate, or evolutionary, understanding. The physiological pathways by which organisms precipitate skeletal minerals and the forms and functions of the skeletons they fashion have been shaped by natural selection through geologic time, and all have constrained continuing evolution in skeleton-forming clades. In this chapter, I outline some major patterns of skeletal evolution inferred from phylogeny and fossils (Figure 1), highlighting ways that our improving mechanistic knowledge of biomineralization can help us to understand this evolutionary record (see Leadbetter and Riding 1986; Lowenstam and Weiner 1989; Carter 1990; and Simkiss and Wilbur 1989 for earlier reviews).
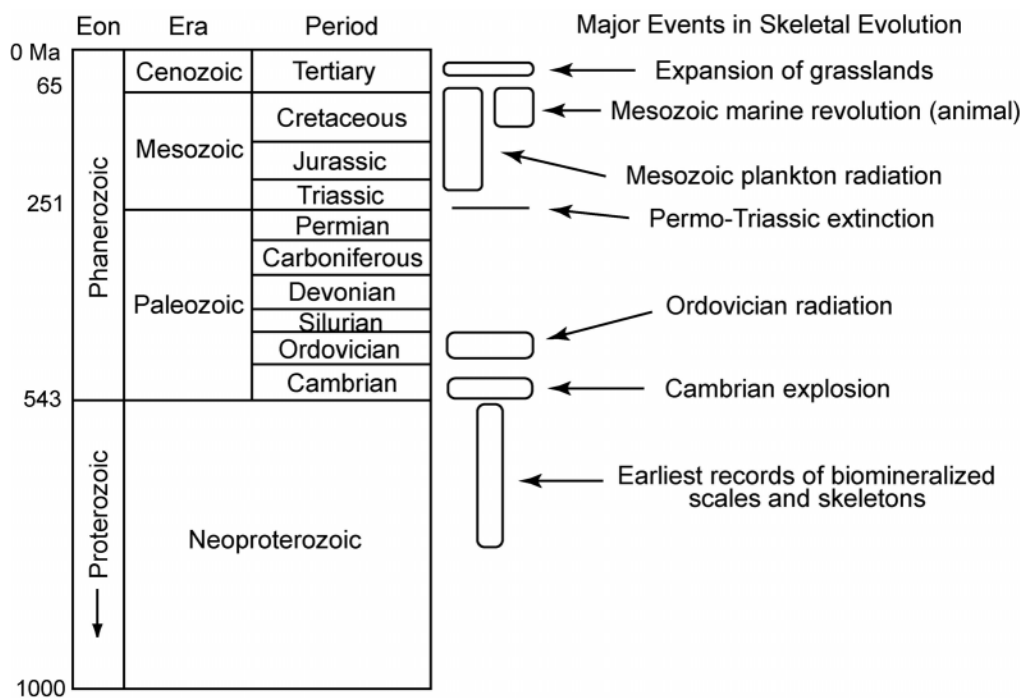
Figure 1. A geologic time scale for the past 1000 million years, showing the principal time divisions used in Earth science and the timing of major evolutionary events discussed in this chapter. Earlier intervals of time—the Mesoproterozoic (1600–1000 million years ago) and Paleoproterozoic (2500–1600 million years ago) eras of the Proterozoic Eon and the Archean Eon (> 2500 million years ago)—are not shown. Time scale after Remane (2000).

My discussion proceeds from two simple observations:

1. Skeletal biomineralization requires energy and so imposes a metabolic cost on skeleton-forming organisms.

2. Mineralized skeletons have evolved in many clades of protists, plants and animals.

If both statements are true, then clearly for many but not all eukaryotic organisms the biological benefits of biomineralization must outweigh its costs. But cost-benefit ratio is not static. It will change through time as a function of environmental circumstance. Thus, if mineralized skeletons confer protection against predators, the energy expended on biomineralization should vary through time as a function of predation pressure. And insofar as the metabolic cost of skeleton formation reflects the physical chemistry of an organism's surroundings, cost-benefit can also change as a function of Earth's environmental history.

THE PHYLOGENETIC DISTRIBUTION OF MINERALIZED SKELETONS

Figure 2 shows the phylogenetic relationships among eukaryotic organisms. The tree is incomplete and parts of it remain contentious. Nonetheless, it provides an essential roadmap for studies of skeletal evolution. The three principal classes of skeletal biominerals—calcium carbonates, calcium phosphates, and silica—all occur widely but discontinuously on the tree. This suggests either that gene cassettes governing biomineralization spread from group to group via horizontal transfer or that skeletal biomineralization evolved independently in different groups using, at least in part, component biochemical pathways that evolved early within the Eucarya.

Carbonate skeletons

Five of the eight major clades in Figure 2 contain species with mineralized skeletons, and all five include organisms that precipitate calcite or aragonite. Accepting this phylogenetic distribution, we can ask how many times carbonate skeletons originated within the eukaryotic domain. To arrive at an answer, we need to draw conclusions about skeletal homology, and we should also differentiate between skeletal structures and the underlying biochemical processes that govern their formation. Skeletons in two taxa can be accepted as independently derived if they share no common ancestor that was itself skeletonized. Thus, foraminiferans and echinoderms unambiguously record two separate origins of $CaCO_3$ skeletons—carbonate biomineralization evolved within the forams well after their differentiation from other cercozoans and, so, long after the opisthokont and cercozoan clades diverged. In contrast, the question of common ancestry for echinoderm and ascidian skeletons is less clear cut. In principle, the two clades could have shared a calcified deuterostome ancestor, although skeletal anatomies in the two groups—spicules in ascidians and the remarkable stereom of echinoderms—differ sharply. A conservative estimate is that carbonate skeletons evolved twenty-eight times within the Eucarya. This includes at least twenty origins among metazoans (as many as eight within the Cnidaria alone; e.g., Romano and Cairns 2000), four within the Plantae (two each in green and red algae), and one each within the cercozoans, haptophytes, heterokonts, and alveolates (the calcified cysts of some dinoflagellates). Given the diversity of problematic skeletons in Lower Cambrian rocks (e.g., Bengtson and Conway Morris 1992) and the likelihood that differing patterns of skeletal precipitation and discontinuous stratigraphic distributions reflect multiple origins of carbonate biomineralization in coralline demosponges (Reitner et al. 1997), the actual number could be significantly higher.
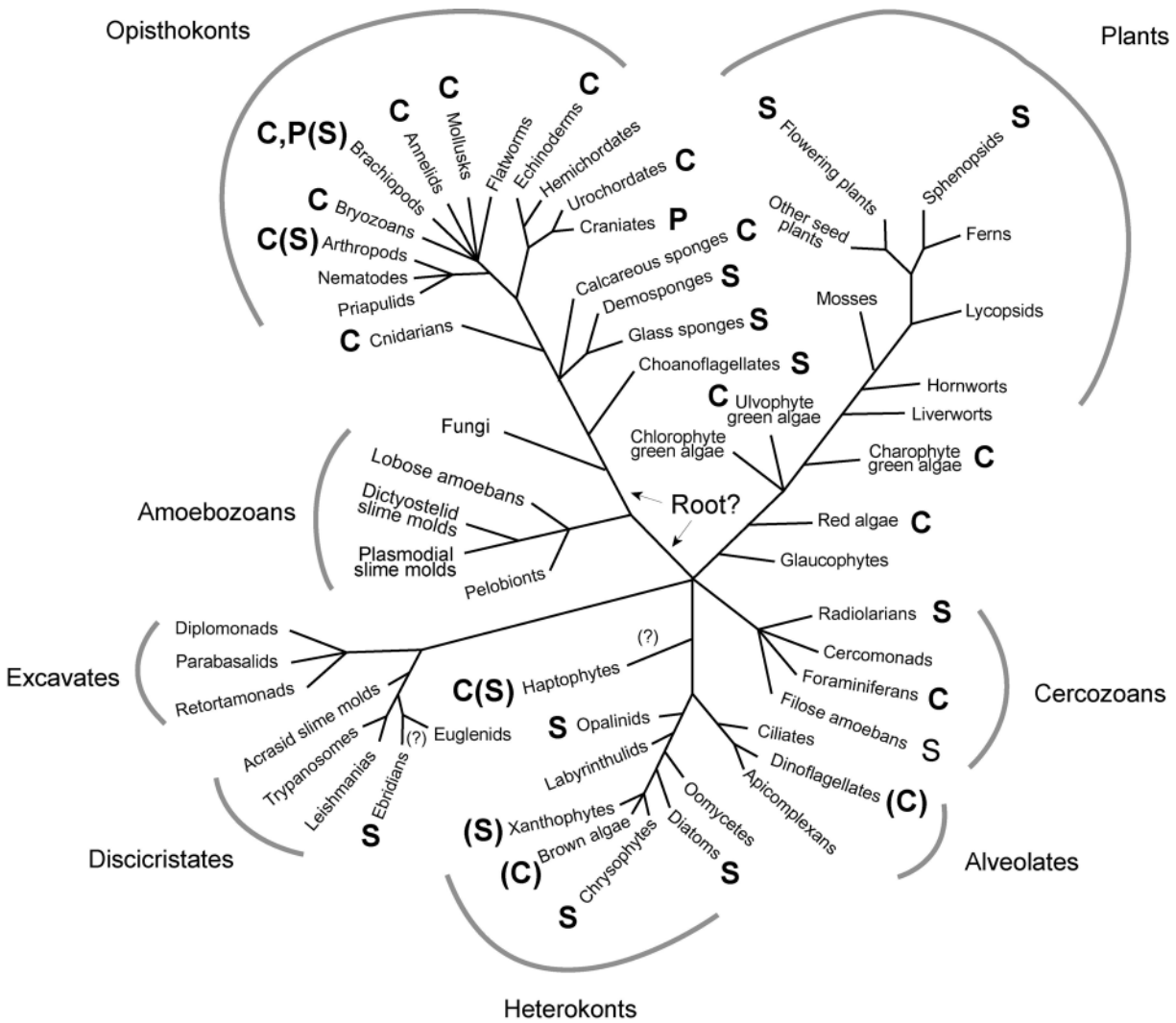
Figure 2. Molecular phylogeny of eukaryotic organisms, showing the phylogenetic distribution of mineralized skeletons. C = calcium carbonate minerals; P = calcium phosphate minerals; S = opaline silica. Letters in parentheses indicate minor occurrences. Phylogeny based principally on Mishler et al. (1994) for the Plantae; Giribet (2001) for opisthokonts; and Baldauf (2003) for the Eucarya as a whole. Data on skeletons principally from Lowenstam and Weiner (1989).

Phylogeny thus points toward repeated innovations in the evolution of carbonate skeletons, but this leaves open the question of homology in underlying molecular process. As pointed out by Westbroek and Marin (1998), skeleton formation requires more than the ability to precipitate minerals; precipitation must be carried out in a controlled fashion in specific biological environments. Skeletal biomineralization requires directed transport of calcium and carbonate, molecular templates to guide mineral nucleation and growth, and inhibitors that can effectively stop crystal growth. All cells share the ability to bind Ca^{2+} ions and regulate calcium concentrations (e.g., MacLennan et al. 1997; Sanders et al. 1999), and both photoautotrophic and heterotrophic eukaryotes regulate their internal inorganic carbon chemistry using carbonic anhydrase and other enzymes (e.g., Aizawa and Miyachi 1986). Thus, the biochemical supply of ions required for calcite or aragonite precipitation appears to be an ancient feature of eukaryotes. Organisms in which carbonate formation has been well studied also synthesize acidic proteins and glycoproteins that provide templates for mineralization (Weiner and Addadi 1997),

guiding what in many cases appears to be essentially diagenetic crystal growth from amorphous precursors (Gotliv et al. 2003). Thus, many animals and protists with no skeleton-forming common ancestors nonetheless share the underlying capacity to synthesize and localize carbonate-inducing biomolecules, although homologies among these molecules remain uncertain.

Biochemical similarities extend, as well, to the molecules that inhibit $CaCO_3$ mineralization. Marin et al. (1996, 2000) proposed that organisms sculpt mineralized skeletons via "anti-calcifying" macromolecules that locally inhibit crystal growth. Because spontaneous calcification of cell and tissue surface may have been a problem in highly oversaturated Proterozoic oceans (Grotzinger 1989; Knoll et al. 1993), Marin et al. (1996) reasoned that molecular inhibitors evolved early as anti-calcification defenses and were later recruited for the physiological control of skeleton growth. [Even today, molecular inhibitors are necessary to retard spontaneous calcification of internal tissues in vertebrates; Luo et al. (1997).] Immunological comparison of anti-calcifying molecules in mollusks and cnidarians supports the hypothesis that this biochemistry already existed in the last common ancestor of cnidarians and bilaterian animals, if not before that.

Thus, in the view of Westbroek and Marin (1998), the many origins of calcareous skeletons reflect multiple independent cooptations of molecular and physiological processes that are widely shared among eukaryotic organisms. Skeletons that are not homologous as *structures* share underlying physiological pathways that are. This powerful idea has to be correct at some level. The details—how much biochemical innovation and diversity underlies carbonate skeletonization across clades—await an expanded program of comparative biological research.

Silica skeletons

Skeletons of opaline silica also enjoy a wide distribution among eukaryotes, occurring in five or (depending on the still debated phylogenetic relationships of ebridians) six of the eight great eukaryotic clades. Biologically, however, SiO_2 skeletons differ in distribution from those made of $CaCO_3$. Silica biomineralization is limited to intracellular precipitation. Thus, microscopic scales and skeletons are abundant in cercozoans (radiolarians and their relatives, as well as the siliceous scales of euglyphid amoebans), ebridians, and heterokonts (reaching their apogee in the exquisite frustules of diatoms). In animals, however, siliceous skeletons are limited to sponge spicules and minor occurrences such as the opalized mandibular blades of boreal copepods (Sullivan et al. 1975) and the micron-scale silica tablets formed intracellularly in the epidermis of some brachiopod larvae (Williams et al. 2001). Within Plantae, the carbonate biomineralization of marine and freshwater algae is replaced by silica phytolith mineralization in the epidermis of some vascular plants, especially grasses, sedges, and the sphenopsid genus *Equisetum* (Rapp and Mulholland 1992). Accepting that choanoflagellates and sponges could share a common ancestor that precipitated silica, we can estimate that silica skeletons evolved at least eight to ten times in eukaryotic organisms. Much has been learned in recent years about silica precipitation by diatoms (e.g., Kröger and Sumper 1998; Kröger et al. 2000, 2002; Zurzolo and Bowler 2001). Frustule formation requires active silica transport to local sites of precipitation (silica deposition vesicles), where opal deposition is mediated by enzymes. The vesicular spaces for mineral formation appear to be modifications of the Golgi-vesicle apparatus shared almost universally by eukaryotes. On the other hand, little is known about intracellular silica transport. Various molecules have been shown to promote the polymerization of silicic acid molecules—polyamines and silaffins in diatoms (Kröger et al. 2000), silicatein and collagen in sponges (Krasko et al. 2000). To date, however, we do not know enough about the comparative biology of these molecular processes to know the

extent to which organisms that produce siliceous skeletons mirror carbonate precipitators in the recruitment of common biochemistries.

Phosphate skeletons

Calcium phosphate mineralization is widespread in the form of amorphous granules used in phosphate storage, gravity perception and detoxification (Gibbs and Bryan 1984; Lowenstam and Weiner 1989). In contrast, phosphatic skeletons are limited to animals and within this kingdom occur prominently only in lingulate brachiopods, vertebrates, and several extinct clades (see below). The absence of wider usage may reflect the metabolic extravagance of deploying nutrient phosphate for skeletons, especially in protists and plants. Phosphatic skeletons may best justify their cost when ontogeny requires constant remodeling, as it does in vertebrates.

Although phosphatic skeletons differ in evolutionary trajectory from those made of calcium carbonate, the two likely share much of the biochemical machinery underlying mineralization. As noted above, calcium transport is ubiquitous in eukaryotes, and so is the basic molecular biology of phosphate control. As evidenced by the capacity of nacre to induce bone formation by human osteoblasts (Lopez et al. 1992), $CaCO_3$ and phosphate precipitating animals also share at least some of the signaling molecules that direct mineralization. Given that vertebrates and mollusks characteristically precipitate different minerals, key features of their skeletal biochemistry must differ—but what those features are and how many of them separate bone from clam shells remains to be seen.

THE GEOLOGIC RECORD OF SKELETONS

Biomineralization in Precambrian oceans

The antiquity of eukaryotic clades. In Figure 3, the eukaryotic tree is trimmed with dates that mark (1) the earliest geological records of constituent taxa and (2) the earliest records of mineralized skeletons within clades. The oldest evidence for eukaryotic biology comes from C_{28}–C_{30} steranes preserved in 2700 million year old shales from northwestern Australia (Brocks et al. 1999). The chemical structures of inferred precursor molecules are inconsistent with biosynthesis by any of the few bacterial groups known to produce sterols. Nonetheless, nothing else is known about the biology of source organisms, which could have been stem group eukaryotes only distantly related to extant clades. Protistan body fossils are rare and poorly characterized in rocks older than ca. 1800–1600 million years, when both problematic macrofossils and unambiguously eukaryotic microfossils enter the record. The macrofossils include centimeter-scale helices, tubular structures, and articulated filaments up to 7 or 8 cm long (Walter et al. 1990; Grey and Williams 1990; Rasmussen et al. 2002), all plausibly eukaryotic but not easily mapped onto the phylogeny in Figure 3. Organically preserved microfossils include forms up to several hundred microns in diameter whose walls display closely packed polygonal plates, branching processes, spines and other ornamentation, and ultrastructures (imaged by TEM) found today only in eukaryotes (Javaux et al. 2001, 2003). Such fossils are protistan, but they also remain problematic at any finer taxonomic scale.

Large populations of filamentous fossils, preserved in ca. 1200 million year old cherts from northern Canada, display patterns of cell differentiation and division that relate them to extant bangiophyte red algae (Butterfield 2000). Florideophyte reds began to diversify no later than 600 million years ago (Xiao et al. in press), but calcified red algae enter the record only during the Ordovician Period (Riding et al. 1998). Similarly, green algae occur in 700–800 million year old shales from Spitsbergen and are possibly recorded by phycoma-like microfossils in rocks older than 1000 million years
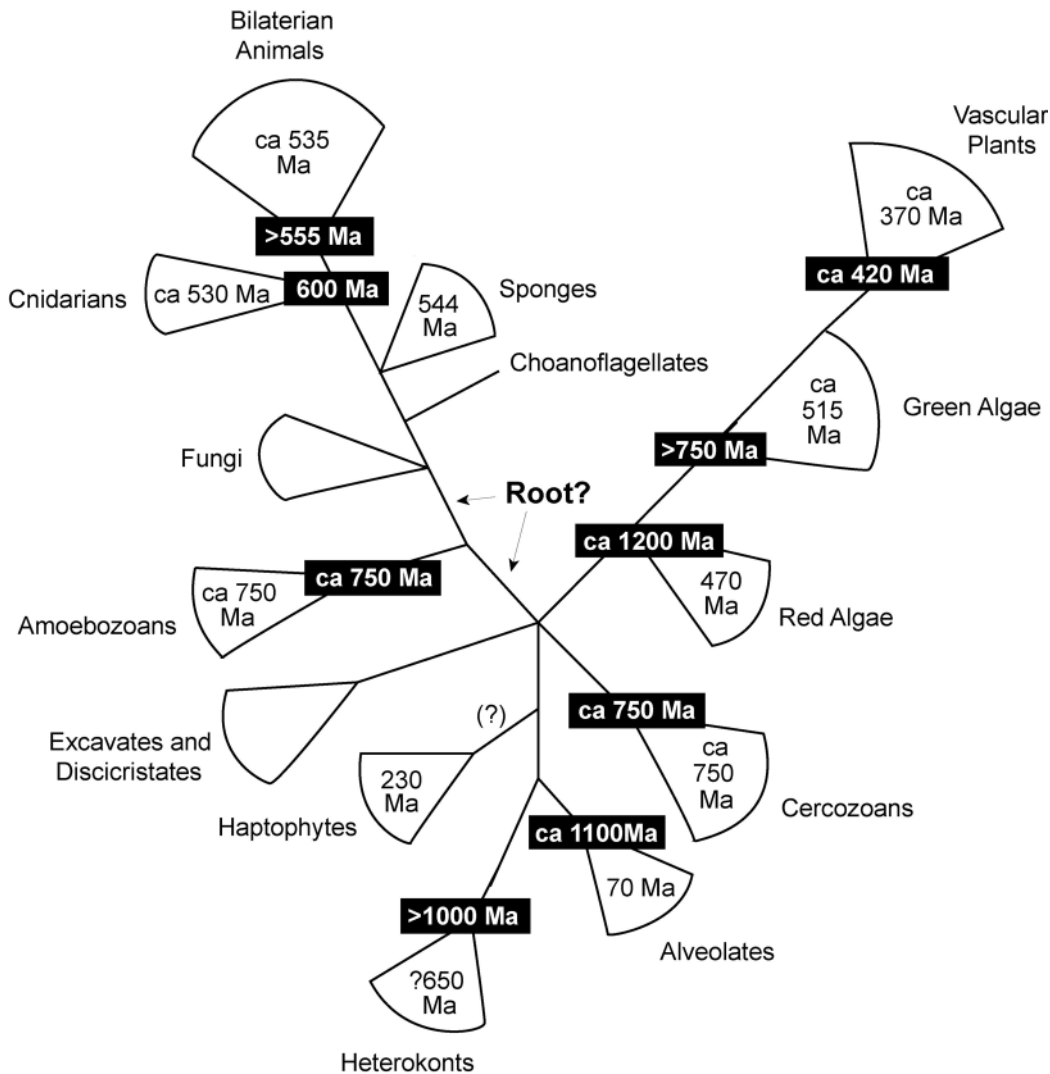
Figure 3. A simplified version of the phylogeny illustrated in Figure 2, with dates showing the earliest geological records of major clades (black boxes) and the earliest known records of biomineralized scales and skeletons within these clades (dates within wedges). First appearances of clades are shown only if they constrain the timing of subsequent divergences on a given branch. Thus, the oldest record of fungi is not shown because its Cambrian age postdates the earliest appearance of cnidarians at 600 million years—fungal divergence from other opisthokonts must have predated the first appearance of recognizable cnidarians.

(Butterfield et al. 1994), yet calcareous dasyclad and caulerpalean greens occur only in Cambro-Ordovician and younger carbonates (Wray 1977). *Vaucheria*-like heterokonts occur in Siberian shales cut by 1000 million year old intrusions (German 1990) and in 700–800 million year old shales from Spitsbergen (Butterfield 2002)—the latter are particularly compelling, as they include most phases of the vaucherian life cycle. In contrast, siliceous scales possibly formed by heterokonts appear only in ca. 610–650 million year old rocks and well skeletonized chrysophytes and diatoms not until the Mesozoic Era (see below).

Rounding out the picture of eukaryotic clade divergence, cercozoan fossils occur in ca. 750 million year old rocks (Porter et al. 2003), well before radiolarians and forams rose to biogeochemical importance. Lobose amoebans, an early branch of the

amoebozoan clade, occur in the same rocks (Porter et al. 2003). Biomarkers ascribed to alveolates have been found in shales as old as 1100 million years (Summons and Walter 1990), but animals are unknown before 600 million years ago (Xiao and Knoll 2000). Save for the late appearance of animals, this paleontological picture of Proterozoic clade divergence is consistent with recent molecular clock estimates (e.g., Wang et al. 1999; Yoon et al. 2002).

The overall pattern, then, appears to be one of early eukaryotic clade differentiation, with later—and in some cases much later—evolution of biomineralized skeletons within clades. Preservational biases have undoubtedly influenced this pattern; skeletal fossils can be recognized in the rock record only when both mechanical and solubility thresholds for preservation and morphological thresholds for identification have been crossed. Nonetheless, the inferred evolutionary pattern must be at least broadly correct, as detailed in the following sections.

The earliest records of mineralized skeletons. Today, calcium carbonate and silica leave the oceans largely as skeletons. This could not have been the case early in Earth history; nonetheless, as expected when chemical weathering continuously introduces calcium and silica into the oceans, limestone, dolomite, and chert are common in Proterozoic sedimentary successions. Proterozoic and Phanerozoic successions differ not so much in the abundance of carbonates and silica as in the facies distributions of preserved deposits. Prior to the radiation of skeleton-forming eukaryotes, $CaCO_3$ and SiO_2 both accumulated preferentially along the margins of the oceans—in tidal flats and coastal lagoons, where evaporation drove precipitation (Maliva et al. 1989; Knoll and Swett 1990). Bacteria undoubtedly facilitated this deposition—the microscopic textures preserved in silicified stromatolites include both encrusted filaments and radially oriented crystal fans nucleated within surface sediments (e.g., Knoll and Semikhatov 1998; Bartley et al. 2000)—but the overall distribution of Proterozoic carbonates and silica reflects primary physical controls on precipitation. In this regard, it is worth noting that surface textures of Proterozoic sandstone beds record the widespread distribution of microbial mats in environments where no stromatolites accreted (e.g., Hagadorn and Bottjer 1997; Noffke et al. 2002); stromatolites formed where carbonate was deposited, not the reverse.

At present, the oldest inferences of protistan biomineralization come from vase-shaped tests preserved in 742±6 million year old rocks of the Chuar Group, Grand Canyon, Arizona (Porter and Knoll 2000; Porter et al. 2003). These fossils are veneered by pyrite (or iron oxides after pyrite) with regularly arranged ovoid holes, interpreted as insertion sites for mineralized scales in originally proteinaceous tests (Figure 4B). The morphology, inferred organic construction, and scale distribution of these fossils closely (and uniquely) resemble the tests of euglyphid filose amoebans (Porter et al. 2003). Further evidence of silica biomineralization is provided by a remarkable assemblage of small (10–30 μm) scales preserved in early diagenetic chert nodules from ca. 630–650 million year old rocks of the Tindir Group, northwestern Canada (Figure 4A; Allison and Hilgert 1986). These variously ornamented microfossils resemble the siliceous scales of chrysophytes, albeit at a larger size.

Horodyski and Mankiewicz (1990) described a possible instance of early carbonate skeletonization in silicified dolomites from the Pahrump Group, California, that are at least broadly correlative with Chuar rocks in the Grand Canyon. The fossils consist of sheet-like cellular structures originally encrusted by finely crystalline calcium carbonate and now preserved texturally in early diagenetic chert nodules. In some specimens, cell walls are preserved as clear chert, sharply differentiated from the carbonate-textured silica within and without. Horodyski and Mankiewicz (1990) proposed that the Pahrump fossils record thalloid algae with carbonate impregnated cell walls. More likely, however, the fossils
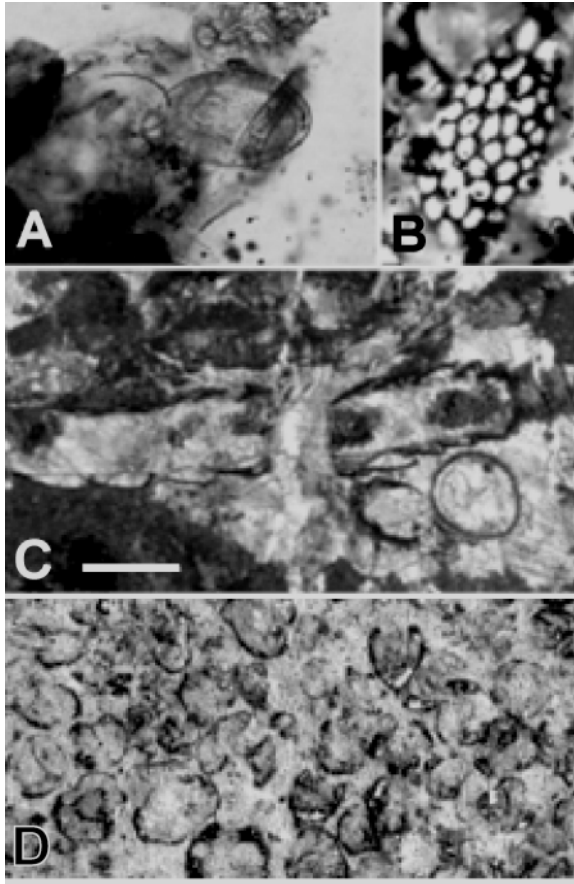
Figure 4. Evidence for skeletal biomineralization in Neoproterozoic rocks: (A) chrysophyte-like scales from ca. 650–630 million year old cherts of the Tindir Group, northwestern Canada; (B) *Melicerion*, test of a scale-forming filose amoeban from rocks just below a 742±6 million year ash bed in the Chuar Group, Grand Canyon, Arizona; (C) *Cloudina*, thin section photograph showing skeletal structure, from 548–543 million year old reefs of the Nama Group, Namibia; and (D) *Namacalathus*, also from the Nama Group, Namibia—note the goblet shaped individual in the upper right part of the image. (See text for references.) Scale bar (found in C) = 35 μm for (A), = 40 μm for (B), = 600 μm for (C), and = 1.5 cm for (D).

record unmineralized thalli whose relatively decay resistant walls were cast by encrusting carbonates soon after burial. Cyanobacterial sheaths preserved in similar fashion occur widely if sporadically in Neoproterozoic rocks around the world (e.g., Knoll and Semikhatov 1998). Ca. 600 million year old rocks of the Doushantuo Formation, China, contain extraordinary fossils of multicellular red and green algae preserved in anatomical detail, and these include florideophyte reds interpreted as stem group members of the (now) skeleton-forming Corallinales. Despite their superb preservation, however, these fossils show no evidence for the precipitation of $CaCO_3$ skeletons (Xiao et al. in press).

Early animals are best known from so-called Ediacaran fossils, problematic remains found globally as casts and molds in latest Proterozoic (575–543 million year old) storm deposits and turbidites (Narbonne 1998). Ediacaran remains and associated trace fossils contain little evidence for mineralized skeletons, prompting the widespread belief that pre-Cambrian animals were exclusively soft-bodied. Coeval carbonates, however, tell a different story. Microbial reefs in Namibia and elsewhere contain abundant and moderately diverse assemblages of calcified metazoans. *Cloudina* is a broadly cylindrical fossil built of funnel-like, apically flaring tubes set one within the next—ontogenetically, but not necessarily phylogenetically, reminiscent of pogonophoran worm tubes (Figure 4C; Grant 1990). The systematic relationships of these fossils are poorly known, but occasional evidence for budding supports a broadly cnidarian interpretation. Two distinct size classes, 0.5–2 and up to 7 mm in cross-sectional diameter, have been distinguished as different species (Germs 1972). Preserved walls are thin (a few tens of microns), but they commonly retain their rounded cross-sections in sediments, displaying only minimal evidence of compaction. Shell hash sometimes shows evidence of brittle fracture,

although folded walls also occur (Conway Morris et al. 1990). Collectively, these observations suggest that *Cloudina* tubes consisted principally of organic materials, with only weak biomineralization. Nonetheless, because *Cloudina* fossils differ in diagenetic behavior from encompassing (originally) aragonitic cements, Grant (1990) proposed they precipitated skeletons of Mg calcite—not the aragonite favored by the physical chemistry of surrounding seawater.

Namacalathus constitutes a second calcified animal that was common in terminal Proterozoic reefs (Figure 4D; Grotzinger et al. 2000). Goblet-shaped fossils up to 2 cm across again suggest a broadly cnidarian biology, although *Namacalathus* continues the theme of problematic relationships established by Ediacaran remains and *Cloudina*. As in *Cloudina*, walls were thin and somewhat flexible, suggesting light and perhaps discontinuous calcification, as by spicules or granules. Many specimens are preserved by void-filling cement, but locally unique overgrowth of outer surfaces by euhedral calcite crystals may suggest original calcitic biomineralization.

Thin calcified plates also occur in terminal Proterozoic platform carbonates of Namibia. A general resemblance to Squamariacean red algae and the possible preservation of conceptacles led Grant et al. (1991) to interpret these fossils as rhodophytes, but like much else in terminal Proterozoic paleontology, this interpretation remains uncertain. More promising, Wood et al. (2002) recently described well skeletonized modular fossils that grew in fissures within Namibian reefs. Christened *Namapoikia*, these remains resemble chaetitid sponges or simple colonial cnidarians; petrology suggests originally aragonitic walls. Finally, latest Proterozoic strata from Siberia and Mongolia contain simple calcareous tubes called anabaritids and cambrotubulids, as well as clusters of siliceous spicules precipitated by early sponges (Brasier et al. 1997).

The diversity of skeletal organisms in terminal Proterozoic successions remains to be documented fully, but it will never be high. On the other hand, the *total* diversity of latest Proterozoic animals was also low, and so the *proportional* representation of skeleton-formers seems not too different from that of the Cambrian Burgess Shale or, for that matter, modern oceans. By the end of the Proterozoic Eon, animals had evolved the physiological pathways required to make skeletons of calcite, aragonite, and silica. Nascent predation may have favored the evolution of mineralized skeletons—Bengtson and Yue (1992) have reported possible predator borings in well-preserved *Cloudina* specimens from China. In light of this, it is surprising that the most heavily mineralized skeletons thus far known from terminal Proterozoic rocks are the modular fossils found in cryptic environments (fissures) within Namibian reef systems.

It is possible to elaborate on individual claims for Proterozoic biomineralization because there are so few of them. Other than the microscopic remains of siliceous scales, there is little evidence to suggest that skeletons played important functional roles before the latest Proterozoic Eon and none to suggest that they loomed large in Proterozoic carbonate and silica cycles. Skeletal biomineralization was part of the initial diversification of animals, but skeleton-forming metazoans began their rise to biological and biogeochemical prominence only during the next, explosive phase of diversity increase.

Biomineralization and the Cambrian explosion

The great watershed in skeletal evolution was the Cambrian Period, when mineralized skeletons appeared for the first time in many groups (see Cloud 1968; Lowenstam and Weiner 1989 for comprehensive reviews of early thinking on this subject). Various hypotheses propose that the Cambrian "explosion" was precipitated by environmental changes favoring skeletal biomineralization. There is, however, no geological evidence to support this conjecture, and, in any case, it isn't clear what physical event would facilitate

the broadly simultaneous evolution of carbonate, phosphatic, siliceous, and agglutinated skeletons in marine animals and protists. It has also been proposed that Cambrian rocks document an explosion of fossils, made apparent by robust skeletons, rather than a true diversification of animals in the oceans. Again, the growing record of latest Proterozoic fossils and trace fossils discourages this idea. More likely, as Bengtson (1994) has argued, the Cambrian diversification of mineralized skeletons was part and parcel of a broader Cambrian radiation of animal diversity, with increases in predation pressure favoring the evolution of protective armor.

Exceptionally well preserved Cambrian fossils such as those of the Burgess (Briggs et al. 1994) and Chengjiang (Chen and Zhou 1997) biotas show that, then as now, most animals did not precipitate mineralized skeletons; only about 15% of Burgess species formed skeletons that would be preserved in conventional fossil assemblages (Bengtson and Conway Morris 1992). Nonetheless, many clades did evolve mineralized skeletons (Figure 5), and these gave rise to the predominant fossil record of the past 500 million years. Skeletal diversity increased tremendously in the sponges, even though this clade must have differentiated from other animals before Ediacaran fossils first entered the record. The Cambrian diversity of siliceous spicules matches or exceeds anything known from subsequent periods (Bengtson et al. 1994; Dong and Knoll 1996), and the carbonate-precipitating archaeocyathids produced the first massively mineralized skeletons known from the geological record. Indeed, by virtue of their skeletal evolution, archaeocyathids qualify as the first metazoan reef formers, although many Cambrian build-ups remained predominantly microbial (Riding and Zhuravlev 1998; Rowland and Shapiro 2002).

Anabaritids, small calcitic tubes with three-fold symmetry found in basal Cambrian rocks, may have been cnidarian, but for the most part, Cambrian rocks contain only
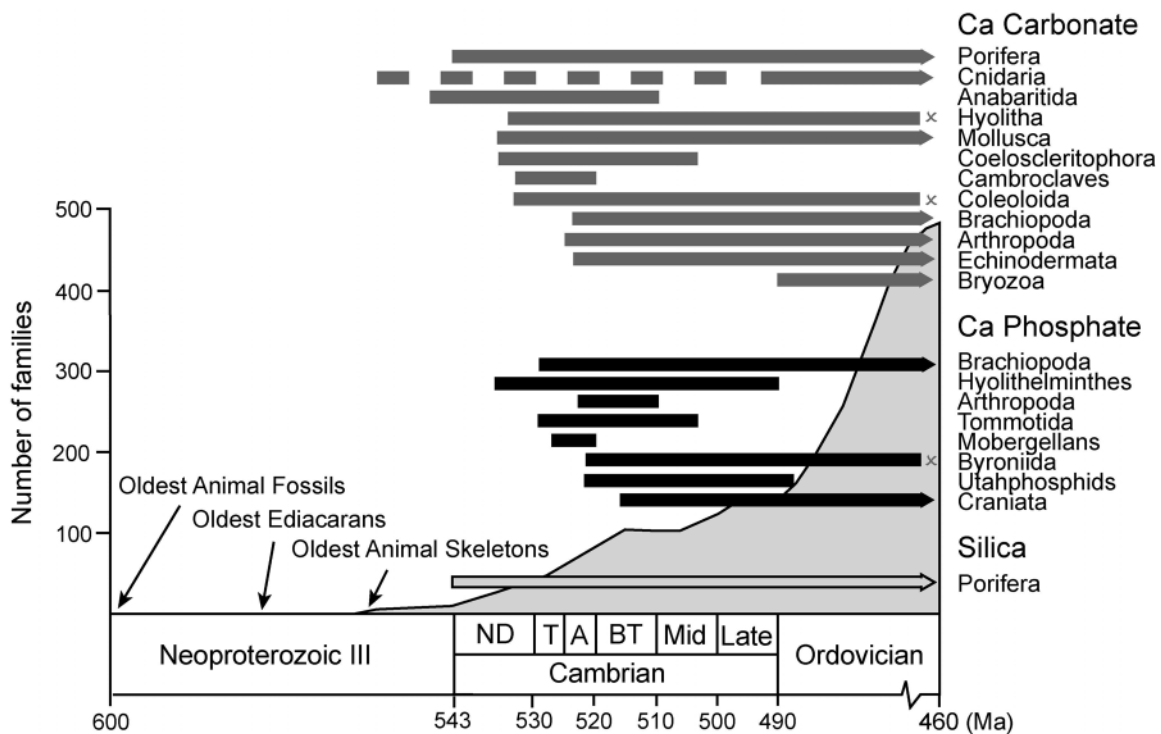
Figure 5. Summary of early skeleton evolution in metazoans, showing the diversity, skeletal mineralogy, and stratigraphic distribution of Cambro-Ordovician animals. Skeleton data modified from Bengtson and Conway Morris (1992); family diversity from Sepkoski (1982).

scattered records of cnidarian (or presumptive cnidarian) biomineralization (Debrenne et al. 1990). Thus, in contrast to their importance in subsequent periods, cnidarian skeletons are not a major feature of the Cambrian fossil record. Bilaterian skeletons are also scarce in lowermost Cambrian deposits, but over the first 25 million years of the period, they increased markedly in abundance and diversity. Earliest Cambrian bilaterians are dominated by extinct groups whose relationships to younger animals remain uncertain. By the end of the Early Cambrian, however, faunas included recognizable stem group members of many extant phyla and classes (Figure 5; Budd and Jensen 2000). Among protists, radiolarians first appear in Cambrian rocks (Dong et al. 1997; Won and Below 1999; Won and Iams 2002), as do agglutinated, but not calcified foraminiferans (McIlroy et al. 2001). Skeletons assigned to the dasyclad green algae have been reported from Cambrian carbonates in Siberia, but, by and large, algal skeletons are not a conspicuous feature of Cambrian rocks (Johnson 1966).

Functionally, Early Cambrian skeletons included spicules, sclerites, tubular and conical exoskeletons, bivalved shells, internal skeletons, and mineral-impregnated cuticle that molted as organisms grew—of the 178 distinct skeletal architectures recognized in marine animals by Thomas and Reif (1993), 89 are known to have appeared within the first 20 million years of the period, and by the Middle Cambrian fully 146 (80%) were present (Thomas et al. 2000). Craniate chordates were part of this mix (Shu et al. 1999), and of these the conodonts, at least, formed dermal bone in the form of tooth-like structures containing dentine (Donoghue et al. 2000). Other major innovations in the vertebrate skeleton postdated the Cambrian.

Many Early Cambrian skeletons are phosphatic, and in the past, this gave rise to speculation that phosphatic mineralization was favored by the chemistry of Early Cambrian oceans. Detailed investigations of preserved shell microstructure, however, show that the phosphate in most Early Cambrian fossils originated by the early diagenetic replacement of originally calcitic, aragonitic, or organic skeletons (e.g., Runnegar 1985; Kouchinsky 2000). Of course, some animals precipitated phosphatic skeletons, and this list includes a number of extinct clades in addition to lingulate brachiopods and craniates. Despite this, the proportional representation of phosphatic skeletons in Early Cambrian ecosystems was not very different from that of younger oceans (Bengtson and Runnegar 1992).

In summary:

(1) The evolution of mineralized skeletons in Cambrian organisms was not instantaneous. Only a few taxa occur in lowermost Cambrian rocks; skeletal abundance and diversity increased dramatically over the succeeding 25 million years.

(2) The body plans characteristic of most extant bilaterian phyla took shape over this same interval, although most Early and Middle Cambrian animals were stem and not crown group members of persistent phyla and classes. Skeletons evolved as principal components of some body plans, constraining the subsequent course of evolution in these clades. That so many different groups evolved mineralized skeletons during this time lends support to the hypothesis that animals deployed "off-the-shelf" biochemistry in skeletal evolution.

(3) All major skeletal biominerals were exploited during this radiation, as were most known skeletal architectures. The diversity of minerals employed in early skeletal evolution discourages the idea that changing ocean chemistry drove Cambrian evolution. Likewise, the fact that protists (including skeletonized protists) diversified along side animals, limits explanations that rely exclusively on developmental genetics (Knoll 1994). The diverse skeletons of Cambrian organisms share only one principal feature in common—they would have protected their owners against the bilaterian animal predators

that took shape during the Cambrian explosion. Thus, ecology must loom large in hypotheses to explain Cambrian biomineralization (Bengtson 1994). This does not preclude a role for physical change in early animal evolution, but does limit its specific application to the evolution of skeletons and skeletal chemistry. In general, Cambrian diversification likely reflects the interplay between genetic possibility and environmental opportunity, including new ecological opportunities introduced by both late Proterozoic increase in atmospheric oxygen tensions and strong carbon cycle perturbation at the Proterozoic-Cambrian boundary (Knoll 2003; Amthor et al. 2003).

An aside on later Cambrian oceans. Interestingly, mineralized skeletons are more apparent in Lower Cambrian sedimentary rocks than they are in many Middle and, especially, Upper Cambrian successions. Much Early Cambrian diversity was lost during major extinctions near the end of the age (Zhuravlev and Wood 1996). The massively calcified archaeocyathids dwindled to a handful of species, and trilobites underwent extensive turnover. Many of the small shelly taxa known from Lower Cambrian rocks disappeared as well, although the role of changing taphonomy in producing this pattern remains poorly known; Porter (2003) has shown that the diversity history of small shelly fossils closely matches the stratigraphic distribution of the phosphatized limestones in which they occur most abundantly. Phosphatized limestones diminished in abundance through later Cambrian time, taking with them the preservational window through which small shelly fossils are viewed.

Moderately mineralized trilobite carapaces and lingulate brachiopods are common in Upper Cambrian deposits, and viewed under the microscope, carbonate sands commonly contain abundant echinoderm debris. But diverse mollusks, calciate brachiopods, and well-preserved echinoderms—all known from older rocks and staples of the younger Paleozoic record—are not common. In contrast, stromatolites and thrombolites are widespread (Kennard and James 1986; Rowland and Shapiro 2002). Trace fossils and exceptional assemblages like the Burgess Shale tell us that diverse animals lived in later Cambrian oceans, and that quite a few of them were large—but large animals did not precipitate robust skeletons.

Rowland and Shapiro (2002) asked why metazoan-built reefs disappeared at the end of the Early Cambrian, a question that can be generalized to include all carbonate precipitating eukaryotes. In answer, they hypothesized that high temperatures and high P_{CO2} associated with a later Cambrian supergreenhouse inhibited carbonate biomineralization, especially by organisms with only limited capacity to buffer the fluids from which they precipitate skeletons. In terms of the framework presented here, this means that the environmentally dictated cost of precipitating carbonate skeletons is thought to have been high for all organisms and prohibitively high for groups such as calcareous sponges, cnidarians, and algae.

Rowland and Shapiro's (2002) innovative idea deserves careful testing by both biologists and Earth scientists. Geologists need to sharpen tools for paleoenvironmental reconstruction in the deep past, and they need to develop better data on the paleolatitudinal distribution of early skeleton-forming organisms. Berner and Kothavala's (2001) model of atmospheric carbon dioxide levels through Phanerozoic time is consistent with the Rowland/Shapiro scenario, as is the widespread distribution of carbonaceous shales in later Cambrian successions. Nonetheless, empirical constraints on Middle and Late Cambrian environmental conditions remain limited. Biologists need to provide better experimental data on the responses of skeletal physiology to elevated temperature and CO_2, measured across a phylogenetically wide range of organisms. Experiments prompted by current threats of global warming point the way (e.g., Langdon et al. 2000; Zondervan et al. 2001; see below).

The Ordovician radiation of heavily calcified skeletons

Although Cambrian evolution produced diverse body plans, species diversity within major clades remained low as the Ordovician Period began. But all this was about to change. During renewed Ordovician diversification, the global diversity of families and genera preserved as fossils increased three- to four-fold (Figure 5; Sepkoski 1982; Miller 1997), crown group members of major invertebrate phyla and classes came to dominate marine ecosystems, and the marine carbonate and silica cycles both came under substantial biomineralogical control.

Animal taxa that radiated during the Ordovician Period include sclerosponges and other new experiments in demosponge calcification; both tabulate and rugose corals; cephalopods, bivalves and gastropods; bryozoans; calciate brachiopods; crinoids and other echinoderms; and fish with dermal armor—establishing the fauna that would dominate oceans for the rest of the Paleozoic Era (Sepkoski and Sheehan 1986). Metazoan reefs returned to the oceans, skeletonized red and green algae became widespread, and radiolarians expanded dramatically, firmly establishing biological control over the marine silica cycle (Maliva et al. 1989; Racki and Cordey 2000). Moreover, both maximum size (e.g., Runnegar 1987) and skeletal mass increased in many groups.

Again, it is helpful to frame these observations in terms of evolutionary costs and benefits. The physiological cost of precipitating such massive skeletons must have been high, although, if, as noted above, Late Cambrian environmental conditions made the costs of carbonate skeletons prohibitive, then relaxation of those conditions might have contributed to Ordovician radiation. In any event, the phylogenetically broad evolution of robust skeletons as part of an overall increase in biological diversity once again suggests that an upward ratcheting of predation pressure contributed to the observed evolutionary pattern; important new predators included nautiloid cephalopods and starfish. (Increase in skeleton mass is a biomechanical requirement of increased body size but cannot explain why groups like corals and bryozoans evolved robust carbonate skeletons *de novo*.) Miller (1997) pointed out that Ordovician diversification took place in the context of increasing tectonic activity and by implication, therefore, increased nutrient flux to the oceans. Increasing nutrient status would certainly help to explain increased body size and predation in Ordovician oceans (see Vermeij 1995 and Bambach 1999 for arguments why this should be so).

Permo-Triassic extinction and its aftermath

The end of an era. For most of the Permian Period, marine biology looked much as it had in for the preceding two hundred million years. Large, well-skeletonized sponges, rugose and tabulate corals, calciate brachiopods, mollusks, and stenolaemate bryozoans characterized benthic communities, while radiolarians contributed a skeletal component to the plankton. Calcified algae played important roles in carbonate build-ups on continental shelves and platforms (Samankassou 1998; Wahlman 2002), and—in contrast to most earlier Paleozoic reefs—so did non-skeletal cementstones, precipitated at least in part under microbial influence in reef cavities and on the seafloor (Grotzinger and Knoll 1995; Weidlich 2002). Evidently, Permian seawater was highly oversaturated with respect to calcium carbonate minerals, a circumstance related in part to low sea levels and, consequently, limited shelf area for skeleton-forming benthos (Grotzinger and Knoll 1995). Despite the broad Paleozoic continuity of the marine biota, several important innovations in skeletal evolution did occur after the Ordovician radiation. By the Devonian Period, foraminiferans had evolved the capacity to precipitate calcitic tests, allowing benthic forams, especially the large, symbiont-bearing fusulinids, to emerge as

major carbonate producers in Late Paleozoic seaways (Culver 1993). And vertebrates evolved phosphatized post-cranial skeletons, providing, among other things, biomechanical support for the colonization of land (Clack and Farlow 2002).

It was not to last. Mass extinction at the end of the Permian Period devastated Paleozoic ecosystems. More than half of all invertebrate families, and perhaps ninety percent or more of existing species, perished in the oceans (Raup 1979; Erwin et al. 2002), and both tetrapods and vascular plants suffered substantial losses on land (Maxwell 1992; Looy et al. 2001). Recent geochronologic data suggest a rapid pulse of extinction (Jin et al. 2000), precipitated by some discrete event or cascade of events (Bowring et al. 1998). Debate continues, however, about both the physical trigger(s) for the extinction and the physiological mechanisms that induced mortality on such a vast scale.

The reason for considering end-Permian mass extinction in a discussion of biomineralization is that extinction and survival at the Permo-Triassic boundary show a pattern of strong selectivity with respect to skeletal physiology. Knoll et al. (1996) asked whether catastrophically high carbon dioxide levels could have furnished a kill mechanism for Permo-Triassic mass extinction. The standard geological approach to such a problem is to search in boundary rocks for geochemical evidence of elevated CO_2, but Knoll and colleagues looked, instead, for physiologically informative pattern in the fossil records of animals that did or did not survive the extinction. Consulting the large experimental literature on hypercapnia in both tetrapods and marine invertebrates, they articulated paleontologically recoverable traits of physiology, anatomy, functional biology, and ecology that correlate with vulnerability to or tolerance for elevated CO_2 levels. From these data, they developed a set of predictions about extinction and survival at the Permo-Triassic boundary.

Within the marine realm, animals with active circulation and elaborated gills (or lungs) for gas exchange compensate for elevated P_{CO2} better than organisms that lack these features. Also, animals that normally experience high internal P_{CO2}, including infauna and metazoans capable of exercise metabolism at high rates, tolerate experimental increases in carbon dioxide differentially well. And among animals that form skeletons of calcium carbonate, species that can exert physiological control over the pH balance of the fluids from which minerals are precipitated fare better than those with limited buffering capacity. Based on these features, Knoll et al. (1996) divided the Late Permian marine fauna into two groups, with high and low expected survival, respectively. As predicted, 81% of genera in the "vulnerable" group disappeared at the boundary, while only 38% of nominated "tolerant" genera became extinct (Figure 6A). The selectivity is even more pronounced when skeletal physiology is considered alone (Figure 6B; Bambach and Knoll, in preparation). Fully 88% of genera disappeared in groups that formed massive carbonate skeletons but had limited capacity to buffer fluids (sponges, cnidarians, bryozoans, calciate brachiopods). In contrast, groups that built skeletons of materials other than calcium carbonate lost only about 10% of their genera. Intermediate taxa—groups like mollusks that have a substantial commitment to carbonate skeletons but some physiological capacity to regulate the chemistry of internal fluids—lost 53% of their genera. Of these, those genera considered vulnerable on the basis of the other criteria noted above went extinct at twice the rate of those otherwise considered tolerant.

To a first approximation, then, Late Permian extinction in the oceans is about biomineralization. Specifically, it appears that the metabolic cost—and for some organisms, even the metabolic feasibility—of building $CaCO_3$ skeletons changed catastrophically at the Permo-Triassic boundary. Most proposed explanations for end-Permian mass extinction do not predict this. Indeed, while oxygen starvation and nutrient collapse, two commonly favored kill mechanisms, can explain the prevalence of small
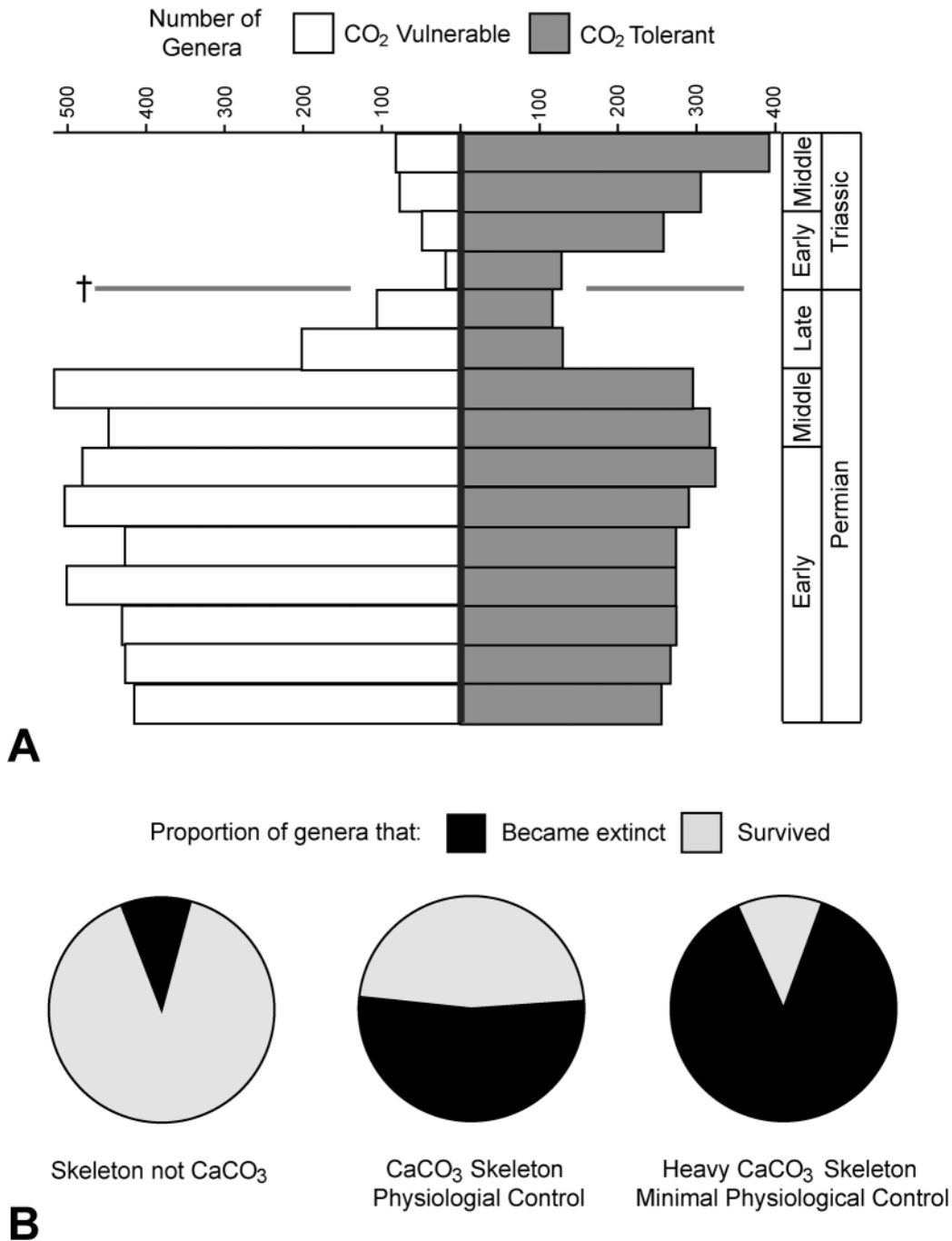
Figure 6. Summary of extinction and survival associated with Permo-Triassic mass extinction, as seen from the perspective of anatomy and physiology. (A) Permian and Early to Middle Triassic diversity of genera within groups predicted to be vulnerable to physiological disruption by rapid increase in carbon dioxide levels (white bars—includes calcifying sponges, corals, brachiopods, bryozoans, echinoderms, and calcareous foraminiferans) and groups predicted to be relatively tolerant to hypercapnic stress (shaded bars—includes mollusks, arthropods, chordates, and protists without $CaCO_3$ skeletons). Note that both absolute genus richness and proportional diversity change across the P-Tr boundary (marked by the cross). Pre-boundary Late Permian diversity decline reflects both true extinction at the end of the Middle Permian and the Signor Lipps effect, a backward smearing of last appearances caused by record loss. Redrawn from Knoll et al. (1996). (B) The relationship between skeletal physiology and Permo-Triassic extinction (Bambach and Knoll, in prep).

sizes in Early Triassic animals, they make biological predictions about extinction selectivity that run counter to the pattern actually observed (Bambach and Knoll in preparation). Moreover, catastrophic carbon dioxide increase provides two distinct kill mechanisms—direct physiological inhibition of metabolism and climate change associated with greenhouse enhancement—so CO_2 increase at the boundary is consistent with both terrestrial and marine patterns of extinction. Other, as yet unarticulated, environmental perturbations may account for observed patterns of extinction equally well, but for now, carbon dioxide deserves a prominent place on the short-list of plausible kill mechanisms. Accepting this, we can ask what sort of trigger could introduce lethal amounts of CO_2 into the atmosphere and surface oceans. Knoll et al. (1996) favored catastrophic overturn of anoxic deep waters, but this idea has not generated widespread enthusiasm among oceanographic modelers. Oxidation of methane released catastrophically from hydrates on the continental shelf and slope might also be suggested, but isotopic constraints on the volume of methane that could have been released suggest that by itself this mechanism cannot provide the necessary trigger (Berner 2002). The same problem applies to carbon dioxide release associated with extensive continental basalt eruption at the Permo-Triassic boundary. The wild card that remains is bolide impact, an attractive mechanism for which empirical evidence remains controversial (Becker et al. 2001; Kaiho et al. 2001; Verma et al. 2002).

Delayed rediversification of the marine fauna. The Early Triassic aftermath of end-Permian mass extinction poses its own set of questions, some of which potentially provide new perspective on the extinction event itself. Given the magnitude of biological disturbance, it is not surprising that basal Triassic rocks are paleontologically depauperate. What is surprising is that the exceptional features of the earliest Triassic biosphere persisted for four to six million years; true ecosystem recovery really didn't begin until the Middle Triassic (Erwin 2001).

Early Triassic marine diversity was lower than at any previous time since the Cambrian Period. Characteristically, Early Triassic faunas consist of small, lightly skeletonized survivors, many with apparently cosmopolitan distributions (Schubert and Bottjer 1995; Rodland and Bottjer 2001). The gastropods, bivalves, and ostracodes found in local abundance in Lower Triassic carbonates are commonly only 1–2 mm long (Lehrmann et al. 2003); ammonoid cephalopods and calciate brachiopods were similarly small and thin walled. Echinoderm debris formed bioclastic sands, but individual crinoid columnals and skeletal plates are tiny. Calcified red and green algae were important carbonate producers in both Late Permian and later Triassic seaways, but with one high paleolatitude exception (Wignall et al. 1998), neither is known from Lower Triassic rocks (Flügel 2002). Similarly, all Paleozoic corals disappeared by the end of the Permian, and the scleractinian corals that would rise to ecological prominence in Mesozoic and Cenozoic ecosystems appear only in Middle Triassic rocks (Stanley 2003), apparently evolving carbonate skeletons *de novo* in at least two distinct actinarian stocks (Romano and Cairns 2000). Thus, no metazoan or algal reefs are known from Lower Triassic rocks. In contrast, microbialites and precipitated carbonates less obviously formed under microbial influence are relatively widely distributed (Schubert and Bottjer 1992; Baud et al. 1997; Kershaw et al. 2002; Lehrmann et al. 1993).

The paucity of skeletal remains doesn't mean that carbonates are rare in Lower Triassic successions; in fact Lower Triassic limestones and dolomites are widespread and regionally thick. Facies development, however, resembles that of Neoproterozoic basins, as well as Upper Cambrian successions that have similarly limited contributions from skeletal algae and animals—carbonate mudstones, generated at least in part by whitings, and oolites occur along with the microbialites noted in the previous paragraph.

CO_2-induced decrease in the saturation state of sea water must, therefore, have been transient, pointing to more directly physiological limitations on calcification.

During the Anisian Age of the Middle Triassic, large, robustly skeletonized floras and faunas reappeared globally. Ecological networks were reestablished in the oceans, but in novel ways which insured that subsequent evolution would travel new paths (Bambach et al. 2002). New reefs were, at first, dominated by *Tubiphytes*, an unusual fossil formed by (?)bacterially induced carbonate encrustation of algae and perhaps other non-skeletal organisms (Senowbari-Daryan and Flügel 1993). Soon, however, scleractinian corals emerged along with both coralline and siliceous sponges as major framework builders (Flügel 2002; Stanley 2003). Biological reorganization was seeded in the plankton as well as the benthos, paving the way for one last momentous change in skeletal evolution.

Two Mesozoic revolutions

A revolution of marine animals. In 1977, Geerat Vermeij outlined what he called the "Mesozoic marine revolution," a change of guard in skeletal faunas, driven by step-wise increase in the abundance and mechanical strength of shell crushing predators. Vermeij's ecological research had convinced him that in marine gastropods, both shell strength and probability of shell damage varied biogeographically with the crushing strength of claws sported by predatory crabs. His insight was to observe that gastropod shell strength also varied in time: beginning in the Cretaceous Period and accelerating toward the present, gastropod taxa with stronger, more highly ornamented, and more readily remodeled shells replaced earlier evolved forms. Other marine groups from coralline red algae to echinoids also changed in ways that reduced their vulnerability to shell-crushing predators. Among bivalves, infaunal groups capable of avoiding predators by burrowing diversified markedly during the Cretaceous and Cenozoic, while epifaunal taxa withdrew to protected environments or disappeared entirely (Stanley 1975).

What predators radiated during this interval? The list includes crabs, lobsters, stomatopods, shell crushing sharks and rays, teleost fish, and shore birds, not to mention naticid and other gastropods that drill through shells to reach their prey (Vermeij 1977). Bambach (1993) has argued that Mesozoic and Cenozoic marine animals were larger and more nutritious than their Paleozoic forebears—Devonian New Englanders would doubtfully have prepared trilobite boils and brachiopod bakes—and that this evolutionary change in the nutritional quality of prey might have facilitated predator evolution. The problem, also noted by Bambach, is one of timing. The shift toward larger and more energetic animals was set in place by selective extinction at the Permo-Triassic boundary and subsequent recovery, but Vermeij's marine revolution took hold only in mid-Cretaceous times, some 150 million years later. Thus, while overall changes in the prey biota may have been necessary for Mesozoic marine revolution, they were probably not sufficient. That so many distinct classes of predator should have diversified at the same time suggests, once again, that some enabling environmental change began 100 million years ago. Bambach (1993, 1999) proposed that the radiation of flowering plants brought more nutrients to continental shelves and platforms. The nutritional quality of angiosperms (N:C) is, on average, higher than that of ferns and other seed plants (Midgley et al. 2002). Moreover, the specialized chemical defenses that flowering plants produce tend to be synthesized in lower concentrations than the more general feeding deterrents characteristic of gymnosperms and ferns (Rhoades 1979), further enhancing the food quality of angiosperm debris. At the same time, Cretaceous and Cenozoic orogenesis increased the mean elevation of continents, increasing weathering rates (Huh and Edmond 1999) and so fueling increased productivity in coastal oceans. Furthermore, both flowering plants (especially sea grasses) and kelps radiated in late Cretaceous and

Cenozoic oceans, providing new in situ resources for animals. In consequence, marine communities may have come to support a new tier of top predators, including shell crushing animals that drove adaptive change in the skeletal biology of prey organisms.

A revolution of marine phytoplankton. A second Mesozoic marine revolution took place in the planktonic realm. For more than three billion years, primary production in the oceans had been dominated by organisms bearing chlorophyll a (cyanobacteria) or chlorophyll a+b (green algae). Beginning at the time of Middle Triassic recovery from end-Permian events, however, phytoplankton containing chlorophyll a+c began to spread, and by the end of the era, three groups—the dinoflagellates, diatoms, and coccolithophorids—would come to dominate the oceans (Falkowski et al. in press). The reasons for this photosynthetic change of guard remain a subject for debate, although the distinct trace metal requirements of Chl a+c algae relative to greens and cyanobacteria may have favored evolutionary replacement in increasingly well oxidized Mesozoic oceans (Quigg et al. in press). Whatever its causes, the phytoplankton revolution stands as a major episode in the history of biomineralization because two groups, the coccolithophorids and the diatoms, rose to biogeochemical dominance in the marine carbonate and silica cycles, respectively.

Dinoflagellates were the first Chl a+c group to diversify. Preserved biomarker molecules suggest that the dinoflagellates existed in Neoproterozoic and Paleozoic oceans (Summons and Walter 1990; Moldowan and Talyzina 1998), although morphologically diagnostic microfossils have not been identified to date. Unambiguous dinoflagellate fossils enter the record in modest diversity during the Middle Triassic (Fensome et al. 1996), in concert with a major increase in dinoflagellate biomarkers in sedimentary organic matter (Moldowan et al. 1996). Species diversity increased by an order of magnitude during the second half of the Jurassic Period, mostly due to the radiation of a single family, the Gonyaulacaceae (Fensome et al. 1996). Cretaceous radiation of a second family, the Peridiniaceae, brought the group to its late Cretaceous diversity acme. Biomineralization within the group, however, never expanded beyond calcareous cysts in a few lineages.

Coccolithophorids similarly show modest Triassic origins and later Mesozoic expansion to a late Cretaceous zenith (Siesser 1993). Unlike the dinoflagellates, however, coccolithophorids evolved calcitic skeletons made of minute scales called coccoliths (Young et al. 1999). The functional biology of coccoliths remains uncertain, although the apparent light dependence of calcification offers some support to hypotheses that tie calcification to CO_2 supply within cells (e.g., Anning et al. 1996). [One can generalize to state that our understanding of skeletal function, and, therefore, of the evolutionary benefits associated with skeletal biomineralization, varies inversely with size.] The ecological expansion of coccolithophorids, joined in the Middle Jurassic by planktonic foraminiferans with calcitic tests, changed the nature of carbonate deposition in the oceans. For the first time, a pelagic carbonate factory delivered carbonate sediments directly to the deep sea floor. Seafloor cementstones, common in later Triassic carbonate platforms, exit the record as coccolithophorids expand, suggesting that coccolithophorid evolution led to a global decrease in the saturation state of seawater with respect to carbonate minerals.

The third Chl a+c group, the diatoms, radiated later than the others, but expanded to unparalleled ecological success. Uncertainty plagues Rothpletz' (1896) report of diatoms in Middle Jurassic rocks, but unambiguous frustules occur in Lower Cretaceous marine rocks from many localities (Harwood and Nikolaev 1995). By late in the Cretaceous Period the group had both radiated in the oceans (Harwood and Nikolaev 1995) and colonized non-marine environments (Chacón-Baca et al. 2002). The fossil record suggests that diatom diversity has continued to expand up to the present (Barron 1993).

Nasselarian radiolaria also diversified in the Cretaceous and Tertiary, as did two additional silica precipitating groups. Silicoflagellates are chrysophyte algae with an internal skeleton of siliceous tubes. Ebridians also form internal skeletons of silica rods; they have sometimes been grouped with dinoflagellates, although recent ultrastructural data suggest euglenid affinities (Hargraves 2002). Regardless of the expanded diversity of silica-precipitating protists, however, diatoms account quantitatively for silica removal from modern seawater, limiting silica concentrations in surface waters to only a few parts per million (Wollast and Mackenzie 1983). The "diatomization" of the marine silica cycle left its mark on evolutionary pattern in other silica users. Cenozoic radiolarians, for example, show a pattern of decreasing use of silica in tests (Harper and Knoll 1974). Siliceous sponges, which had been major reef builders in Jurassic seas, largely vacated shelf environments (Maliva et al. 1989), and the morphological diversity of siliceous spicules decreased (Maldonado et al. 1999). Interestingly, when grown experimentally in waters with presumed pre-Cretaceous concentrations of dissolved silica, modern Mediterranean sponges precipitate spicules with morphologies not seen as fossils since the Mesozoic (Maldonado et al. 1999).

What, if any, links connect the two Mesozoic biological revolutions? Perhaps changing nutrient status and patterns of oceanographic circulation influenced marine life on continental shelves *and* in the open ocean. But compelling answers remain a distant prospect. To date, hardly anyone has even asked the question.

The future

With biological revolutions in animals and phytoplankton, the modern biology, ecology, and biogeochemistry of skeletal organisms in the oceans was in place. On land, the modern pattern emerged somewhat later, with the mid-Tertiary expansion of grasses. Annual production of siliceous phytoliths now rivals that of marine diatom frustules (Conley 2002), a biological expansion of silica use perhaps recorded most clearly in the changing tooth morphology of mammalian grazers (Janis 1995).

Today, however, one last revolution appears set to change the cost/benefit balance of carbonate skeletons in tropical oceans. Since the beginning of the industrial revolution, carbon dioxide levels in the atmosphere and surface ocean have been rising, and they may be rising too fast for some skeleton formers to adapt. (The deleterious effects of environmental change nearly always hinge as much on rates as they do on magnitude.) Increased carbon dioxide leads to a decrease in carbonate concentration, and hence in the saturation state of seawater with respect to calcite and aragonite (Gattuso and Buddemeier 2000; Andersson et al. 2003). In light of this, it is not surprising that experimental growth of coccolithophorids, red algae, and symbiont-bearing corals at CO_2 levels predicted for the next century resulted in pronounced downturns in calcification (Gattuso et al. 1998; Kleypas et al. 1998; Riebesell et al. 2000; Langdon et al. 2000; Marubini et al. 2003). As P_{CO_2} continues its rapid rise, the physiological cost of carbonate precipitation may once again become prohibitively high, especially for poorly buffered organisms like benthic algae and cnidarians—the same groups that suffered disproportionately at the end of the Permian Period. As they shed light on Earth's evolutionary past, then, experimental studies of growth in skeleton-forming organisms may illuminate the biological future that our grandchildren will inherit.

DISCUSSION AND CONCLUSIONS

From the proceeding sections, it should be clear that the fossil record is not simply a history of organisms preserved by virtue of their mineralized skeletons. The evolutionary fates of skeletonized animals, plants, and protists have actually been tied, in no small

measure, to the physiological pathways by which those skeletons formed. At least three times in the past 600 million years, increases in predation pressure have fueled evolutionary changes in both the phylogenetic distribution and the functional biology of mineralized skeletons. Environmental perturbations have also decreased, at least temporarily, the saturation state of the oceans with respect to calcite and aragonite, challenging organisms that have only limited physiological control over the fluids from which they precipitate carbonate skeletons.

The evolutionary influence of marine chemistry may go beyond selective extinction. Two decades ago, Sandberg (1983) recognized large scale secular variations in the carbonate chemistry of the oceans. During the earliest Cambrian, the mid-Mississippian to Middle Jurassic, and the last 35 million years, non-skeletal carbonates (ooids, penecontemporaneous cements) have been precipitated largely as aragonite and Mg-calcite. During the intervening intervals (late Early Cambrian to mid-Mississippian and Late Jurassic to the Oligocene), non-skeletal carbonates formed predominantly as calcite. Sandberg (1983) ascribed this geological pattern to secular variations in P_{CO2}, but Stanley and Hardie (1998) have argued instead that seawater Mg/Ca, itself governed by hydrothermal ridge activity, controls the mineralogy of carbonate precipitation in the oceans. Moreover, Stanley and Hardie (1998) noted that the skeletal mineralogy of major carbonate producers has varied through time in synchrony with the pattern of non-skeletal precipitation (Fig. 7). In the Paleozoic "calcite" sea, calcitic corals and sponges dominated reefs. During the ensuing "aragonitic" interval, however, major carbonate producers included aragonite-precipitating demosponges, algae, and scleractinian corals. Corals declined in distribution and ecological importance during the "calcitic" interval of the late Mesozoic and early Tertiary, but came back as principal reef builders when "aragonitic" conditions returned. In contrast, calcite use in coccoliths shows a polyphyletic decline from the Cretaceous to the present (Houghton 1991).

Some caveats are in order. Not all skeletal organisms appear to have noticed the oscillations in seawater chemistry. As Stanley and Hardie (1998) emphasized, it is specifically those organisms that precipitate massive skeletons under conditions of limited physiological control that show the predicted stratigraphic pattern. These of course, are the same groups that suffered disproportionately at the end of the Permian and which were so conspicuously absent from Late Cambrian and Early Triassic seafloors. For carbonate producers, physiology is destiny.

Note also that ocean chemistry correlates with the initial appearances of sponges, cnidarians, and algal taxa, but not necessarily with the last appearances of individual clades. In this regard, it is important to recognize that there is no evidence for a secular shift in mineralogy within skeleton-forming lineages. The groups highlighted by Stanley and Hardie (1998) all belong to larger clades that also include non-calcifying taxa. Thus, apparent shifts from calcite to aragonite skeletons in corals, in sponges, and in red and green algae actually reflect extinction followed by the *de novo* evolution of mineralized skeletons from unmineralized ancestors. It appears that in the recruitment of macromolecules to guide *de novo* carbonate precipitation, natural selection favored molecules that would minimize the physiological cost of precipitation. [Minor element chemistry does not seem to be so rigorously controlled. When Stanley et al. (2002) grew coralline red algae in simulated Cretaceous sea water, the algae precipitated skeletons of low Mg calcite, as predicted for the Cretaceous "calcite" sea, rather than the Mg-calcite formed today. In red algae, templating macromolecules appear to govern the overall mineralogy of carbonate precipitation, but they do not stringently control cation incorporation into precipitated minerals.]
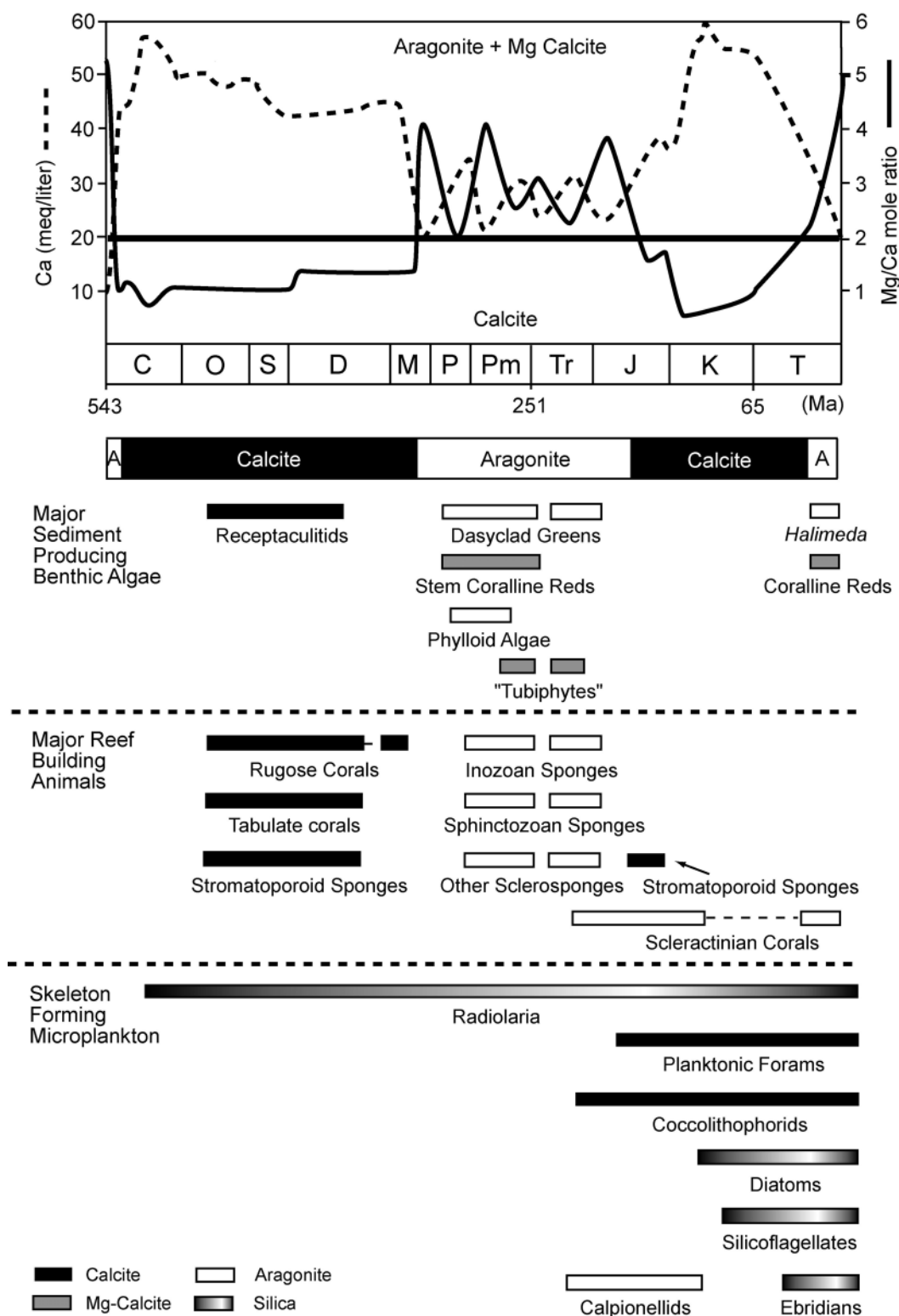
Figure 7. The stratigraphic relationship between ocean chemistry and skeletal mineralogy in major sediment producing benthic algae and animals, modified from Stanley and Hardie (1998). The figure shows Stanley and Hardie's (1998) estimates of Ca abundance and Mg/Ca in ancient oceans, as well as the principal time intervals dominated by "calcite" and "aragonite" seas. Aragonite and Mg-calcite are favored when the Mg/Ca mole ratio is above 2; calcite is favored at ratios below 2. Also shown are the time distributions of principal skeleton–forming protists; calpionellids are thought to be tintinnids with calcified tests (see text for references).

Harper et al. (1997) have claimed a role for seawater chemistry in the skeletal evolution of bivalved mollusks, but it is an influence of a different sort. Bivalves precipitate skeletal minerals from physiologically controlled fluids, so environmental influence on shell formation is not at issue. But for epifaunal bivalves, carbonate dissolution potentially weakens shells, thereby increasing the success rates of predators. Ancestral bivalves secreted aragonitic shells, but through time epifaunal bivalves show a pattern of increasing calcite use in shell laminae—a propensity that is potentially counterintuitive, given the superior mechanical strength of aragonite. Noting that infaunal bivalves show no comparable trend, Harper et al. (1997) proposed that the evolutionary pattern of increasing calcite incorporation was driven by calcite's greater resistance to dissolution, especially during the long Paleozoic and Mesozoic intervals of "calcite" oceans.

From the examples presented here, it can be seen that a number of key events in the history of life reflect the changing costs and benefits of skeletal biomineralization. Paleontologists have identified principal patterns of skeletal evolution, and biologists have provided functional explanations of this pattern, at least for larger organisms. The challenge—and the opportunity—for the future is to link paleontological insights more firmly to the molecular biology and physiology of skeletal biomineralization and to the physical history of the biosphere.

ACKNOWLEDGMENTS

REFERENCES

Aizawa K, Miyachi S (1986) Carbonic anhydrase and carbon concentrating mechanisms in microalgae and cyanobacteria. FEMS Microbiol Rev 39:215–233

Allison CW, Hilgert JW (1986) Scale microfossils from the early Cambrian of northwest Canada. J Paleontol 60:973–1015

Amthor JE, Grotzinger JP, Schroder S, Bowring SA, Ramezani J, Martin MW, Matter A (2003) Extinction of *Cloudina* and *Namacalathus* at the Precambrian-Cambrian boundary in Oman. Geology 31:431–434

Andersson AJ, Mackenzie FT, Ver LM (2003) Solution of shallow-water carbonates: An insignificant buffer against rising atmospheric CO_2. Geology 31:513–516

Anning T, Nimer N, Merrett MJ, Brownlee C (1996) Costs and benefits of calcification in coccolithophorids. J Mar Systems 9:45–56

Baldauf SL (2003) The deep roots of eukaryotes. Science 300:1703–1706

Bambach RK (1993) Seafood through time: changes in biomass, energetics, and productivity in the marine ecosystem. Paleobiology 19:372–397

Bambach RK (1999) Energetics in the global marine fauna: a connection between terrestrial diversification and change in the marine biosphere. Geobios 32:131–144

Bambach RK, Knoll AH (in review) Physiological selectivity during the end-Permian mass extinction. Earth Planet Sci Lett

Bambach RK, Knoll AH, Sepkoski JJ (2002) Anatomical and ecological constraints on Phanerozoic animal diversity in the marine realm. Proc Nat Acad Sci USA 99:6854–6859

Barron JA (1993) Diatoms. *In:* Fossil Prokaryotes and Protists. Lipps J (ed) Blackwell Scientific, Oxford, p 155–167

Baud A, Cirilli S, Marcoux J (1997) Biotic response to mass extinction: the lowermost Triassic microbialites. Facies 36:238–242

Becker L, Poreda RL, Hunt AG, Bunch TE, Rampino M (2001) Impact event at the Permian-Triassic boundary: evidence from extraterrestrial gases in fullerenes. Science 291:1530–1533

Bengtson S (1994) The advent of animal skeletons. *In*: Early Life on Earth, Nobel Symposium 84. Bengtson S (ed) Columbia University Press, New York, p 421–425

Bengtson S, Conway Morris S (1992) Early radiation of biomineralizing phyla. *In*: Origin and Early Evolution of the Metazoa. Lipps JH, Signor PW (eds) Plenum, New York, p 447–481

Bengtson S, Runnegar B (1992) Origins of biomineralization in metaphytes and metazoans. *In*: The Proterozoic Biosphere: A Multidisciplinary Study. Schopf JW, Klein C (eds) Cambridge University Press, Cambridge, p 447–451

Bengtson S, Yue Z (1992) Predatorial borings in late Precambrian mineralized xoskeletons. Science 257:267–369

Bengtson S, Conway Morris S, Cooper BJ, Jell PA, Runnegar BN (1990) Early Cambrian fossils from South Australia. Mem Assoc Australas Palontol 9:1–364

Berner RA (2002) Examination of hypotheses for the Permo-Triassic boundary extinction by carbon cycle modeling. Proc Nat Acad Sci USA 99:4172–4177

Berner RA, Kothavala Z (2001) GEOCARB III: A revised model of atmospheric CO_2 over Phanerozoic time. Am J Sci 301:182–204

Bowring SA, Erwin DH, Jin YG, Martin MW, Davidek K, Wang, W (1998) U/Pb zircon geochronology and tempo of the end-Permian mass extinction. Science 280:1039–1045

Brasier M, Green O, Shields G (1997) Ediacaran sponge spicule clusters from southwestern Mongolia and the origins of the Cambrian fauna. Geology 25:303–306

Briggs DEG, Erwin DH, Collier FJ (1994) The Fossils of the Burgess Shale. Smithsonian Institution Press, Washington

Brocks JJ, Logan GA, Buick R, Summons RG (1999) Archean molecular fossils and the early rise of eukaryotes. Science 285:1033–1036

Budd GE, Jensen S (2000) A critical reappraisal of the fossil record of the bilaterian phyla. Biol Rev 75:253–295

Butterfield NJ (2000) *Bangiomorpha pubescens* n. gen., n. sp; implications for the evolution of sex, multicellularity, and the Mesoproterozoic/Neoproterozoic radiation of eukaryotes. Paleobiology 26:386–404

Butterfield NJ (2002) A *Vaucheria*-like fossil from the Neoproterozoic of Spitsbergen. Geol Soc Am Abstr Progr 34:169

Butterfield NJ, Knoll AH, Swett K (1994) Paleobiology of the Upper Proterozoic vanbergfjellet Formation, Spitsbergen. Fossils and Strata 34:1–84

Carter JG (ed) (1990) Skeletal Biomineralization, Patterns, Processes and Evolutionary Trends. Van Nostrand Reinhold and Company, NewYork

Chacón-Baca E, Beraldi-Campesi H, Knoll AH, Golubic S, Cevallos-Ferriz SR (2002) 70 million year old non-marine diatoms from northern Mexico. Geology 30:279–281

Chen J, Zhou G (1997) Biology of the Chengjiang fauna. Bull Nat Mus Nat Sci (Taiwan) 10:11–106

Clack JA, Farlow (2002) Gaining Ground: The Origin and Early Evolution of Tetrapods. Indiana University Press, Bloomington, Indiana

Cloud PE (1968) Pre-metazoan evolution and the origins of the Metazoa. *In*: Evolution and Environment. Drake T (ed) Yale University Press, New Haven, p 1–72

Conley DJ (2002) Terrestrial ecosystems and the global biogeochemical silica cycle. Global Biogeochem Cycles 16(4):1121, doi:10.1029/2002GB001894

Conway Morris S, Mattes BW, Chen M (1990) The early skeletal organism *Cloudina*: new occurrences from Oman and possibly China. Am J Sci 290A:245–260

Culver SJ (1993) Foraminifera. *In*: Fossil Prokaryotes and Protists. Lipps J (ed) Blackwell Scientific, Oxford, p 203–247

Debrenne F, Lafuste J, Zhuravlev A (1990) Coralomorphes et spongiomorphes á l'aube du Cambrien. Bull Mus Natn Hist Nat Paris, 4e Sér 12(sec C, nr 1):17–39

Dong X, Knoll AH (1996) Middle and Late Cambrian sponge spicules from Hunan, China. J Paleontol 70:173–184

Dong X, Knoll AH, Lipps J (1997) Late Cambrian radiolaria from Hunan, China. J Paleontol 71:753–758.

Donoghue PCJ, Forey PL, Aldridge RJ (2000) Conodont affinity and chordate phylogeny. Biol Rev 75:191–251

Erwin DH (2001) Lessons from the past: biotic recoveries from mass extinctions. Proc Nat Acad Sciences USA 98:5399–5403

Erwin DH, Bowring SA, Jin YG (2002) End-Permian mass extinctions: a review. Geol Soc Am Spec Papers 356: 363–383

Falkowski PG, Schofield O, Katz ME, van Schotteberge B, Knoll AH (in press) Why is the land green and the ocean red? *In*: Coccolithophores: From Molecular Process to Global Impact. Thierstein H, Young JR (eds) Springer Verlag, Heidelberg

Fensome RA, MacRae RA, Moldowan JM, Taylor FJR, Williams GL (1996) The early Mesozoic radiation of the dinoflagellates. Paleobiology 22:329–338

Flügel E (2002) Triassic reef patterns. *In*: Phanerozoic Reef Patterns, SEPM Special Publication 72. Kiessling W, Flügel, Golonka J (eds) SEPM Press, Tulsa, Oklahoma, p 391–463

Gattuso J-P, Buddemeier RW (2000) Calcifcation and CO_2. Nature 407:311–312

Gattuso J-P, Frankignoulle M, Bourge I, Romaine S, Buddemeier RW (1998) Effect of calcium carbonate saturation of seawater on coral calcification. Global Planet Change 18:37–46

German TN (1990) Organic World One Billion Year Ago. Nauka, Leningrad

Germs GJB (1972) New shelly fossils from Nama Group, South West Africa. Am J Sci 272:752–761

Gibbs PE, Bryan GW (1984) Calcium phosphate granules in muscle cells of *Nephtys* (Annelida, Polychaeta)—a novel skeleton? Nature 310:494–495

Giribet G (2002) Current advances in the phylogenetic reconstruction of metazoan evolution: a new paradigm for the Cambrian explosion? Mol Phylogenet Evol 23:345–357

Gotliv BA, Addadi L, Weiner S (2003) Mollusk shell acidic proteins: in search of individual functions. Chembiochem 4:522–529

Grant SWF (1990) Shell structure and distribution of *Cloudina*, a potential index fossil for the terminal Proterozoic. Am J Sci 290A:261–294

Grant SWF, Knoll AH, Germs GJB (1991) A probable calcified metaphyte from the latest Proterozoic Nama Group, Namibia. J Paleontol 65:1–18

Grey K, Williams IR (1990) Problematic bedding-plane markings from the Middle Proterozoic Manganese Subgroup, Bangemall Basin, Western Australia. Prec Res 46:307–328

Grotzinger JP (1989) Facies and evolution of Precambrian carbonate depositional systems: emergence of the modern platform archetype. *In*: Controls on Carbonate Platform and Basin Development. SEPM Special Publication 44. Crevello PD, Wilson JL, Sarg JF, Read JF (eds) SEPM Press, Tulsa, Oklahoma, p 79–106

Grotzinger JP, Knoll AH (1995) Anomalous carbonate precipitates: Is the Precambrian the key to the Permian? Palaios 10:578–596

Grotzinger JP, Knoll AH (1999) Proterozoic stromatolites: evolutionary mileposts or environmental dipsticks? Ann Rev Earth Planet Sci 27:313–358

Grotzinger JP, Watters W, Knoll AH (2000) Calcareous metazoans in thrombolitic bioherms of the terminal Proterozoic Nama Group, Namibia. Paleobiology 26:334–359

Hagadorn JW, Bottjer DJ (1997) Wrinkle structures: microbially mediated sedimentary structures in siliciclastic settings at the Proterozoic-Phanerozoic transition. Geology 25:1047–1050

Hargraves PE (2003) The ebridian flagellates *Ebria* and *Hermesinum*. Plankton Biol Ecol 49:9–16

Harper EM, Palmer TJ, Alphey JR (1997) Evolutionary response by bivalves to changing Phanerozoic sea-water chemistry. Geol Mag 134:403–407

Harper HE, Knoll AH (1975) Silica, diatoms, and Cenozoic radiolarian evolution. Geology 3:175–177

Harwood DM, Nikolaev VA (1995) Cretaceous diatoms: morphology, taxonomy, biostratigraphy. *In*: Siliceous Microfossils, Short Courses in Paleontology 8. Blome CD, Whalen PM, Reed KM (eds) Paleontological Society, Tulsa OK, p 81–106

Horodyski RJ, Mankiewicz C (1990) Possible late Proterozoic skeletal algae from the Pahrump Group, Kingston Range, southeastern California. Am J Sci 290A:149–169

Houghton SD (1991) Calcareous nannofossils. *In*: Calcareous Algae and Stromatolites. Riding R (ed). Springer Verlag, Heidelberg, p 217–266

Huh Y, Edmond JM (1999) The fluvial geochemistry of the rivers of Eastern Siberia: III. tributaries of the Lena and Anabar draining the basement terrain of the Siberian Craton and the Trans-Baikal Highlands. Geochim Cosmochim Acta 63:967–987

Janis CM (1995) Correlations between craniodental morphology and feeding behavior in ungulates: reciprocal illumination between living and fossil taxa. *In:* Functional Morphology in Vertebrate Paleontology. Thomason JJ (ed) Cambridge University press, Cambridge, p 76–98

Javaux EJ, Knoll AH, Walter MR (2001) Ecological and morphological complexity in early eukaryotic ecosystems. Nature 412:66–69

Javaux E, Knoll AH, Walter MR (2003) Recognizing and interpreting the fossils of early eukaryotes. Origins Life Evol Biosphere 33:75-94

Jin YG, Wang Y, Wang W, Shang QH, Cao CQ, Erwin DH (2000) Pattern of marine mass extinction near the Permian-Triassic boundary in south China. Science 289:432–436

Johnson JH (1966) A review of Cambrian algae. Quart Colorado School Mines 61:1–162

Kaiho K, Kajiwara Y, Nakano T, Miura Y, Kawahata H, Tazaki K, Ueshima M, Chen ZQ, Shi GR (2001) End-Permian catastrophe by a bolide impact: Evidence of a gigantic release of sulfur from the mantle. Geology 29:815–818

Kennard JM, James NP (1986) Thrombolites and stromatolites: two distinct types of microbial structures. Palaios 1:492–503

Kershaw S, Guo L, Swift A, Fan J (2002) Microbialites in the Permian-Triassic boundary interval in central China: structure, age, and distribution. Facies 47:83–90

Kleypas JA, Buddemeier RW, Archer D, Gattuso J-P, Langdon C, Opdyke BN (1999) Geochemical consequences of increased atmospheric carbon dioxide on coral reefs. Science 284:118–120

Knoll AH (1994) Proterozoic and Early Cambrian protists: evidence for accelerating evolutionary tempo. Proc Nat Acad Sci USA 91:6743–6750

Knoll AH (2003) Life on a Young Planet: The First Three Billion Years of Evolution on Earth. Princeton University Press, Princeton NJ

Knoll AH, Semikhatov MA (1998) The genesis and time distribution of two distinctive Proterozoic stromatolite microstructures. Palaios 13:407–421

Knoll AH, Swett K (1990) Carbonate deposition during the late Proterozoic era: An example from Spitsbergen. Am J Sci 290A:104–132

Knoll AH, Bambach R, Canfield D, Grotzinger JP (1996) Comparative Earth history and late Permian mass extinction. Science 273:452–457

Knoll AH, Fairchild IJ, Swett K (1993) Calcified microbes in Neoproterozoic carbonates: implications for our understanding of the Proterozoic-Cambrian transition. Palaios 8:512–525

Kouchinsky A (2000) Shell microstructures in Early Cambrian mollusks. Acta Palaeontol Pol 45:119–150

Krasko, A, Lorenz B, Batel R, Schröder HC, Müller IM, Müller WEG (2000) Expression of silicatein and collagen genes in the marine sponge *Suberites domuncula* is controlled by silicate and myotrophin. Eur J Biochem 267:4878–4887

Krőger N, Sumper M (1998) Diatom cell wall proteins and the biology of silica biomineralization. Protist 149: 213–219

Krőger N, Deutzmann R, Bergsdorf C, Sumper M (2000) Species-specific polyamines from diatoms control silica morphology. Proc Nat Acad Sci USA 97:14133–14138

Krőger N, Lorenz S, Brunner E, Sumper M (2002) Self-assembly of highly phosphorylated silaffins and their function in silica morphogenesis. Science 298:584–586

Langdon C, Takahashi T, Sweeney C, Chipman D, Goddard J, Marubini F, Aceves H, Barnett H (2000) Effect of calcium carbonate saturation state on the calcification rate of an experimental coral reef. Global Biogeochem Cycles 14:639–654

Leadbetter BSC, Riding R (1986) Biomineralization in Lower Plants and Animals. The Systematics Association Special Volume 30. Clarendon Press, Oxford

Lehrmann DL, Payne JL, Felix SV, Dillett PM, Wang H, Yu Y, Wei J (2003) Permian-Triassic boundary sections from shallow-marine carbonate platforms of the Nanpanjiang Basin, south China: Implications for oceanic conditions associated with the end-Permian extinction and its aftermath. Palaios 18:138–152

Looy CV, Twitchett RJ, Dilcher DL, Konijnenburg-Van Cittert JHA, Visscher H (2001) Life in the end-Permian dead zone. Proc Nat Acad Sci USA 98:7879–7883

Lopez E, Vidal B, Berland S, Camprasse S, Camprasse G, Silve C (1992) Demonstration of the capacity of nacre to induce bone formation by human osteoblasts *in vitro*. Tissue and Cell 24:667–679

Lowenstam HA, Weiner S (1989) On Biomineraliztion. Oxford University Press, Oxford

Luo G, Ducy P, McKee MD, Pinero GJ, Loyer E, Behringer RR, Karsenty G (1997) Spontaneous self-calcification of arteries and cartilage in mice lacking matrix GLA protein. Nature 386:78–81

Maldonado M, Carmona MG, Uriz MJ, Cruzado A (1999) Decline in Mesozoic reef-building sponges explained by silicon limitation. Nature 401:785–788

MacLennan DH, Rice WJ, Green NM (1997) The mechanism of Ca^{2+} transport by sarco(endo)plasmic reticulum Ca^{2+}-ATPases. J. Biol Chem 272:28815–28818

Maliva R, Knoll AH, Siever R (1990) Secular change in chert distribution: a reflection of evolving biological participation in the silica cycle. Palaios 4:519–532

Marin F, Smith M, Isa Y, Muyzer G, Westbroek P (1996) Skeletal matrices, muci, and the origin of invertebrate calcification. Proc Nat Acad Sci USA 93:1554–1559

Marin F, Corstjens P, de Gaulejac B, de Vrind-de Jong EW, Westbroek P (2000) Mucins and molluscan calcification: molecular characterization of mucoperlin, a novel mucin-like protein from the nacreous layer of the fan mussel *Pinna nobilis* (Bivalvia, Pteriomorpha). J Biol Chem 275:20667–20675

Marubini F, Ferrier-Pages C, Cuif JP (2003) Suppression of skeletal growth in scleractinian corals by decreasing ambient carbonate-ion concentration: a cross-family comparison. Proc Royal Soc London B270:179–184

Maxwell MD (1992) Permian and Early Triassic extinction of non-marine tetrapods. Paleontology 35:571–583

McIlroy D, Green OR, Brasier MD (2001) Palaeobiology and evolution of the earliest agglutinated Foraminifera: *Platysolenites*, *Spirosolenites* and related forms. Lethaia 34:13–29

Midgley JJ, Midgley G, Bond WJ (2002) Why were dinosaurs so large? A food quality hypothesis. Evol Ecol Res 4:1093-1095

Miller AI (1977) Dissecting global diversity patterns: examples from the Ordovician radiation. Annu Rev Ecol Syst 28:85–104

Mishler BD, Lewis LA, Buchheim MA, Renzaglia KS, Garbary DJ, Delwiche CF, Zechman FW, Kantz TS, Chapman RL (1994) Phylogenetic relationships of the "green algae" and "bryophytes." Ann Missouri Bot Gard 81:451–483

Moldowan JM, Talyzina NM (1998) Biogeochemical evidence for dinoflagellate ancestors in the Early Cambrian. Science 281:1168–1170

Moldowan JM, Dahl J, Jacobson SR, Huizinga BJ, Fago FJ, Shetty R, Watt DS, Peters KE (1996) Chemostratigraphic reconstruction of biofacies: Molecular evidence linking cyst-forming dinoflagellates with pre-Triassic ancestors. Geology 24:159–162

Narbonne GM (1998) The Ediacaran biota: a terminal Proterozoic experiment in the evolution of life. GSA Today 8:1–7

Noffke N, Knoll AH, Grotzinger JP (2002) Sedimentary controls on the formation and preservation of microbial mats in siliciclastic deposits: a case study from the Upper Neoproterozoic Nama Group, Namibia. Palaios 17:533–544

Porter SM (in press) Closing the 'phosphatization' window: implications for interpreting the record of small shelly fossils. Paleobiology

Porter SM, Knoll AH (2000) Testate amoebae in the Neoproterozoic Era: evidence from vase-shaped microfossils in the Chuar Group, Grand Canyon. Paleobiology 26: 360–385

Porter SM, Meisterfeld R, Knoll AH (2003) Vase-shaped microfossils from the Neoproterozoic Chuar Group, Grand Canyon: a classification guided by modern testate amoebae. J Paleontol 77:205–225.

Quigg A, Finkel ZV, Irwin AJ, Rosenthal Y, Ho T-Y, Reinfelder JR, Schofield O, Morel FMM, Falkowski PG (2003) The evolutionary inheritance of elemental stoichiometry in marine phytoplankton. Nature 425:291-294

Racki G, Cordey F (2000) Radiolarian palaeoecology and radiolarites: is the present the key to the past? Earth Sci Rev 52:83–120

Rapp GS, Mulholland SC (1992) Phytolith Systematics: Emerging Issues. Plenum, New York

Raup DM (1979) Size of the Permo-Triassic bottleneck and its evolutionary implications. Science 206:217–218

Rasmussen B, Bengtson S, Fletcher IR, McNaughton NJ (2002) Discoidal impressions and trace-like fossils more than 1200 million years old. Science 296:1112–1115

Remane J (2000) International stratigraphic chart. International Union of Geosciences. IUGS Secretariat, Geological Survey of Norway, Trondheim, Norway

Reitner J, Wörheide, Lange R, Thiel W (1997) Biomineralization of calcified skeletons in three Pacific coralline demosponges—an approach to the evolution of basal skeletons. Cour Forch-Inst Senckenberg 201:371–383

Rhoades DR (1979) Evolution of plant chemical defense against herbivores. *In*: Herbivores: their interaction with secondary plant metabolites. Rosenthal GH, Janzen DH (eds) Academic Press, New York, p 3–54

Riding R, Zhuravlev AYu (1995) Structure and diversity of oldest sponge-microbe reefs: Lower Cambrian, Aldan River, Siberia. Geology 23:649–652

Riding R, Cope JCW, Taylor PD (1998) A coralline-like red alga from the lower Ordovician of Wales. Palaeontology 41:1069–1076

Riebesell U, Zondervan I, Rost B, Tortell PD, Zeebe RE, Morel FMM (2000) Reduced calcification of marine plankton in response to increased atmospheric CO_2. Nature 407:364–367

Rodland DL, Bottjer DJ (2001) Biotic recovery from the end-Permian mass extinction: behavior of the inarticulate brachiopod as a disaster taxon. Palaios 15: 95–101

Romano SL, Cairns SD (2000) Molecular phylogenetic hypotheses for the evolution of scleractinian corals. Bull Mar Sci 67:1043–1068

Rothpletz A (1896) Über die Flysch-Fucoiden und einige andere fossile Algen, sowie über liasische, Diatomeen führende Hörenschwämme. Deutsch Geol Ges 48:858–914

Rowland SM, Shapiro RS (2002) Reef patterns and environmental influences in the Cambrian and earliest Ordovician. *In*: Phanerozoic Reef Patterns, SEPM Special Publication 72. Kiessling W, Flügel, Golonka J (eds) SEPM Press, Tulsa, Oklahoma, p 95–128

Runnegar B (1985) Shell microstructures of Cambrian mollusks replicated by phosphate. Alcheringa 9:245–257

Runnegar B (1987) Rates and modes of evolution in the Mollusca. *In*: Rates of Evolution. Campbell KS, Day MF (eds) Allen and Unwin, London, p 39–60

Sandberg PA (1983) An oscillating trend in Phanerozoic non-skeletal carbonate mineralogy. Nature 305:19–22

Sanders D, Brownlee C, Harper JF (1999) Communicating with calcium. Plant Cell 11:691–706

Samankassou E (1996) Skeletal framework mounds of dasycladalean alga *Anthracoporella*, Upper Paleozoic, Carnic Alps, Austria. Palaios 13:297–300

Schubert JK, Bottjer DJ (1992) Early Triassic stromatolites as post-mass extinction disaster forms. Geology 20:883–886

Schubert JK, Bottjer DJ (1995) Aftermath of the Permian-Triassic mass extinction event: paleoecology of Lower Triassic carbonates in the western USA. Palaeogeogr Palaeoclimatol Palaeoecol 116:1–39

Senowbari-Daryan B, Flügel E (1993) *Tubiphytes* Maslov, an enigmatic fossil: classification, fossil record and significance through time, Part I: discussion of Late Paleozoic material. Soc Paleontol Ital Boll Spec Vol 1:353–382

Siesser W (1993) Calcareous nannoplankton. *In*: Fossil Prokaryotes and Protists. Lipps J (ed) Blackwell Scientific, Oxford, p 169–201

Sepkoski JJ (1982) A compendium of fossil marine families. Milwaukee Publ Mus Contr Biol Geol 51:1–125

Sepkoski JJ, Sheehan (1992) Diversification, faunal change, and community replacement during the Ordovician radiation. *In*: Biotic Interactions in Recent and Fossil Communities. Tevesz MJS, McCall PL (eds) Plenum, New York, p 673–717

Shu DG, Luo HL, Morris SC, Zhang XL, Hu SX, Chen L, Han J, Zhu M, Li Y, Chen LZ (1999) Lower Cambrian vertebrates from South China. Nature 402:42–46

Simkiss K, Wilbur KM (1989) Biomineralization: Cell Biology and Mineral Deposition. Academic Press, New York

Stanley GD (2003) The evolution of modern corals and their early history. Earth-Sci Rev 60:195–225

Stanley SM (1975) Adaptive themes in the evolution of the Bivalvia. Annu Rev Earth Planetary Sci 3:361–385

Stanley SM, Hardie LA (1998) Secular oscillations in the carbonate mineralogy of reef-building and sediment-producing organisms driven by tectonically forced shifts in seawater chemistry. Palaeogeogr Palaeoclimatol Palaeoecol 144:3–19

Stanley SM, Ries JB, Hardie LA (2002) Low-magnesium calcite produced by coralline algae in seawater of Late Cretaceous composition. Proc Nat Acad Sci USA 99:15323–15326

Sullivan BK, Miller CB, Peterson WT, Soeldner AH (1975) A scanning electron microscope study of the mandibular morphology of boreal copepods. Marine Biol 30:175–182

Summons RE, Walter MR (1990) Molecular fossils and microfossils of prokaryotes and protists from Proterozoic sediments. Am J Sci 290A:212–244

Thomas RDK, Reif WE (1993) The skeleton space: a finite set of organic designs. Evolution 47:341–360

Thomas RDK, Shearman RM, Stewart GW (2000) Evolutionary exploitation of design options by the first animals with hard skeletons. Science 288:1239–1242

Tinbergen N (1963) On aims and methods of ethology. Zeitschr Tierpsychol 20:410–413

Verma HC, Upadhyay C, Tripathi RP, Shukla AD, Bhandari N (2002) Evidence of impact at the Permian/Triassic boundary from Mössbauer spectroscopy. Hyperfine Interactions 141:357–360

Vermeij GJ (1977) The Mesozoic marine revolution: evidence from snails, predators and grazers. Paleobiology 3:245–258

Vermeij GJ (1995) Economics, volcanos, and Phanerozoic revolutions. Paleobiology 21:125–152

Wahlman GP (2002) Upper Carboniferous-Lower Permian reefs (Bashkiri-Kungarian) mounds and reefs. *In*: Phanerozoic Reef Patterns, SEPM Special Publication 72. Kiessling W, Flügel, Golonka J (eds) SEPM Press, Tulsa, Oklahoma, p 271–228

Walter MR, Du R, Horodyski RJ (1990) Coiled carbonaceous megafossils from the Middle Proterozoic of Jixian (Tinjian) and Montana. Am J Sci 290A:133–148

Wang DYC, Kumar S, Hedges SB (1999) Divergence time estimates for the early history of animal phyla and the origin of plants, animals and fungi. Proc Royal Soc London B266:163–171

Weidlich O (2002) Middle and Late Permian reefs—distributional patterns and reservoir potential. *In*: Phanerozoic Reef Patterns, SEPM Special Publication 72. Kiessling W, Flügel, Golonka J (eds) SEPM Press, Tulsa, Oklahoma, p 339–390

Weiner S, Addadi L (1997) Design strategies in mineralized biological materials. J Mater Chem 7:689–702

Westbroek P, Marin F (1998) A marriage of bone and nacre. Nature 392:861–862

Wignall PB, Morante R, Newton R (1998) The Permo-Triassic transition in Spitsbergen: $\delta^{13}C_{org}$ chemostratigraphy, Fe and S geochemistry, facies, fauna and trace fossils. Geol Mag 135:47–62

Williams A, Luter C, Cusack M (2001) The nature of siliceous mosaics forming the first shell of the brachiopod *Discinisca*. J Structur Biol 134:25–34

Wollast R, Mackenzie FT (1983) The global cycle of silica. *In*: Silicon Geochemistry and Biochemistry. Astor SR (ed) Academic Press, New York, p 39–76

Won MZ, Below R (1999) Cambrian radiolaria from the Georgina Basin, Queensland, Australia. Micropaleontology 45:325–363

Won MZ, Iams WJ (2002) Late Cambrian radiolarian faunas and biostratigraphy of the Cow Head Group, western Newfoundland. J Paleontol 76:1–33

Wood RA, Grotzinger JP, Dickson JAD (2002) Proterozoic modular biomineralized metazoan from the Nama Group, Namibia. Science 296:2383–2386

Wray JL (1977) Calcareous Algae. Elsevier, Amsterdam

Xiao S, Knoll AH (2000) Phosphatized animal embryos from the Neoproterozoic Doushantuo Formation at Weng'an, Guizhou Province, South China. J Paleontol 74:767–788

Xiao S, Knoll AH, Yuan X, Pueschel C (in press) Phosphatized multicellular algae in the Neoproterozoic Doushantuo Formation, China, and the early evolution of florideophyte red algae. Am J Bot

Yoon HS, Hackett JD, Pinto G, Bhattacharya D (2002) The single, ancient origin of chromist plastids. Proc Nat Acad Sci, USA 99:15507–15512

Young JR, Davis SA, Bown PR, Mann (1999) Coccolith ultrastructure and biomineralisation. J Struc Biol 126:195–215

Zhuravlev AY, Wood RA (1996) Anoxia as the cause of the mid-Early Cambrian (Botomian) extinction event. Geology 24:311–314

Zondervan I, Zeebe RE, Rost B, Riebesell (2001) Decreasing marine biogenic calcification: a negative feedback on rising atmospheric pCO$_2$. Global Biogeochem Cycles 15:507–516

Zurzolo C, Bowler C (2001) Exploring bioinorganic pattern formation in diatoms. A story of polarized trafficking. Plant Physiol 127:1339–1345