CHAPTER

8

The Geological Succession of Primary Producers in the Oceans

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In the modern oceans, diatoms, dinoflagellates, and coccolithophorids play prominent roles in primary production (Falkowski *et al.* 2004). The biological observation that these groups acquired photosynthesis via endosymbiosis requires that they were preceded in time by other photoautotrophs. The geological observation that the three groups rose to geobiological prominence only in the Mesozoic Era also requires that other primary producers fueled marine ecosystems for most of Earth history. The question, then, is What did primary production in the oceans look like before the rise of modern phytoplankton groups?

In this chapter, we explore two records of past primary producers: morphological

fossils and molecular biomarkers. Because these two windows on ancient biology are framed by such different patterns of preservational bias and diagenetic selectivity, they are likely to present a common picture of stratigraphic variation only if that view reflects evolutionary history.

I. RECORDS OF PRIMARY PRODUCERS IN ANCIENT OCEANS

A. Microfossils

Microfossils, preserved as organic cell walls or mineralized tests and scales, record the morphologies and (viewed via transmission electron microscopy) ultrastructures of ancient microorganisms. Such fossils can provide unambiguous records of phytoplankton in past oceans—diatom frustules, for example—and they commonly occur in large population sizes, with numerous occurrences that permit fine stratigraphic resolution and wide geographic coverage.

Set against this is a number of factors that limit interpretation. Not all photoautotrophs produce preservable cell walls or scales, and, of those that do, not all generate fossils that are taxonomically diagnostic. Thus, although many modern diatoms precipitate robust frustules of silica likely to enter the geologic record, others secrete weakly mineralized shells with a correspondingly lower probability of preservation. Similarly, whereas dinoflagellates as a group have left a clear record of dinocysts, many extant species do not produce preservable cysts and others form cysts that would not be recognized unambiguously as dinoflagellate in fossil assemblages. (The phylogenetic affinities of fossil dinocysts are established by the presence of an archeopyle, a distinctive excystment mechanism peculiar to but not universally found within dinoflagellates.) Especially in the early history of a group, character combinations that readily distinguish younger members may not be in place. Thus, stem group diatoms without well developed frustules might well leave no morphologic record at all in sediments.

By virtue of their decay-resistant extracellular sheaths and envelopes, many cyanobacteria have a relatively high probability of entering the fossil record, and some benthic lineages are both readily preservable and morphologically distinctive (Knoll and Golubic 1992). On the other hand, important picoplankton such as *Prochlorococcus* are unlikely to leave recognizable body (or, as it turns out, molecular) fossils. A number of algal clades include good candidates for fossilization, especially groups with distinctive resting stages (phycomate prasinophytes, dinoflagellates) or mineralized skeletons (diatoms, coccolithophorids, coralline reds, caulerpalean and dasyclad greens). Other primary producers fossilize occasionally, but only under unusual depositional or diagenetic circumstances (e.g., Butterfield 2000; Xiao *et al.* 2002, 2004; Foster and Afonin 2006), and still others rarely if ever produce morphologically interpretable fossils.

Diagenesis can obliterate fossils as well as preserve them: organic walls are subject to post-depositional oxidation and mineralized skeletons may dissolve in undersaturated pore waters. The result is that presence and absence cannot be weighted equally in micropaleontology. The presence of a fossil unambiguously shows that the cell from which it derived lived at a certain time in a particular place, but absence may reflect true absence, low probability of fossilization, or obfuscating depositional or diagenetic conditions. For older time intervals, tectonic destruction of the sedimentary record imposes an additional challenge; in particular, subduction inexorably destroys oceanic crust and the sediments that mantle it, so that deep sea sediments are common only in Jurassic and younger ocean basins.

B. Molecular Biomarkers

The chemical constituents of biomass produced by living organisms can be incorporated

into sediments and ultimately into sedimentary rocks that can survive for billions of years. Where these compounds are preserved in recognizable forms, they represent another opportunity for organisms to leave a trace of themselves in the fossil record. Organic biomarkers are the diagenetically altered remains of the products of cellular biosynthesis and may be aptly termed molecular fossils. Most biomarkers are derived from lipids and are potentially stable over billion-year time scales under ideal conditions (Brocks and Summons 2004).

Given the variety of organic compounds produced by cells, and the vast quantities of sedimentary organic matter in a rock record that stretches back billions of years, biomarkers are a potentially rich source of information concerning the diversity and ecology of ancient communities. However, the process of organic matter incorporation into rocks and its transformation during deep burial imposes some strong constraints on the kinds of information that can be recovered millions of years after the fact. The classes of molecules that contain molecular sequence information, nucleic acids and most proteins, do not survive long in the geologic environment. DNA can survive for at least a few hundred thousand years, especially in reducing environments such as euxinic sediments (e.g., Coolen *et al.* 2004) where heterotrophy is curtailed by a lack of electron acceptors but is not an option where the aim is to look at changes on million-year or longer time scales. Other kinds of biomolecules, however, prove remarkably resilient in the rock record.

Any molecule with a hydrocarbon skeleton has the potential to be preserved over long periods. For the most part, this means the hydrocarbon portions of membrane lipids, which are the major constituent of extractable organic matter (bitumen) in sedimentary rocks. Diagenesis quickly strips these compounds of their reactive polar functionalities, and over longer periods causes stereochemical and structural rearrangements, but hydrocarbon skeletons

can remain recognizable as the products of particular biosynthetic pathways on time scales that approach the age of the Earth (e.g., Brocks and Summons 2004; Peters *et al.* 2005).

The character of the information contained in molecular fossils is variable. Some are markers for the presence and, to the extent they can be quantified relative to other inputs, abundance of particular organisms. The taxonomic specificity of such biomarkers ranges from species to domain level. Others are markers for the operation of a particular physiology or biosynthetic pathway that may have a broad and/or patchy taxonomic distribution. Still other kinds of biomarkers are most strongly associated with specific depositional settings, making their presence more indicative of paleoenvironmental conditions than of any particular biology. Interpretation of the molecular fossil record depends on our ability to recognize biomarker compounds, link them to biosynthetic precursors, and then to make inferences about what the presence of those molecules in the rock record tells us about contemporary biology and geochemistry.

Turning to biomarkers that might establish a molecular fossil record of primary production in marine settings, several classes of compounds are promising for their combination of biochemical and/or taxonomic specificity. Pigments are natural candidates, representing markers of the photosynthetic machinery itself. Input of chlorophyll to sediments can result in several kinds of molecular fossils, including porphyrins and the pristane and phytane skeletons of the chlorophyll side-chain (Figure 1). It was the recognition of vanadyl porphyrin as the molecular fossil of chlorophyll that led Alfred Treibs (1936) to make the first compelling chemical argument for the biogenic origin of petroleum. Other pigments, such as carotenoids, are subject to very selective preservation, generally requiring the presence of reduced sulfur species; the functional groups that confer many of their biophysical properties and taxonomic specificity are
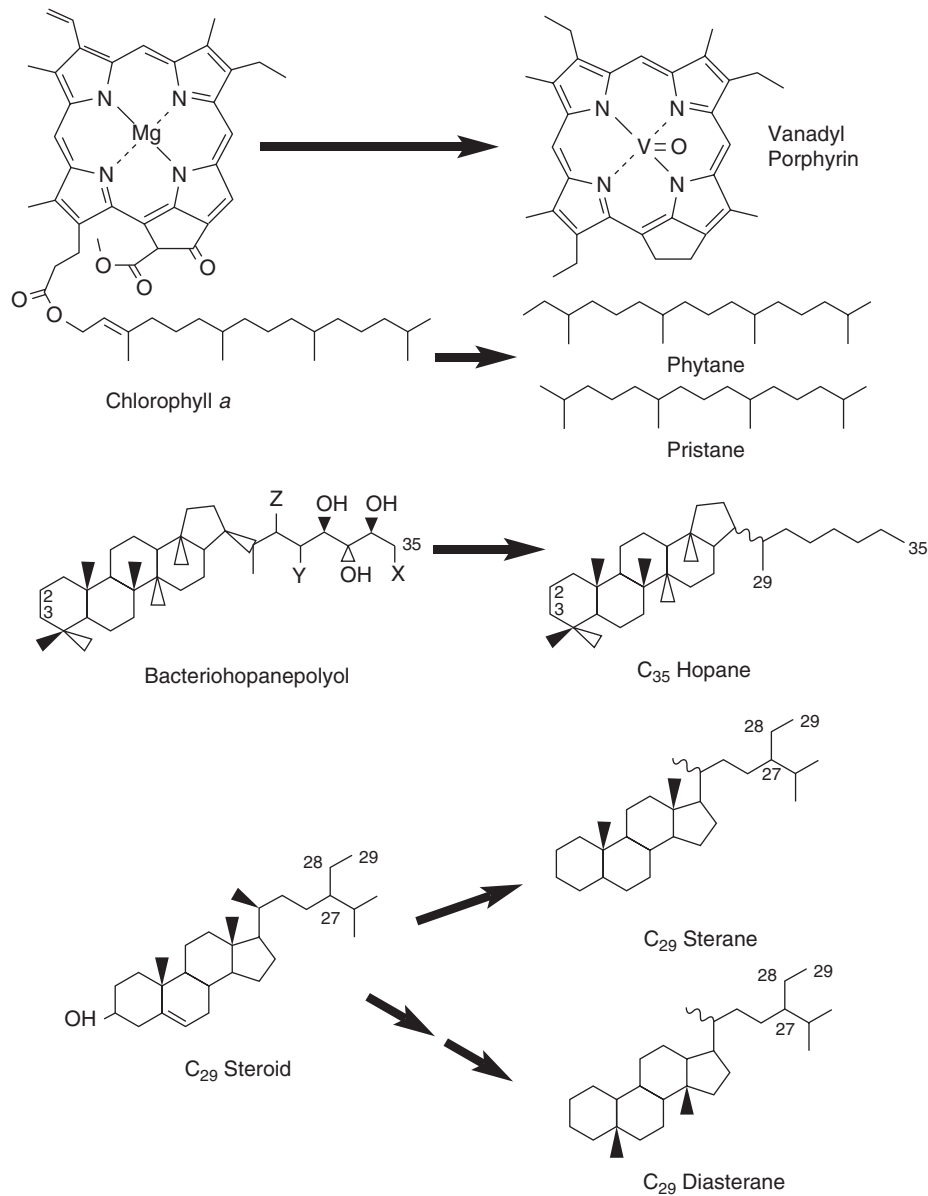
FIGURE 1.   Structures of diagnostic phytoplankton lipids (left) and their fossil counterparts (right).

lost through chemical reduction processes early in diagenesis (e.g. Kohnen *et al.* 1991, 1993; Hebting *et al.* 2006).

Although the preservation of pigment-derived biomarkers is spotty and information is steadily lost over time as diagenesis proceeds, another class of extraordinarily durable molecules provides us with much

of the molecular fossil record of primary producers, particularly in Paleozoic and older rocks. These are the polycyclic triterpenoids produced by the cyclization of the isoprenoid squalene and found in the membranes of both eukaryotes and bacteria. The main types are the steroids, which are ubiquitous among the Eucarya but known

from only a very few bacteria, and the hopanoids, including the bacteriohopanepolyols (BHPs), produced by a wide variety of autotrophic and heterotrophic bacteria. These molecules have the great advantages of a durable polycyclic skeleton that is clearly a biological product and a well-characterized diagenetic fate involving a number of rearrangements that provide information about the postburial history of the organic matter. The structures of some commonly used biomarker lipids and their fossil counterparts are shown in Figure 1. Table 1 summarizes current knowledge of the biological affinities of hydrocarbons commonly found in marine sediment samples, excluding biomarkers derived from terrestrial organisms.

Molecular fossils suffer from some of the same limitations as body fossils. Not all ecologically and biogeochemically important groups leave distinctive molecular fingerprints, making them difficult to follow in time. Moreover, the structures of lipids are not nearly as diverse as body fossils; different, often distantly related or physiologically disparate organisms can produce similar patterns of lipids. Generally, biomarkers will reflect an average of inputs to sediments, which can be influenced by factors including bottom water oxygenation, sediment mineralogy, and grain surface area available for sorptive protection (Hedges and Keil 1995). These inputs are attenuated by remineralization of organic matter as it sinks: this reworking is >95% complete by 3000 m depth (Martin et al. 1987). The high degree of water-column degradation of organic matter in deep basins means that, even where deep-water sediments survive subduction, they commonly contain little organic matter; hence, the biomarker record of open-ocean primary production is poor. The problem of interpreting absence can be acute, because in biomarker analysis, absence can only be defined in terms of detection limits and, hence, is conditionally dependent upon the analytical technology available.

Much of what is known about the diagenesis and preservation of biomarkers derives from studies of the origin and composition of petroleum (e.g., Peters et al. 2005). Petroleum geologists were initially interested in identifying the source rocks from which hydrocarbon accumulations originated. Information on the thermal histories of source rocks is also key for modeling hydrocarbon generation. Biomarkers provide a way to determine both parameters through complementary analyses of sedimentary bitumen in source rocks and their derived oil accumulations. Companies serving the petroleum exploration industry have developed and maintained databases of bitumen and oil composition that can be used to compare oils to bitumen in their source horizons and model the thermal histories of petroleum deposits and that can be employed as a predictive tool when exploring in frontier regions. An example is the commercial "Oils" database generated by GeoMark Research, which records geochemical analyses of more than 10,000 crude oil samples from every known petroliferous basin on the globe (www.geomarkresearch.com). The "Oils" data comprise the contents of S, Ni, and V; the carbon isotopic compositions of bulk saturated and aromatic hydrocarbons; and quantitative analysis of approximately 100 individual hydrocarbons, including n-alkanes, acyclic isoprenoids, steroids, and triterpenoids. Abundances of the latter biomarkers, which have been determined using a rigorously reproducible analytical protocol, allow calculation of 23 diagnostic molecular ratios that can be used to predict paleoenvironmental features of an oil's source rock without direct knowledge of the rock itself (Zumberge 1987) or to evaluate hydrocarbon charge histories from field to basin scales (e.g., Zumberge et al. 2005). Averaging of data from numerous oil samples within a well, field, or an entire basin helps to overcome anomalies in individual hydrocarbon samples that reflect differences in maturity and losses from evaporation, water

washing, or biodegradation. Although it is not widely appreciated, the global ubiquity of sedimentary bitumen and oil accumulations of all sizes means that hydrocarbons can also serve as a source of information on trends in the global carbon cycle (e.g., Andrusevich *et al.* 1998, 2000) and patterns in the evolution and environmental distributions of organisms, as discussed further later. The data illustrated in Figures 2, 3, 4, 5, and 6 come from the "Oils" database and represent the averages of numerous samples from a global selection of prominent Cenozoic to Proterozoic petroleum systems, both marine and lacustrine.

Inspection of trends in the "Oils" database suggests that some aspects of the composi-

tion of sedimentary hydrocarbons appear to be relatively invariant with age, changing instead with source rock lithology and sedimentary environment. These features are mostly reflected in the abundance patterns of bacterial and archaeal biomarkers. An example is depicted in Figure 2, which plots the relative abundance of a diagnostic bacteriohopane hydrocarbon (30-norhopane) as a function of paleolatitude. 30-Norhopane can arguably originate in several ways, but one particularly prolific source would be those BHPs with a hydroxyl substituent at position "Z" (Figure 1); this makes them prone to oxidative cleavage, leading to a C_{29} hydrocarbon (Rohmer *et al.* 1992). Such precursor BHPs occur commonly in proteobacteria,
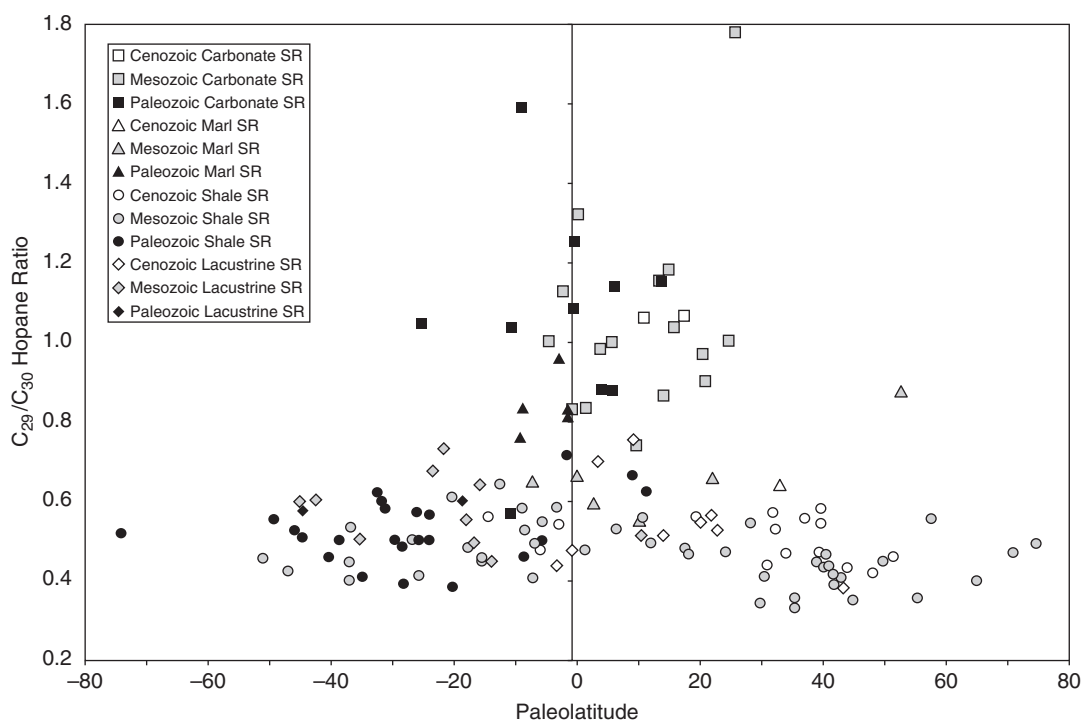
FIGURE 2. This figure depicts a diagnostic biomarker ratio derived from the averaged analyses of numerous oil samples representing important commercial petroleum accumulations plotted versus their paleolatitude. Samples are grouped according to geological era and classified according to the lithology and environment of the source rock, namely marine distal shales, marine marls, marine carbonates, or lacustrine sediments. The ratio of hopanes with 29 carbons to those with 30 carbons tends to be highest in carbonates and marls and in samples from low paleolatitude. Oils sourced from marine distal shales invariably show a C_{29}/C_{30} hopane ratio <0.7, whereas marine carbonates tend to have values of 0.8 or more. This pattern holds irrespective of age over the duration of the Phanerozoic.
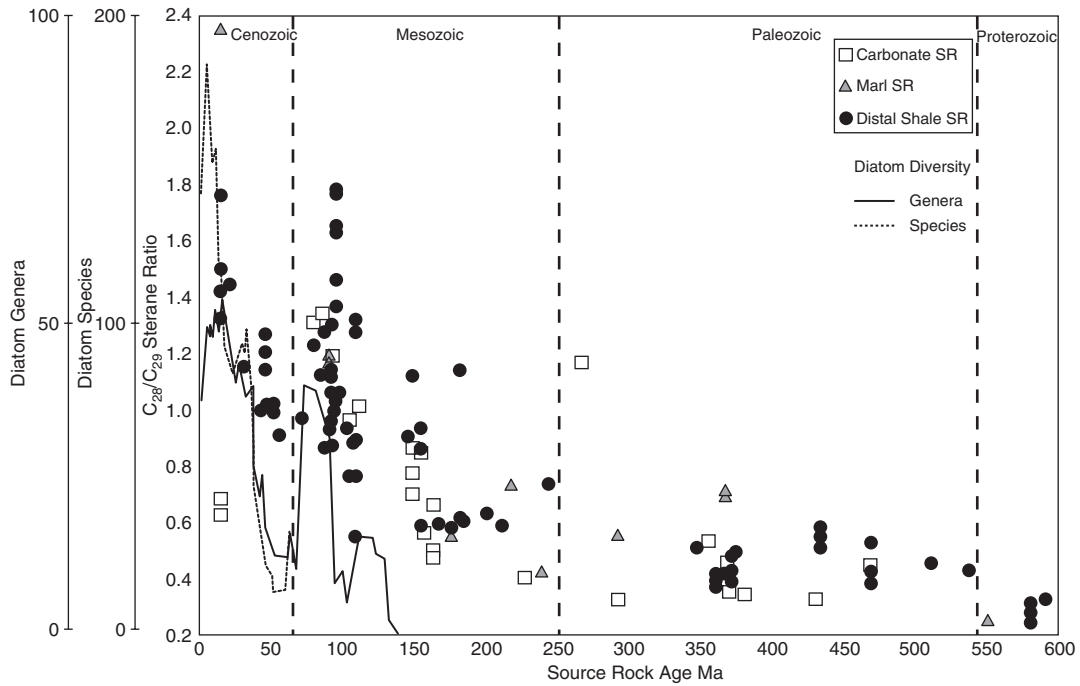
FIGURE 3. The secular increase in the abundance of C_{28} relative to C_{29} steranes over the Phanerozoic Eon, particularly during the last 250 million years, in petroleum systems from the GeoMark Oils database. Overlain are the fossil diatom species and genera diversity curves from Katz *et al*. (2004).
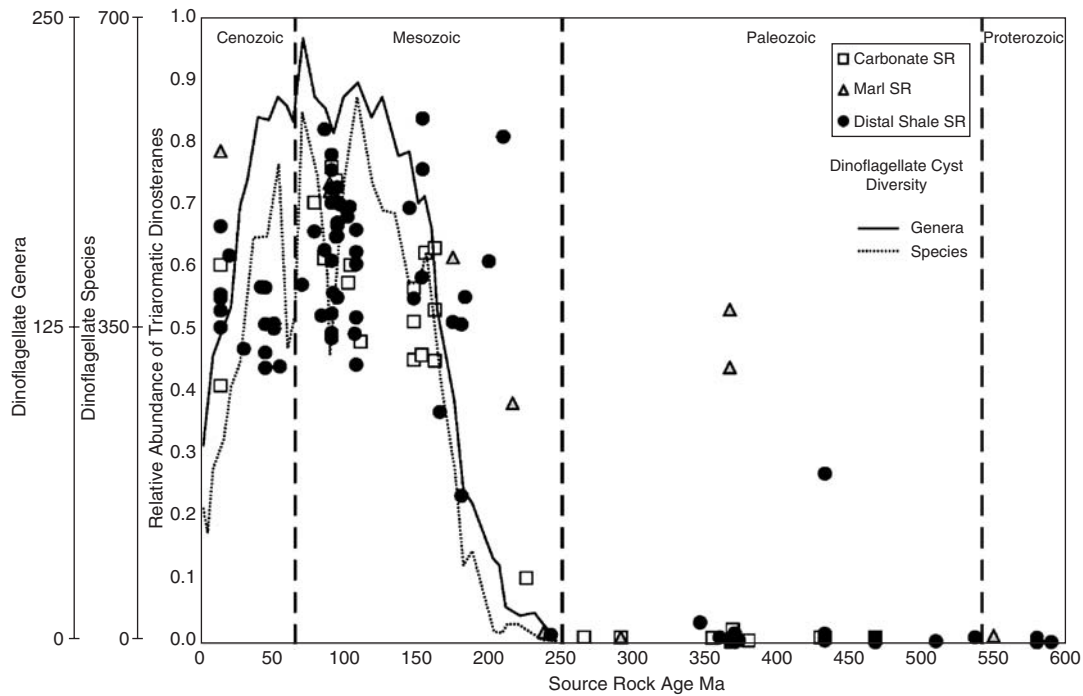
FIGURE 4. The relative abundance of aromatic dinosteranes over the Phanerozoic Eon from the GeoMark Oils database, showing marked increase during the early Mesozoic. Note concordance with genera- and species-level dinoflagellate fossil cyst diversity curves of Katz *et al*. (2004). Paleozoic occurrences of dinosteranes in petroleum sources are infrequent but merit further attention.

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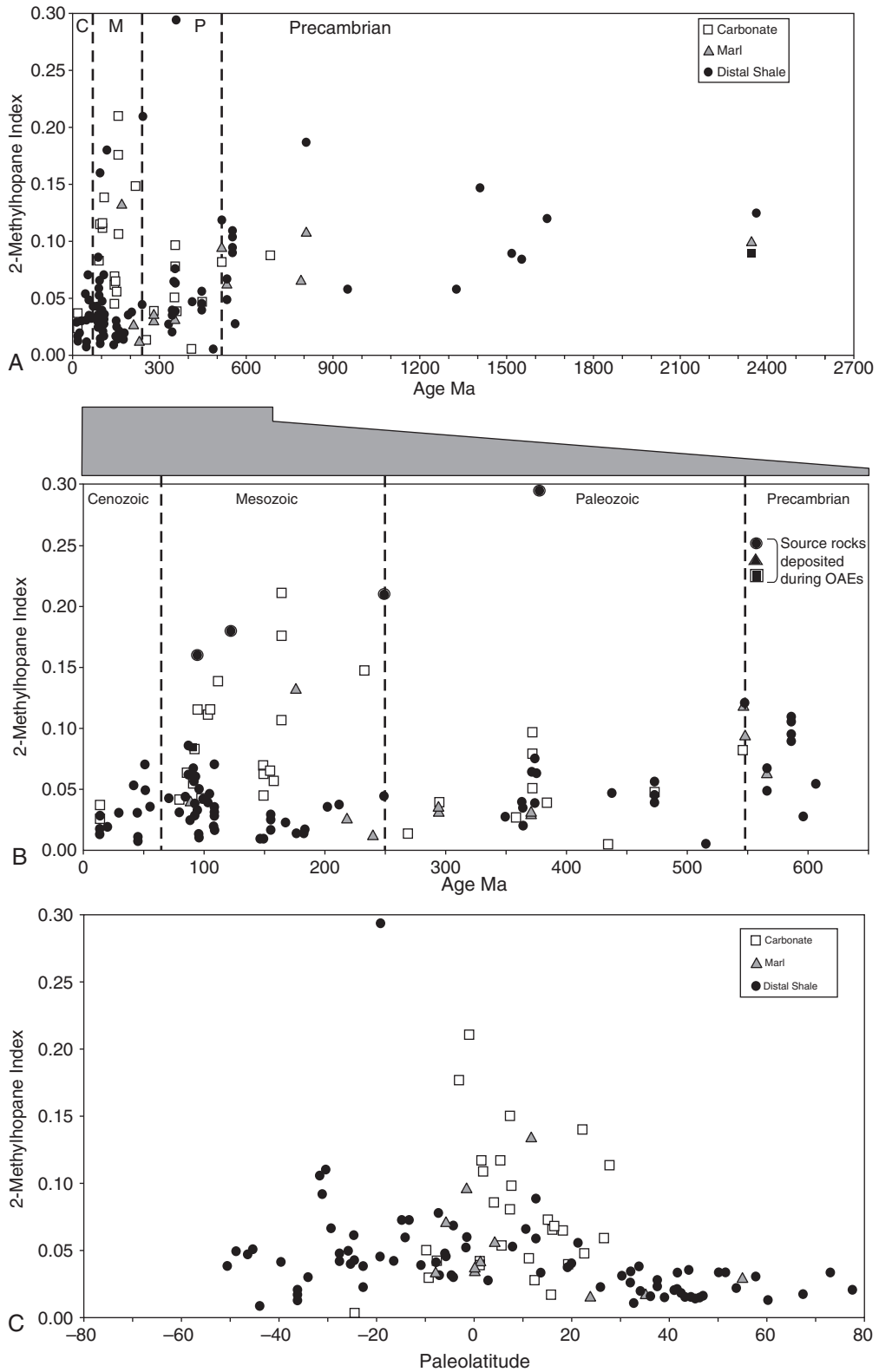
FIGURE 5. For legend see next page

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FIGURE 5. (Cont'd)   **(A)** C_{30} 2-methylhopane (2-MeHI) index (=C_{30} 2-MeHI/(C_{30} 2-MeHI + C_{30} desmethyl hopane) through geologic time. Values are generally elevated throughout the Precambrian, with distal shales reaching below 0.05 only during the Phanerozoic. Compilation includes data from the GeoMark Oils database and Kuypers *et al.* (2004) **(B)** Expansion of the time scale of **(A)** to focus on the Phanerozoic. Source rocks deposited during oceanic anoxic events (OAEs) are highlighted and often show elevated 2-MeHI indices. **(C)** 2-MeHI indices of Phanerozoic petroleum systems by source rock lithology and paleolatitude. The highest 2-MeHI values are generally found at low latitudes, often in carbonate depositional environments.

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including methylotrophs. They appear to be especially common in carbonate-precipitating sedimentary environments; the ratio of C_{29}/C_{30} hopane tends to be highest in oils from carbonates, intermediate in marls, and lowest in distal shales (Subroto *et al.* 1991). This relationship holds independent of the geological age of the source rocks. Carbonates accumulate predominantly in low latitudes, explaining the paleogeographic correspondence shown in Figure 2.

In contrast to the trends shown by biomarkers from prokaryotes, acyclic and cyclized terpenoids and steroids (Figure 1) derived from planktonic algae and vascular plants show strong age-related trends (e.g., Summons and Walter 1990; Brocks and Summons 2004). For example, the oleanoid triterpenoids such as β-amyrin are important in the predation-defense mechanisms of flowering plants. Oleanane, a hydrocarbon derived from these triterpenoids,

is sometimes abundant in oils from rocks deposited on continental margins, showing a marked increase in oils formed from Cenozoic rocks that reflects the Cretaceous radiation of the angiosperms (Moldowan *et al.* 1994). Low levels of oleanane in rocks as old as Jurassic age, however, suggests either that early flowering plants were sporadic inhabitants of Mesozoic environments or that oleanoid triterpenoid synthesis originated in their phylogenetic precursors (e.g., Peters *et al.* 2005). Observations concerning algal biomarkers are discussed later.

II. THE RISE OF MODERN PHYTOPLANKTON

A. Fossils and Phylogeny

In modern oceans, three algal groups dominate primary production on continental shelves: the diatoms, dinoflagellates, and
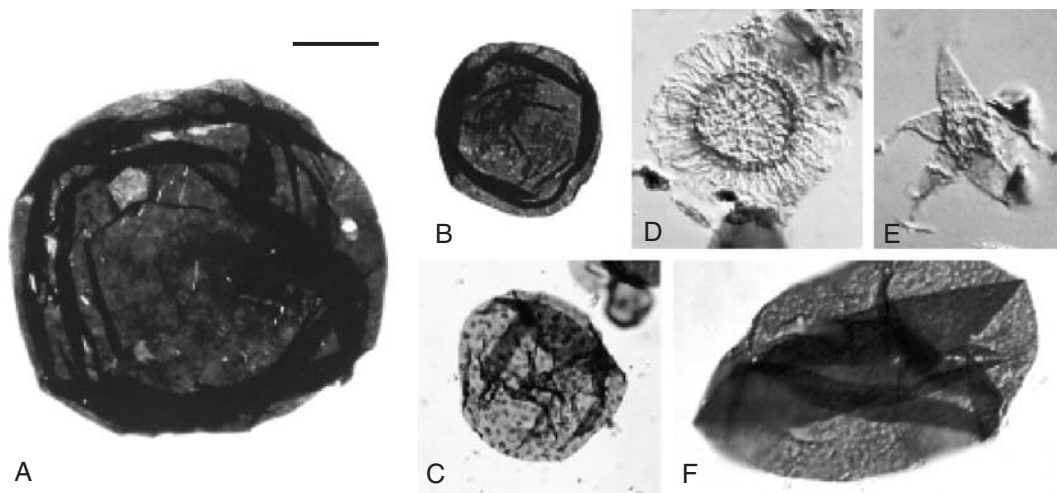
FIGURE 6.   Proterozoic and Early Cambrian protistan microfossils. **(A)** and **(B)** are Neoproterozoic leiospherid acritarchs; **(C–F)** are Early Cambrian acritarchs **(C–E)** and a prasinophyte phycoma (**F**; *Tasmanites*). Scale bar = 40 microns.

coccolithophorids. As detailed elsewhere in this volume, fossils clearly suggest that these groups all rose to taxonomic and ecological prominence only during the Mesozoic Era (Delwiche, 2006; de Vargas *et al*. 2006; Kooistra *et al*. 2006). Could there have been, however, an earlier "cryptic" evolutionary history for these groups? For example, might nonmineralizing stem group diatoms or haptophytes have been ecologically important but paleontologically uninterpretable in Paleozoic oceans? Might the significance of Paleozoic dinoflagellates be obscured by fossils that are abundant and diverse but lack archeopyles?

Several reports claim microfossil evidence for Paleozoic diatoms, dinoflagellates, and haptophytes, but such fossils are rare and subject to alternative interpretation as contaminants (the mineralized skeletons) or different taxa (organic fossils). Stratigraphic research indicates that the Paleozoic silica cycle differed substantially from that of the Cretaceous and Tertiary periods, with sponges and radiolarians dominating biological removal of silica from the oceans (Maliva *et al*. 1989). Similarly, sediments preserved in obducted slices of Paleozoic seafloor at best contain only limited evidence for pelagic carbonate deposition. Such observations cannot eliminate the possibility that rare diatoms, coccolithophorids, or calcareous dinoflagellates lived in Paleozoic oceans, but they clearly indicate that these groups did not perform the biogeochemical roles they have played since the Mesozoic Era.

Complementing this, molecular clock estimates for diatom and coccolithophorid diversification, calibrated by well-preserved fossils, suggest that these groups have no long Paleozoic "prehistory" (de Vargas *et al*. 2006; Kooistra *et al*. 2006). On the other hand, some molecular clock analyses suggest divergence times for the plastids in photosynthetic chromoalveolates well back into the Proterozoic (Douzery *et al*. 2004; Yoon *et al*. 2004). If these estimates are even broadly correct, they must be accommodated in one of two ways. Either the molecular clocks date divergence within a closely related group of unicellular red algae that subsequently and individually were incorporated as plastids in chromalveolate algae, or photosynthetic chromalveolates emerged from a single Proterozoic endosymbiosis (Cavalier-Smith 1999) but remained ecologically unimportant or paleontologically unrecognizable until much later.

B. Biomarkers and the Rise of Modern Phytoplankton

The rise to ecological prominence of the three chlorophyll *c*-containing eukaryotic plankton lineages left several imprints in the molecular fossil record, especially in the distributions of steranes with different side-chain alkylation patterns. A secular increase in the ratio of C_{28} to C_{29} steranes (24-methylcholestanes versus 24-ethylcholestanes), first noted by Grantham and Wakefield (1988), has been attributed to increasing production by chlorophyll *c* algae (which dominate C_{28} sterane input) relative to green algae, which synthesize primarily C_{29} steroids (Volkman 2003). An updated plot of the C_{28}/C_{29} sterane ratio versus geological age, and based on averages from 123 petroleum systems worldwide, is shown in Figure 3 along with data for diatom diversity. The C_{28}/C_{29} sterane ratio remains below 0.4 in the Neoproterozoic and, with one exception, below 0.7 through the Paleozoic. Corresponding to the diversification of diatoms in the later half of the Mesozoic, there is a rise in the C_{28}/C_{29} sterane ratio to values as high as 1.8, followed by an apparent drop in the Paleocene and Eocene. Values climb again in the Miocene, accompanying a second rise in the numbers of diatom genera and species.

Other biomarkers show marked increases in abundance in the Cretaceous that also likely reflect diatom radiation. These include 24-norcholestanes (Holba *et al*. 1998a, b), the so-called highly branched isoprenoids (HBIs; Sinninghe Damsté *et al*. 1999a, b; Belt *et al*. 2000; Allard *et al*. 2001), long-chain

diols, and mid-chain hydroxyl methy-lalkanoates (Sinninghe Damsté *et al.* 2003). The secular increase in 24-norcholestane abundance (Moldowan *et al.* 1991; Holba *et al.* 1998a, 1998b) was observed and linked to the diatom radiation well before a precursor sterol was recognized in a culture of the centric diatom *Thalassiosira aff. antarctica* (Rampen *et al.* 2005). In fact, in the study of Rampen *et al.* (2005) only one, that is *T. aff. antarctica,* of 100 different diatom taxa was found to produce 24-norcholesta-5, 22-dien-3β-ol .

The detail of novel sterol production by diatoms provides an interesting window into the connections among biomarkers, taxonomy, and the physiological roles of lipids. In a recent study of diatom sterols, Suzuki *et al.* (2005) reported that environmental samples of diatoms collected from the North Pacific Ocean and the Bering Sea contained 24-norsterols. Further, samples of the diatom *Coscinodiscus marginatus,* initially devoid of 24-norcholesterol, contained significant amounts of this and the related steroid 27-nor-24-methylcholesta-5,22-dien-3β-ol after storage at 3°C for 30 days. These authors attributed the latter change to bacterial biodegradation. Due to the ubiquity of 24-norsteranes in Mesozoic sediments (Holba *et al.* 1998a, 1998b), and no other evidence for selective side-chain biodegradation of sterols (biodegrading bacteria are unlikely to select for removal of C_{26} and C_{27} of the apparent precursor 24-methylcholesta-5,22-dien-3β-ol and leave other sterols untouched), it seems far more likely that there is a direct as opposed to diagenetic source for the 24-norsteroids in sediments. The rarity of 24-norsterols in cultured diatoms (Rampen *et al.* 2005) more likely reflects the fact that sterol biosynthesis responds to physiological conditions and that laboratory culture conditions have as yet not mimicked the natural conditions, such as low temperature and, perhaps, low light under which 24-norsterols are produced by some diatoms. The enigma surrounding the origins of 24-norsteroids, and the ultimate detection of

24-norcholesta-5,22-dien-3β-ol by Rampen *et al.* (2005) in a cold water diatom species, provide a timely reminder that biomarkers not only reflect the presence of particular algal taxa but also reflect the environmental conditions under which they thrive. A corollary to this is that cultured organisms might not always produce the same assemblage of lipids as their counterparts growing under natural conditions.

The other major class of diatom-specific biomarkers is the HBI. So far as is currently known, the occurrence of HBI is confined to four genera, namely *Navicula*, *Haslea,* and *Pleurosigma* within the pennates and *Rhizosolenia* among the centrics (Volkman *et al.* 1994; Belt *et al.* 2000; Sinninghe Damsté *et al.* 2004). Both molecular phylogeny and fossils indicate that ce ntric diatoms predate pennates (Kooistra *et al.* 2006). Therefore, the genus *Rhizosolenia* is considered the likely source of the first recorded fossil HBI at about 91 Ma ago—which predates recorded fossil tests of Rhizosolenid diatoms by about 20 million years (Sinninghe Damsté *et al.* 2004). This discrepancy in timing could reflect incomplete paleontological sampling, which systematically underestimates first appearances, HBI synthesis by a morphologically distinct stem group relative of the rhizosolenids, or both. Biosynthetic pathways are such a fundamental characteristic of organisms that they might be detectable through chemical fossils before the first classical fossils of a clade are ever recognizable.

Dinosteroid biomarkers, derived from the 4-methylsterols of dinoflagellates (Robinson *et al.* 1984), show an analogous pattern of secular increase in the Mesozoic, in accord with microfossil evidence for later Triassic dinoflagellate radiation. As in the case of diatom HBI, however, several reported occurrences of dinosteranes predate fossil cysts, in some cases by hundreds of millions of years (Summons *et al.* 1992; Moldowan and Talyzina 1998; Talyzina *et al.* 2000). These deserve close attention as they may establish a genuine pre-Mesozoic history

of dinoflagellates, as predicted by molecular phylogenies and clocks. Some aspects of this putative history are considered further later. In Figure 4, data derived from the "Oils" database show the pattern of secular variation in triaromatic dinosteroid abundances, along with a recent compilation of dinoflagellate cyst diversity (Katz et al. 2004).

The third group of modern plankton, the haptophytes, produces distinctive lipids in the form of long-chain (n-C_{37} to C_{39}), unsaturated ketones known as alkenones (Volkman et al. 1980; Marlowe et al. 1984). These can be abundant and easily recognized in Recent and Cenozoic sediments that have not experienced extensive diagenesis, and they form the basis of a widely used paleotemperature proxy (Brassell et al. 1986). Their distinctiveness, however, lies in the carbonyl functionality and one to four unsaturations, which are easily reduced and inherently unstable over geological time scales (Prahl et al. 1989). Thus, the oldest reported detection is in Cretaceous sediments (Farrimond et al. 1986), and we would not expect to be able to recognize them in Paleozoic or older rocks.

The molecular and morphological records of eukaryotic predominance in shelf primary production are mirrored by indications of relatively low cyanobacterial contributions. Some cyanobacteria are known to biosynthesize BHPs and analogues with an extra methyl group attached to the 2 position of the A ring (2-MeBHP); the hydrocarbon cores of these molecules provide a potentially useful tracer for cyanobacterial input to sedimentary organic matter (Summons et al. 1999). Apart from a few notable exceptions, values of the 2-methylhopane (2-MeHI) index fraction of hopanoids methylated at the 2 position relative to their desmethyl counterparts) tend higher in Proterozoic samples than they are in Paleozoic and, especially Jurassic and younger oils (Figure 5A). This is especially true of samples from shales. (Examination of the Phanerozoic record [Figure 5B] shows that higher

2-MeHI values are found in oils from carbonate lithologies, formed predominantly at low paleolatitudes [Figure 5C].) The exceptions are associated with widespread anoxia in the oceans (Figure 5B). Kuypers et al. (2004a, 2004b) and Dumitrescu and Brassell (2005) studied biomarkers associated with Cretaceous oceanic anoxic events (OAEs) and found that the relative abundances of 2-methylhopanoids, as measured by the 2-MeHI, were distinctively enhanced, along with nitrogen (N) isotopic evidence for cyanobacterial primary productivity (Kuypers et al. 2004b). Mass extinction at the Permian-Triassic boundary is also associated with widespread anoxia in shallow oceans (Wignall and Twitchett 2002). In Figure 5, the two data points for the Permian Triassic transition represent unpublished data from the Perth Basin, Australia, and the boundary stratotype in Meishan, China; in these sections high 2-MeHI correlate with independent molecular, iron speciation, and sulfur isotopic evidence for intense euxinia (Grice et al. 2005). The highest 2-MeHI value (0.29) recorded in the GeoMark Oils database comes from the Larapintine Petroleum System, Australia, which includes oils from the Late Devonian reef complex of the Canning Basin (Edwards et al. 1997) sourced from black shales deposited near to Frasnian-Famennian boundary, another event characterized by geological and geochemical evidence for pervasive euxinia (e.g., Bond et al. 2004). The samples from the Cretaceous OAEs, Permian-Triassic boundary, and Frasnian-Fammenian shale all contain abundant isorenieratane and aryl isoprenoids derived from the brown pigmented strains of the green sulfur bacteria (Chlorobiaceae), considered diagnostic for photic zone euxinia (e.g., Summons and Powell 1987; Koopmans et al. 1996; Kuypers et al. 2004a; Grice et al. 2005; van Breugel et al. 2005). Kuypers et al. (2004b) hypothesize that the N cycle was compromised while euxinic conditions prevailed during the Cretaceous OAEs, creating an unusual opportunity for the

proliferation of N-fixing cyanobacteria. The disparate occurrences described previously suggest a more general correlation between high 2-MeHI and photic zone euxinia, a topic we return to in our discussion of Proterozoic primary production.

Although cyanobacteria appear to have been minor contributors to primary production on most Mesozoic and Cenozoic continental shelves, they remain the dominant phytoplankton in open-ocean, oligotrophic environments today. Whether this is a recent or long-standing situation is difficult to discern given the paucity of the deep-sea sedimentary records and the absence of 2Me-BHP in cyanobacterial picoplankton (Summons, unpublished data).

C. Summary of the Rise of Modern Phytoplankton

Fossils, molecular biomarkers, molecular clocks for individual clades, and the sedimentary silica record all tell a consistent story: the modern phytoplankton has Mesozoic roots. How we interpret this transformation depends in no small part on what we think came before.

III. PALEOZOIC PRIMARY PRODUCTION

A. Microfossils

Microfossils of presumptive eukaryotic phytoplankton are both abundant and diverse in Paleozoic marine rocks (Figure 6C–F). A number of forms, including *Tasmanites*, *Pterospermella*, and *Cymatiosphaera*, have morphologies and ultrastructures that relate them to prasinophyte phycomata (Tappan 1980). Indeed, in well-studied microfossil assemblages from Lower Cambrian shales, at least 20% of described morphotaxa and more than half of all individual fossils are likely prasinophytes (e.g., Volkova *et al.* 1983; Knoll and Swett 1987; Moczydlowska 1991). Others, with regularly distributed processes, tantalizingly

resemble dinocysts, but lack archeopyles. Still other acritarchs (the group name given to closed, organic-walled microfossils of uncertain systematic relationships) (Evitt 1963) do not closely resemble known cysts of modern phytoplankton. Collectively, these microfossils show evidence of marked Cambrian and Ordovician radiations that parallel the two-stage diversification of marine animals (Knoll 1989). For reasons that remain obscure, acritarch diversity drops near the end of the Devonian and remains low for the remainder of the Paleozoic Era (Molyneux *et al.* 1996).

Moldowan and Talyzina (1998) innovatively attempted to break the phylogenetic impasse regarding Cambrian microfossils. Extracts from fossiliferous clays of the Lower Cambrian Lükati Formation, Estonia, contain low abundances of dinosterane and 4a-methyl-24-ethylcholestane, both known to originate from the sterols of dinoflagellates (Robinson *et al.* 1984; Summons *et al.* 1987). Moldowan and Talyzina (1998) divided the microfossil populations in a Lükati sample into three groups—tasmanitids (Figure 6F; interpreted as prasinophyte phycomata), a low fluorescence group dominated by leiosphaerid acritarchs (also possible phycomata of prasinophytes like the extant *Halosphaera*), and a high fluorescence fraction containing abundant process-bearing acrtiarchs (e.g., Figure 6D)—and analyzed the sterane content of these subassemblages. The tasmanitid and low fluorescence fractions contained relatively abundant C_{29} steranes but little or no dinoflagellate lipid. In contrast, the high fluorescence fraction contained relatively high abundances of dinosterane, suggesting that the dominant, process-bearing acritarchs are dinocysts sans archeopyles. It is not clear that sterols play a structural role in cyst walls, making selective adsorption a real possibility. Moreover, whereas dinosterane and 4a-methyl-24-ethylcholestane abundances in these samples are relatively high, their concentrations are absolutely low. Thus, the specific attribution of acritarch taxa to

the dinoflagellates remains speculative. Nonetheless, these analyses do clearly suggest that dinoflagellates were present in coastal Cambrian oceans and may have left a morphological as well as biogeochemical record. Given the low abundances of dinoflagellate biomarkers, it is possible that the constituent dinoflagellates were largely heterotrophs, not primary producers.

B. Paleozoic Molecular Biomarkers

The molecular fossil record prior to the rise of the chlorophyll c lineages broadly corroborates the microfossil evidence for the occurrence and potential ecological importance of other eukaryotic phytoplankton in the Paleozoic. In particular, the high abundance of C_{29} steranes relative to C_{27} and C_{28} homologues suggests a greater role for green algae in marine primary production at this time. This signal is observed in globally distributed rocks and petroleum systems from the latest Neoproterozoic into the Paleozoic and wanes in the later Paleozoic, although the depositional bias for much of this time is toward low paleolatitudes (Figure 7). In a study of tasmanite oil shales from different locations in Tasmania, Revill *et al.* (1994) found that C_{27} and C_{29} steranes were present in roughly equal abundance and dominated over C_{28}. All the samples were shales with a high total organic carbon content, with the visible organic matter primarily comprising *Tasmanites punctatus* microfossils. These early Permian deposits, which were geographically localized, contained abundant dropstones and evidence
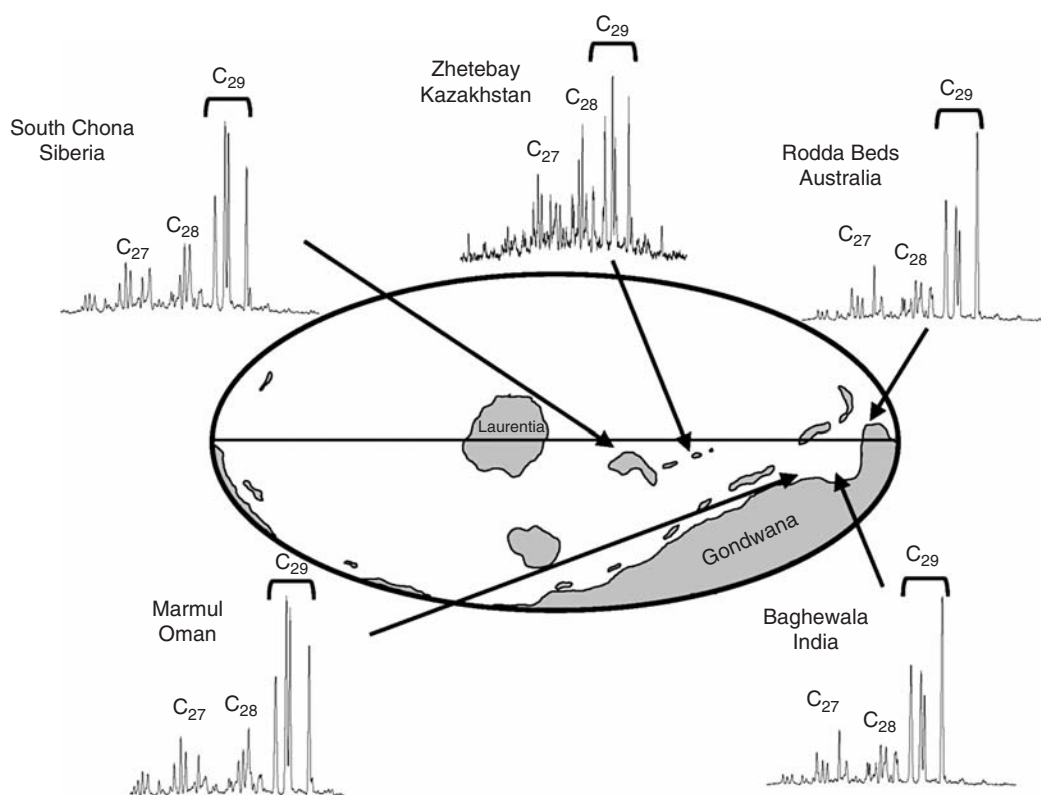

FIGURE 7. Dominance of C_{29} steranes in late Neoproterozoic/Early Cambrian petroleum systems. Paleogeography shows concentration of depositional systems to low paleolatitudes during this time. Continental reconstruction redrawn after C. Scotese, available at www.scotese.com.

of low temperature minerals, were clearly glacial in origin. Thus, the *Tasmanites punctatus* may have occupied an ecological niche similar to that occupied by modern sea-ice diatom communities (Revill *et al*. 1994).

Dinosteranes are generally below detection in the Paleozoic marine sediments and oils that have been examined and reported to date. In contrast, triaromatic dinosteroids have been found in significant abundance in several lower Paleozoic sedimentary rocks and petroleum samples. This speaks to the occurrence of either stem or crown group dinoflagellates in Paleozoic oceans. An additional factor in observed dinosterane abundances may be preservational bias. Saturated dinosteroids, dinosteranes, may only be preserved under strongly reducing conditions. A wider search for triaromatic dinosteroids, and authentication of the Paleozoic petroleum data through reanalysis and careful checking of pedigrees, may expose a more extensive pattern of occurrence and, hence a richer early history for these plankton than is evident from the distribution of fossilized cysts.

C. Paleozoic Summary

Biomarker data for oils and some sediments suggest that dinoflagellates existed in Paleozoic oceans, but with few exceptions, lipids thought to be sourced by dinoflagellates occur in low abundances, raising the question whether Paleozoic dinoflagellates functioned to any great extent as primary producers. The same is true of possible stem-group heterokonts. Thus, although Chl a+c phytoplankton may well have existed in Paleozoic oceans, they do not appear to have played anything like the ecological role they have assumed since the Mesozoic Era began. In contrast, microfossil and biomarker molecules both suggest that green algae played a greater role in marine primary production than they have in the past 100 million years, and biomarkers also suggest a significant role for cyanobacterial production on continental shelves. Macro-

fossils, predominantly of calcareous skeletons, further indicate that red and green algae were ecologically important in the shallow shelf benthos (Wray 1977).

IV. PROTEROZOIC PRIMARY PRODUCTION

Fossils (whether morphological or molecular) are less abundant in Proterozoic rocks than they are in Phanerozoic samples, and Proterozoic sedimentary rocks, themselves, are less abundantly preserved than their younger counterparts. Nonetheless, fossils have been reported from hundreds of Proterozoic localities (Mendelson and Schopf 1992), allowing us to recognize at least broad patterns of stratigraphic and paleoenvironmental distribution. Indeed, Proterozoic micropaleontology has developed to the point where it has become predictive, in the sense that knowledge of age and environmental setting permits reasonable prediction about the fossil content of a given rock sample (e.g., Knoll *et al*. 2006).

A. Prokaryotic Fossils

By the earliest Proterozoic Eon, cyanobacteria must have been important contributors to primary production—there is no other plausible source for the O_2 that began to accumulate in the atmosphere and surface oceans 2.45–2.32 Ga. Consistent with this observation, it has been appreciated since the early days of Precambrian paleontology that cyanobacteria-like microfossils are abundant and widespread constituents of Proterozoic fossil assemblages (Figure 8; Schopf 1968). Not all cyanobacteria have diagnostic morphologies, but some do and others are likely candidates for attribution given knowledge of taphonomy (processes of preservation) and depositional environments represented in the record. By mid-Proterozoic times, if not earlier, all major clades of cyanobacteria existed in marine and near-shore terrestrial environments,
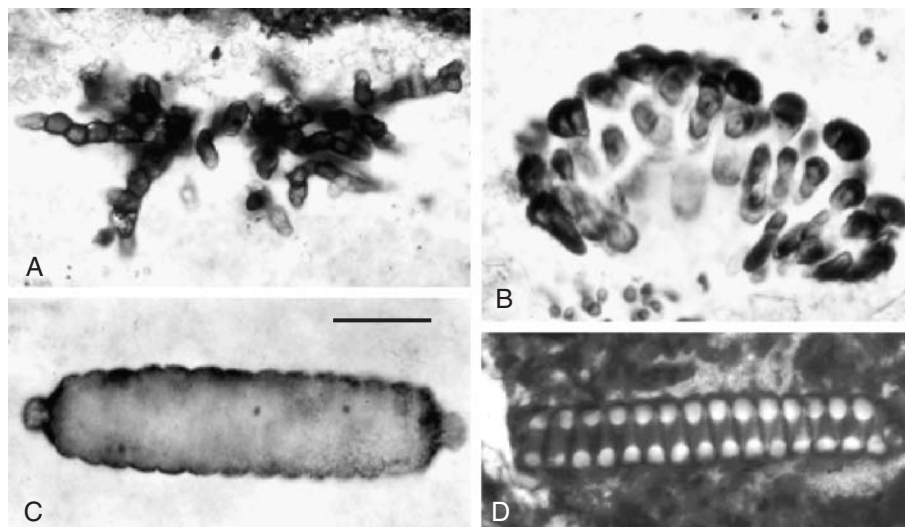
FIGURE 8. Cyanobacteria in Proterozoic sedimentary rocks. **(A)** 700–800 million-year-old endolithic pleurcapsalean fossil. **(B)** 1500 million-year-old mat building cyanobacterium closely related to modern *Entophysalis*. **(C)** 1500 million-year-old short richome. **(D)** *Spirulina*-like fossil in latest Proterozoic (<600 Ma) phosphorite. Scale bar = 15 microns in **(A–C),** and = 25 microns in **(D).**

including those that differentiate akinetes and heterocysts (Tomitani *et al*. 2006). The best characterized Proterozoic cyanobacteria come from early diagenetic chert nodules in carbonate successions (e.g., Schopf 1968; Zhang 1981; Knoll *et al*. 1991; Sergeev *et al*. 1995, 2002; Golubic and Seong-Joo 1999). These fossils are largely benthic and largely coastal marine. Stromatolites, however, indicate a much wider distribution of benthic cyanobacteria in the photic zone. (A role for cyanobacteria or of organisms in general is difficult to establish in the precipitated stromatolites found in Earth's oldest well preserved sedimentary successions; however, the likelihood that cyanobacteria were major architects of Proterozoic stromatolites that accreted primarily by trapping and binding is high) (Grotzinger and Knoll 1999). Microfossils are less useful for evaluating the contributions of cyanobacteria to the phytoplankton of Proterozoic oceans because many were small, nondescript, and likely to settle on the seafloor in places where interpretable preservation was improbable. Given the distribution of planktonic clades

on a phylogenetic tree calibrated by well-documented fossils, however, it is likely that cyanobacteria were important constituents of the phytoplankton in Proterozoic oceans (Sanchez-Baracaldo *et al*. 2005; Tomitani *et al*. 2006; see later).

B. Eukaryotic Fossils

Two problems shadow attempts to understand the Proterozoic history of photosynthetic eukaryotes. Given the polyphyletic evolution of at least simple unicellular and multicellular characters, convergence complicates interpretation of many Proterozoic protistan fossils. In addition, given the oft-observed reality that stem group organisms display only a subset of the characters that collectively identify crown group members of clades, early fossils may challenge finer scale systematic attribution, even though they may be unambiguously eukaryotic.

Despite these problems, a small number of fossil populations provide calibration points for eukaryotic phylogenies. *Bangiomorpha pubescens* (Butterfield 2000) is a large

population of multicellular microfossils found in tidal flat deposits of the ca. 1200 Ma Hunting Formation, Arctic Canada. These erect filaments, preserved via rapid burial by carbonate mud and subsequent silicification, display patterns of thallus organization, cell division, and cell differentiation that ally them to the bangiophyte red algae. Complementing this, a moderate diversity of cellularly preserved florideophyte red algal thalli occurs in <600 Ma phosphorites of the Ediacaran Doushantuo Formation, China (Xiao *et al.* 2004). Shifting to another branch of the eukaryotic tree, several taxa of vase shaped microfossils in the ca. 750 Kwagunt Formation, Grand Canyon, Arizona, can be related to lobose testate amoebae, placing a minimum constraint on the timing of amoebozoan divergence (Porter *et al.* 2003).

Accepting the presence of red algae by 1200 Ma, one might expect to observe green algal fossils in younger Proterozoic rocks. Several candidate taxa have been described, of which *Proterocladus,* a branching coenocytic thallus organized much like living *Cladophora,* is most compelling (Butterfield *et al.* 1994). *Palaeovaucheria clavata,* described from >1005 ±4 Ma shales in Siberia (Herman 1990), as well as ca. 750–800 Ma shales from Spitsbergen (Butterfield 2004), has a branching filamentous morphology and pattern of reproductive cell differentiation very similar to that of the extant xanthophyte alga *Vaucheria.* Kooistra *et al.* (2006) speculate that this similarity arose via convergence in a green algal clade; either interpretation places the origin of green algae earlier than 1000 Ma.

Fossils show that eukaryotic photoautotrophs were present in the benthos no later than the Mesoproterozoic Era (1600–1000 Ma), but what about the phytoplankton? Unicellular taxa occur in all three divisions of the Plantae, making it likely that such cells existed by the time that *Bangiomorpha* evolved. Of these, however, only the phycomate prasinophytes are likely to have left a tractable fossil record in marine

sedimentary rocks. As noted previously, the three major types of ornamented phycoma known from living prasinophytes have fossil records that extend backward to the Early Cambrian, but there is little evidence of earlier origin. In contrast, extant *Halosphaera* develop smoothly spheroidal phycomata that could easily be represented among leiosphaerid acritarchs in Proterozoic rocks (Figure 6A and B; Tappan, 1980). Ultrastructural and microchemical studies (e.g., Javaux *et al.* 2004; Marshall *et al.* 2005) provide our best opportunity to test this hypothesis.

Chromalveolates may be recorded in a very different way. In 1986, Allison and Hilgert reported small (7–40 μm in maximum dimension), apparently siliceous ovoid scales in cherts of the Tindir Group, northwestern Canada, now judged to be >635 and <710 Ma (Kaufman *et al.* 1992). The scales resemble those formed by living prymnesiophytes and (at a smaller size range) chrysophytes, likely documenting early diversification somewhere within the chromalveolate branch of the eukaryotic tree.

Fossils of any kind are rare in rocks older than about 2000 million years, but unambiguous fossils of eukaryotes occur in shales as old as 1650–1850 Ma (Knoll *et al.* 2006); little is known about their systematic relationships or physiology. Compilations of total diversity (e.g., Knoll 1994; Vidal and Moczydlowska 1997), assemblage diversity (Knoll *et al.* 2006), and morphospace occupation (Huntley *et al.* 2006) through time agree that a moderate diversity of eukaryotic organisms existed in Mesoproterozoic oceans. By ca. 1200 Ma if not earlier, this diversity included photosynthetic eukaryotes. Diversity appears to have increased modestly in the Neoproterozoic, but the major radiations within preservable seaweed and phytoplankton groups took place only at the end of the Proterozoic Era and during the ensuing Cambrian and Ordovician Periods (Knoll *et al.* 2006).

C. Proterozoic Molecular Biomarkers

Rocks containing organic matter amenable to biomarker analysis grow increasingly rare as we sample more deeply into the Proterozoic, and many of those available have undergone extensive heating such that only the most recalcitrant molecules remain. Nevertheless, a molecular fossil record of primary production is emerging for this long interval of Earth history. A major feature of the record is the high relative abundance of 2-MeHI in organic-rich distal shales throughout the Proterozoic (Figure 5), which, in conjunction with the microfossil record and geochemical evidence for oxic surface waters in oceans, provides strong evidence for the importance of cyanobacterial production. There has been such limited sampling of Paleo- and Mesoproterozoic sediments that it has not been possible to examine these for correlations with lithology, as has been accomplished for the Phanerozoic (Figure 5C).

Steranes have been reported from a number of Proterozoic successions (e.g., Summons and Walter 1990; Hayes *et al*. 1992; Dutkiewicz *et al*. 2003) and are generally found in low abundance, reflecting at least in part the thermal maturity of their host rocks. These molecular fossils establish the presence of eukaryotes in Proterozoic oceans, but the scarcity of detailed records limits the inferences that can be drawn concerning ecological role or taxonomic affinities (because group-distinctive markers are generally below detection limits). The geologic record of steroid biosynthesis extends into the Late Archean, several hundred million years before the first recognized protistan fossils. However, there continue to be doubts about the syngeneity of these steroids because of the advanced maturity of all the sections studied so far and because of the potential for the bitumens found there to have migrated from younger sequences or to be contaminants from drill and handling (e.g., Brocks *et al*. 2003a, 2003b). In contrast, the Roper and McArthur Basins of northern Australia contain rocks of low to moderate thermal maturity, more consistent with the probability of finding genuinely syngenetic biomarkers. Given that studies of the Roper and McArthur Basin sediments and oils consistently show the presence of steroids (Summons *et al*. 1988a, 1988b; Dutkiewicz *et al*. 2003) along with other evidence for the *in situ* (Summons *et al*. 1994) character of the bitumens, there seems little doubt that steroid biosynthesis operated as long ago as 1640 Ma. Preservation is a major limitation for both body and molecular fossil records at this point. Nonetheless, sterane abundances in rocks of this age appear to be low independent of maturity level and do not approach Phanerozoic abundances until the Neoproterozoic Era. Based on a few exceptionally well-preserved deposits of organic material in Mesoproterozoic shales, there appear to have been times and places where producer communities were very different from those that characterize later periods. Brocks *et al*. (2005) have reported biomarkers of anaerobic, sulfide-utilizing phototrophs in the carbonate facies of the Barney Creek Formation, Australia, suggesting that euxinic waters extended well into the photic zone. Molecular markers of eukaryotes and cyanobacteria in those portions of the Barney Creek Formation are exceptionally scarce, raising the possibility that, in at least some environments during the Proterozoic, production by anoxygenic photoautotrophs may have been quantitatively important. In fact, the scarcity of steroids and 2-methylhopanoids in samples with most abundant biomarkers for phototrophic sulfur bacteria is also consistent with the highly euxinic conditions they require. The extent to which this scenario reflects global versus local conditions awaits further elucidation, but it is consistent with geochemical proxies for oceanic redox conditions, observed globally (e.g., Logan *et al*. 1995; Arnold *et al*. 2003; Shen *et al*. 2003; Gellatly and Lyons 2005).

In contrast to the scarcity of suitable organic-rich rocks in the Paleoproterozoic

and Mesoproterozoic successions, the Neoproterozoic is replete with well-characterized organic matter in low maturity sections from Australia, North America, Oman (e.g., Grantham *et al*. 1987) and eastern Siberia (Summons and Powell 1992; see Summons and Walter 1990 and Hayes *et al*. 1992, for reviews). Of particular note are the oldest commercial petroleum accumulations in Siberia and Oman. These late Neoproterozoic oils display striking biomarker patterns characterized by particularly abundant steroidal hydrocarbons. Predominance of C_{29} steranes over other homologues is a feature of oils from the South Oman Salt Basin that has received much attention since it was first reported by Grantham (1986). Examination of Neoproterozoic petroleum samples worldwide suggests that this is a globally significant feature (Figure 7) that records the rise of green algae to ecological prominence. Further, samples that show the strong predominance of C_{29} steranes are also generally characterized by anomalously light carbon isotopic compositions, [AU1] in the range of −33 to −37% PDB. It is likely no coincidence that the oldest commercial petroleum deposits bear the prominent signature of a green algal contribution to petroleum-prone organic matter and that some green algae are known for their capacity to biosynthesize decay resistant aliphatic biopolymers in their cell wall (algaenans; Derenne *et al*. 1991, 1992; Gelin *et al*. 1996, 1997, 1999), a likely source of acyclic hydrocarbons in these oils (e.g. Höld *et al*. 1999).

D. Summary of the Proterozoic Record

Microfossil and biomarker records are consistent in showing that cyanobacteria and eukaryotic microorganisms were both present in Proterozoic oceans. Fossils indicate that the primary endosymbiotic event establishing the photosynthetic Plantae took place no later than ca. 1200 Ma, in broad agreement with molecular clock estimates appropriately ornamented by error estimates (Hackett *et al*. 2006). Thus, eukaryo- [AU2]

tic algae contributed to primary production during at least the last 600 million years of the Proterozoic Era. Yet, preserved biomarkers are dominated by cyanobacteria and other photosynthetic bacteria, suggesting that eukaryotes played a limited quantitative role in primary production. Increasing amounts of C_{29} steranes appear in later Neoproterozoic samples, typified by the high sterane to hopane ratios and strong C_{29} sterane predominances in oils from the South Oman Salt Basin and eastern Siberia (e.g., Grantham 1986; Summons and Powell 1992); this suggests that green algae began to play an increasing role in primary production by 600–700 Ma. The timing of this transition is not well constrained but, in Oman, it begins prior to the Marinoan glaciation and extends to the Neoproterozoic-Cambrian boundary (Grosjean *et al*. 2005, and unpublished data), falsifying the hypothesis that the green algal proliferation was a response to the Acraman impact event in Australia (McKirdy *et al*. 2006). In short, algae may have emerged as major contributors to global primary production only during the late Neoproterozoic to Early Paleozoic interval distinguished by marked increases in fossil diversity.

V. ARCHEAN OCEANS

We evaluate the Archean geobiological record cautiously, as available data are sparse. Sedimentary rocks are limited in volume, especially for the early Archean, and most surviving strata have been altered by at least moderate metamorphism. Thus, any interpretation must be provisional.

The expectation from both phylogeny and the Proterozoic biogeochemical record is that prokaryotic primary producers are likely to have governed early marine ecosystems. Cyanobacteria have the ecological advantage of obtaining electrons from ubiquitous water molecules, but there is no reason to believe that cyanobacteria were the primordial photoautotrophs (see Blankenship *et al*.

2006). Indeed, the question of when cyano-bacteria, with their coupled photosystems, evolved remains contentious. In an early ocean dominated by anoxygenic photobacteria, the availability of electron donors (Fe^{++}, H_2, H_2S) would have limited primary production (Kharecha et al. 2005).

The four principal lines of evidence used to contract an evolutionary history of Proterozoic oceans apply equally to the Archean record: microfossils, biomarker molecules, sedimentary textures that record microbe/sediment interactions on the ancient seafloor (e.g., stromatolites), and stable isotopic signatures (Knoll 2003b). Few microfossils have been reported from Archean cherts and shales. Somewhat poorly preserved fossils occur in latest Archean cherts from South Africa (Lanier 1986; Klein et al. 1987; Altermann and Schopf 1995); these could include cyanobacteria, but other alternatives cannot be rejected. More controversial are the nearly 3500 Ma carbonaceous microstructures interpreted as bacterial, and possibly cyanobacterial trichomes by Schopf (1993). Recently, not only their systematic interpretation but their fundamental interpretation as biogenic has been called into question (Brasier et al. 2002, 2005, 2006). Debate about these structures continues (e.g., Schopf et al. 2002a, 2002b, in response to Brasier et al. 2002), but few believe that these structures, whatever their origin, provide phylogenetic or physiological insights into early life.

The stromatolite record is similar. At least 40 occurrences of stromatolites have been reported from Archean rocks (Schopf 2006)—not a lot given that the record is 1 billion years long. Those younger than about 3000 Ma include structures that accreted by the trapping and binding of fine particles; such textures are more or less uniformly associated with microbial activity. Bedding surfaces on siliciclastic rocks of comparable age similarly include textures attributable to microbial mat communities (Noffke et al. 2006). Older stromatolites are largely precipitated structures whose bio-genicity is harder to establish. Conoidal forms in ca. 3450 Ma rocks from Western Australia (Hofman et al. 1999; Allwood et al. 2006) and "roll-up structures" (sediment sheets that were ripped up and rolled into a cylinder by currents, suggesting microbially mediated cohesion of poorly lithified laminae) in comparably old rocks from South Africa (Tice and Lowe 2004) may well require biological participation to form, but the taxonomic and physiological nature of the participants remains uncertain (see Tice and Lowe 2006, for an argument that anoxygenic photobacteria fueled Early Archean mat ecosystems).

No biogeochemically informative organic molecules are known from Early Archean rocks. Late Archean biomarkers have been reported; controversy surrounding their identification and interpretation has two distinct aspects. The first relates to their provenance and whether or not all the organic matter present in ancient sediments is coeval, as recognized by Brocks et al. (2003a, 2003b). This question can best be addressed through studies of cores recently drilled and curated under controlled conditions. For example, the Agouron-Griqualand Paleoproterozoic Drilling Project (AGPDP) and the NASA Astrobiology Institute Drilling Project (ABDP) have recovered fresh cores from South Africa and the Pilbara Craton of Western Australia, respectively, which are being studied for a range of paleobiologic proxies, including analyses of preserved organic matter. One aim of this research is to control or eliminate contamination by hydrocarbons from younger sediments; a second aim is to test for relationships between extractable hydrocarbons and rock properties that could not exist in the case of contamination.

The second aspect of the controversy revolves around the degree to which biosynthetic pathways may have evolved over long time scales. It is fair to state that there must have been evolution in the structure and function of lipids over geological time. However, key enzymes in the biosynthetic

pathways leading to sterols (Summons *et al.* 2006) and other triterpenoids in extant organisms are highly conserved. The known geological record of molecular fossils, especially steranes and triterpanes, is notable for the limited number of structural motifs that are recorded. With a few exceptions, the carbon skeletons are the same as those found in the lipids of extant organisms, and no demonstrably extinct structures have been reported. Furthermore, the patterns of occurrence sterane and triterpane isomers are rigid over billion-year time scales and correlate strongly with environments of deposition, suggesting that diagenetic pathways connecting functional lipids to their fossil biomarker counterparts are also conserved. We also have evidence, through the occurrence of rearranged steranes (diasteranes) and unconventional steroids such as the 2-alkyl and 3-alkyl steranes (Summons and Capon 1988, 1991) and their aromatic counterparts (Dahl *et al.* 1995), that fossil steranes originated from precursors that carried a 3-hydroxyl group and unsaturation in the tetracyclic ring system, as extant sterols do. Thus, there is no evidence for major changes in the known record of chemical fossils that could be attributed to the inception, evolution, or alternative lipid biosynthetic pathways to the 24-alkylated steroids or hopanoids (Kopp *et al.* 2005). Accordingly, if biomarkers that have been identified are confirmed to be indigenous to late Archean rocks, this will constitute robust evidence for the presence of algae and bacteria early in Earth history. The fact that molecular oxygen is an absolute requirement for the biosynthesis of algal sterols also implies that oxygenic photosynthesis must have been present at the time (Summons *et al.* 2006).

The carbon isotopic abundances of Early Archean carbonates and organic matter are comparable to those of younger rocks, indicating fractionation like that imparted by Rubisco-based autotrophy. Indeed, C-isotopic signatures that are consistent with carbon fixation by Rubisco extend backward to nearly 3800 Ma metamorphosed sediments from southwestern Greenland (Rosing and Frei 2004). The question is whether these signatures *require* such an interpretation. Other biochemical pathways for carbon fixation exist and at least some of them impart isotopic signatures that are equally consistent with Archean data (e.g., Knoll and Canfield 1998). It has been known for 2 decades that abiotic syntheses of organic matter, like that demonstrated by Miller (1953), fractionate C-isotopes (Chang *et al.* 1982); the degree of fractionation appears to vary widely as a function of initial conditions. More recently, McCollom and Seewald (2006) have shown that Fischer-Tropsch-type (FTT) synthesis can produce organic compounds depleted in ^{13}C relative to their carbon source to a degree similar to that associated with biological carbon fixation. In these experiments, formic acid was reacted with native iron at 250°C and 325 bar, and a series of *n*-alkanes were produced that were depleted by ~36% relative to the reactant carbon. This isotopic discrimination is in the range observed for the difference in $\delta^{13}C$ values of coexisting carbonate minerals and organic matter in some Archean deposits. This finding emphasizes the importance of understanding the depositional context (e.g., sedimentary versus hydrothermal) of this very ancient carbonaceous matter when assessing its biogenicity.

We conclude that the origin of life predates the known record of preserved sedimentary rocks, but the nature of that life—and, in particular, the nature of primary producers in the oceans—remains uncertain. All known geobiological records from Archean rocks are consistent with an early evolution of cyanobacteria, but few if any require such an interpretation (Knoll 2003a). Indeed, Kopp *et al.* (2005) have hypothesized that cyanobacteria originated only in association with the initial accumulation of free oxygen in the atmosphere, 2320–2450 Ma (Holland 2006). Careful geobiological analyses of well-preserved Archean rocks remain a priority for continuing research.

VI. CONCLUSIONS

In combination, paleontological and organic geochemical data suggest that the second half of Earth history can be divided into three major eras, with respect to marine photosynthesis. Limited data from Paleoproterozoic and Mesoproterozoic rocks suggest that cyanobacteria and other photosynthetic bacteria dominated primary production at that time, with anoxygenic photosynthetic bacteria playing an important role at least locally in water masses subtended by a euxinic oxygen-minimum zone. Indeed, available data suggest that cyanobacteria continued as principal photoautotrophs well into the Phanerozoic Eon and long after photosynthesis originated in eukaryotic cells. C_{29} sterane abundances indicate that green algae joined but did not entirely displace cyanobacteria as major primary producers during the latest Proterozoic and Cambrian; the second phase of primary production history thus initiated persisted until the Mesozoic radiation of modern phytoplankton dominants. Later Triassic oceans may have been the first in which cyanobacteria played a relatively minor role in continental shelf production. (Of course, they remain important today in the open gyre systems little recorded by pre-Jurassic sedimentary rocks.) The degree to which Chl a+c algae participated in Neoproterozoic and Paleozoic marine ecosystems remains unresolved, but if present their role must be have much smaller than it has been during the past 200 million years.

The observation that the oceans have experienced two major shifts over the past billion years in the composition of primary producers, and the corollary that at least some clades emerged as ecologically dominant primary producers long after their evolutionary origin invites discussion of possible drivers. The importance of cyanobacteria in Proterozoic primary production can be attributed to at least two circumstances, their early diversification and environmental circumstances in Proterozoic oceans. Prior to the proliferation of eukaryotic algae, cyanobacteria would, of course, have had an open playing field, flourishing in oxygenated surface waters from coastline to mid-ocean gyres, although ceding deeper, at least intermittently euxinic parts of the photic zone to green and purple photosynthetic bacteria. Why, however, does it appear that cyanobacteria continued as dominant features of the photosynthetic biota on continental shelves long after red and green algae entered the oceans? At least in part, the answer may have to do with the nutrient structure of oceans in which, beneath an oxygenated surface layer, the oxygen minimum zone (Brocks *et al*. 2005), if not the entire deep ocean (Canfield, 1998), had a high propensity for developing euxinia. Under these conditions, one would expect little fixed N to resurface during upwelling (Anbar and Knoll 2002; Fennel *et al*. 2005), providing strong selective advantage for cyanobacteria able to fix N and scavenge low concentrations of fixed N effectively from seawater.

Increasing oxygenation of the oceans during the Neoproterozoic Era (Canfield *et al*. 2006; Fike *et al*. 2006) would have begun to alleviate the N budget, as the mid-level waters that source upwelling would have been increasingly likely to remain oxic, limiting denitrification and anammox reactions that strip fixed N from ascending anoxic water masses. More ammonium would have been returned to the surface, and nitrate would have begun to accumulate for the first time. In consequence, eukaryotes would have spread more completely across benthic environments and into the phytoplankton, as recorded in the geological record (Knoll *et al*. 2006).

Dinoflagellates, diatoms, and coccolithophorids exhibit many features that collectively account for their ecological success in modern oceans (Delwiche 2006; de Vargas *et al*. 2006; Kooistra *et al*. 2006). Why, then, do we not see evidence for similar success in Paleozoic seas? One possibility is that the secondary endosymbioses that led to these

group groups took place only at the beginning of the Mesozoic Era or shortly earlier. Such a scenario is consistent with clade-specific molecular clocks for diatoms and coccolithophorids but is inconsistent with the hypothesis that secondary endosymbiosis involving red algal photosymbionts occurred only once, in the early history of the chromalveoates (Hackett *et al.* 2006). Regardless of the timing of clade origination, however, we need to consider environmental factors, for the simple reason that it is hard to conceive of biological barriers would have prevented secondary endosymbiosis long before the Mesozoic began.

Black shale distributions may provide perspective on this issue. Multiregional to globally widespread black shales are essentially absent from Cenozoic successions, but occur at about seven discrete stratigraphic horizons in the Mesozoic record (Jones and Jenkyns 2001). In contrast, there are at least seven black shale horizons in the Devonian record alone and many more in other parts of the Paleozoic, especially the Cambrian and Ordovician (Berry and Wilde 1978). Prior to the dawn of the Cambrian, *most* shales were carbonaceous (e.g., Knoll and Swett 1990; Abbott and Sweet 2000). If the redox structure of the oceans influenced the selective environment of green versus Chl a+c phytoplankton, then it may be that only in Mesozoic oceans did environmental conditions routinely favor the latter. As noted previously, fossils and biomarkers indicate that greens and cyanobacteria transiently reestablished themselves as principal primary producers during the Mesozoic OAEs; green sulfur bacteria also proliferated during episodes of photic zone euxinia. Moreover, unlike chromalveolate photoautotrophs, both green algae and cyanobacteria show a pronounced preference for ammonium over [AU3] nitrate in metabolism (Litchman 2006). Thus, the long-term redox evolution of the oceans may govern the composition of marine primary producers through time.

Whatever their drivers, the two observed transitions in the marine photosynthetic biota provide an important framework and stimulus for continuing paleobiological investigations of animal evolution. Latest Proterozoic and Cambrian phytoplankton radiation may not simply be a response to animal evolution (e.g., Peterson and Butterfield 2005) but also a driver. Well-documented (Bambach 1993) increases in body size among Mesozoic (versus Paleozoic) marine invertebrates may reflect the Mesozoic radiation of larger net plankton, while the so-called Mesozoic Marine Revolution among mostly Cretaceous and Cenozoic marine animals may specifically reflect the rise to ecological prominence of diatoms (see Finkel 2006). Vermeij (1977) first docu- [AU4] mented the major evolutionary changes in skeletonized marine fauna during this interval and ascribed it to a late Mesozoic radiation of predators able to penetrate shells. Bambach (1993), however, argued that the required radiation of top predators could only occur as a consequence of increased primary production and, hence, increasing nutrient status in the oceans. Bambach (1993) suggested that evolving angiosperms increased nutrient fluxes to the oceans, and although this likely did occur (see Knoll 2003c), the evolution of a high-quality food source and efficient nutrient transporter in the form of diatoms likely played at least an equal role.

A. Directions for Continuing Research

Over the past decade, both paleontologists and organic geochemists have made inroads into problems of photosynthetic history. Nonetheless, there continue to be more questions than answers. Future research will require more and independent studies of fossils and hydrocarbon distribution on Archean and Proterozoic rocks. However, it will also require phylogenetic, biosynthetic, and functional studies of sterols and BHPs (especially 2-Me-BHP) in living organisms that will increase our ability to interpret ancient records. In comparable fashion, continuing research on Proterozoic and Paleo-

zoic microfossils will need to stress wall ultrastructure (Arouri *et al*. 1999; Talzyina 2000; Javaux *et al*. 2004) and microchemical analysis (e.g., FTIR, hydropyrolysis, x-ray and, perhaps, Raman spectroscopy; Love *et al*. 1995; Schopf *et al*. 2002a, 2002b; Boyce *et al*. 2003; Marshall *et al.,* 2005) interpreted in light of corresponding analyses of living cells and younger, taxonomically unambiguous, fossils.

Finally, as noted previously, the evolution of photosynthetic organisms did not take place in a passive or unchanging ocean nor did it occur in an ecological vacuum. Improved understanding of Earth's redox history and the evolutionary record of animals (and land plants) (Falkowski *et al*. 2004) will provide the framework needed to interpret the evolutionary history of marine photoautotrophs as it continues to emerge.

Acknowledgments

References

Abbott, S.T., and Sweet, I.P. (2000). Tectonic control on third-order sequences in a siliciclastic ramp-style basin: an example from the Roper Superbasin (Mesoproterozoic), northern Australia. A*ustral. J. Earth Sci*. **47:** 637–657.

Allard, W.G., Belt, S.T., Massé, G., Naumann, R., Robert, J.-M., and Rowland, S. J. (2001). Tetraunsaturated sesterterpenoids (Haslenes) from Haslea ostrearia and related species. *Phytochemistry* **56:** 795–800.

Allison, C.W., and Hilgert, J.W. (1986). Scale microfossils from the Early Cambrian of northwest Canada. *J. Paleontol*. **60:** 973–1015.

Allwood, A.C., Walter, M.R., Kamber, B.S., Marshall, C.P., and Burch, I.W. (2006). Stromatolite reef from the Early Archaean era of Australia. *Nature* **441:** 714–718.

Altermann, W., and Schopf, J.W. (1995). Microfossils from the Neoarchean Campbell Group, Griqualand West sequence of the Transvaal Supergroup, and their paleoenvironmental and evolutionary implications. *Precambrian Res*. **75:** 65–90.

Anbar, A.D., and Knoll, A.H. (2002). Proterozoic ocean chemistry and evolution: a bioorganic bridge? *Science* **297:** 1137–1142.

Andrusevich, V.E., Engel, M.H., Zumberge, J.E., and Brothers, L.A. (1998). Secular, episodic changes in stable isotopic composition of crude oils. *Chem. Geol.* **152:** 59–72.

Andrusevich, V.E., Engel, M.H., and Zumberge, J.E. (2000). Effects of paleolatitude on the stable carbon isotope composition of crude oils. *Geology* **28:** 847–850.

Aquino Neto, F.R., Trigüis, J., Azevedo, D.A., Rodrigues, R., and Simoneit B.R.T. (1992). Organic geochemistry of geographically unrelated Tasmanites. *Org. Geochem*. **18:** 791–803. [AU5]

Arnold, G.L., Anbar, A.D., Barling, J., and Lyons, T.W. (2003). Molybdenum isotope evidence for widespread anoxia in mid-Proterozoic oceans. *Science* **304:** 87–90.

Arouri, K., Greenwood P.F., and Walter, M.R. (1999). A possible chlorophycean affinity of some Neoproterozoic acritarchs. *Org. Geochem*. **30:** 1323–1337.

Arouri, K., Greenwood, P.F., and Walter, M.R. (2000b). Biological affinities of Neoproterozoic acritarchs from Australia: microscopic and chemical characterisation. *Org. Geochem*. **31:** 75–89. [AU6]

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

Belt, S.T., Allard, W.G., Massé, G., Robert, J.-M., and Rowland S. J. (2000). Highly branched isoprenoids (HBIs): identification of the most common and abundant sedimentary isomers. *Geochim. Cosmochim. Acta* **64:** 3839–3851.

Berry, W.B.N., and Wilde, P. (1978). Progressive ventilation of the oceans—an explanation for the distribution of the Lower Paleozoic Black Shales. *Am. J. Sci.* **278:** 257–275.

Bisseret, P., Zundel, M. and Rohmer, M. (1985). Prokaryotic triterpenoids. 2. 2B-Methylhopanoids from *Methylobacterium organophilum* and *Nostoc muscorum*, a new series of prokaryotic triterpenoids. *Eur. J. Biochem*. **150:** 29–34.

Blankenship, R., Sadekar, S., and Raymond, J. (2006). The evolutionary transition from anoxygenic to oxygenic photosynthesis. *Evolution of Aquatic Photosutotrophs*. P. Falkowski and A.H. Knoll, eds. London, Academic Press, pp. xxx-xxx. [AU7]

Bond, D., Wignall, P.B., and Racki, G. (2004). Extent and duration of marine anoxia during the Frasnian-Famennian (Late Devonian) mass extinction in Poland, Germany, Austria and France. *Geol. Mag*. **141:** 173–193.

Boyce, C.K., Cody, G.D., Fogel, M.L., Hazen, R.M., and Knoll, A.H. (2003). Chemical evidence for cell wall lignification and the evolution of tracheids in Early Devonian plants. *Int. J. Plant Sci.* **164:** 691–702.

Brasier, M., McLoughlin, N., Green, O., and Wacey, D. (2006). A fresh look at the fossil evidence for early Archaean cellular life. *Phil. Trans. R. Soc. B* **361:** 887–902.

Brasier, M.D., Green, O.R., Jephcoat, A.P., Kleppe, A.K., van Kranendonk, M.J., Lindsay, J.F., Steele, A., and Grassineau, N.V. (2002). Questioning the evidence for Earth's oldest fossils. *Nature* **416:** 76–81.

Brasier, M.D., Green, O.R., Lindsay, J.F., McLoughlin, N., Steele, A., and Stoakes, C. (2005). Critical testing of earth's oldest putative fossil assemblage from the similar to 3.5 Ga Apex Chert, Chinaman Creek, western Australia. *Precambrian Res.* **140:** 55–102.

Brassell, S.C., Eglinton, G., Marlowe, I.T., Pflaumann, U., and Sarnthein, M. (1986). Molecular stratigraphy: a new tool for climatic assessment. *Nature* **320:** 129–133.

Brocks J.J., Love G.D., Snape C.E., Logan G.A., Summons R.E., and Buick R. (2003a) Release of bound aromatic hydrocarbons from late Archean and Mesoproterozoic kerogens via hydropyrolysis. *Geochim. Cosmochim. Acta* **67:** 1521–1530.

Brocks, J.J., Love, G.D., Summons, R.E., Knoll, A.H., Logan, G.A., and Bowden, S. (2005). Biomarker evidence for green and purple sulfur bacteria in an intensely stratified Paleoproterozoic ocean. *Nature* **437:** 866–870.

Brocks, J.J., and Summons, R.E. (2004). Sedimentary hydrocarbons, biomarkers for early life. *Treatise in Geochemistry.* Vol. 8. H.D. Holland and K. Turekian, eds. Amsterdam, Elsevier, pp. 65–115.

Brocks, J.J., Summons, R.E., Logan, G.A., and Buick, R. (2003b). Molecular fossils in Archean rocks II: composition, thermal maturity and integrity of hydrocarbons extracted from sedimentary rocks of the 2.78 2.45 billion years old Mount Bruce Supergroup, Pilbara Craton, Western Australia. *Geochim. Cosmochim. Acta* **67:** 4289–4319.

Butterfield, N.J. (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, N.J. (2004). A vaucheriacean alga from the middle Neoproterozoic of Spitsbergen: implications for the evolution of Proterozoic eukaryotes and the Cambrian explosion. *Paleobiology* **30:** 231–252.

Butterfield, N.J., Knoll, A.H., and Swett, N. (1994). Paleobiology of the Neoproterozoic Svanbergfjellet Formation, Spitsbergen. *Fossils Strata* **34:** 1–84.

Canfield, D.E. (1998). A new model for Proterozoic ocean chemistry. *Nature* **396:** 450–453.

Canfield, D.E., Poulton, S.W., and Narbonne, G.M. (2006) Late Neoproterozoic deep-ocean oxygenation [AU8] and the rise of animal life. *Science* in press.

Cavalier-Smith, T. (1999). Principles of protein and lipid targeting in secondary symbiogenesis: euglenoid, dinoflagellate, and sporozoan plastid origins and the eukaryote family tree. *J. Euk. Microbiol.* **46:** 347–366.

Chang, S., Des Marais, D., Mack, R., Miller, S.L., and Strathearn, G.E. (1982). Prebiotic organic syntheses and the origin of life. *Earth's Earliest Biosphere: Its Origin and Evolution.* J.W. Schopf, ed. Princeton, NJ, Princeton University Press, p. 53–92.

Coolen, M.J.L., Muyzer, G., Rijpstra, W.I.C., Schouten, S., Volkman, J.K., and Sinninghe Damsté, J.S. (2004). Combined DNA and lipid analyses of sediments reveal changes in Holocene haptophyte and diatom populations in an Antarctic lake. *Earth Planet. Sci. Lett.* **223:** 225–239.

Dahl J., Moldowan J.M., Summons R.E., McCaffrey M.A., Lipton P.A., Watt D.S., and Hope J.M. (1995). Extended 3β-alkyl steranes and 3-alkyl triaromatic steroids in oils and rock extracts. *Geochim. Cosmochim. Acta* **59:** 3717–3729.

Delwiche, C.F. (2006) The origin and evolution of dinoflagellates. *Evolution of Aquatic Photosutotrophs.* P. Falkowski and A.H. Knoll, A.H., eds. London, Academic Press, pp. xxx-xxx.   [AU9]

Derenne, S., Largeau, C., Casadevall, E., Berkaloff, C., and Rousseau, B. (1991).Chemical evidence of kerogen formation in source rocks and oil shales via selective preservation of thin resistant outer walls of microalgae: origin of ultralaminae. *Geochim. Cosmochim. Acta* **55:** 1041–1050.

Derenne, S., Le Berre, F., Largeau, C., Hatcher, P. G., Connan, J., and Raynaud, J.-F. (1992). Formation of ultralaminae in marine kerogens via selective preservation of thin resistant outer walls of microalgae. *Org.Geochem.* **19:** 345–350.

de Vargas, C., Probert, I, Aubrey, M.-P., and Young, J. (2006). Origin and evolution of coccolithophores: from coastal hunters to oceanic farmers. *Evolution of Aquatic Photosutotrophs.* P. Falkowski and A.H. Knoll, eds. London, Academic Press, London, pp. xxx-xxx.   [AU10]

Douzery, E.J.P., Snell, E.A., Bapteste, E., Delsuc, F., and Philippe, H. (2004). The timing of eukaryotic evolution: does a relaxed molecular clock reconcile proteins and fossils? *Proc. Nat. Acad. Sci. U S A* **101:** 15386–15391.

Dumitrescu, M., and Brassell, S.C. (2005). Biogeochemical assessment of sources of organic matter and paleoproductivity during the early Aptian oceanic anoxic event at Shatsky Rise, ODP Leg 198. *Org. Geochem.* **36:** 1002–1022.

Dutkiewicz, A., Volk, H., Ridley, J., and George, S. (2003). Biomarkers, brines, and oil in the Mesoproterozoic, Roper Superbasin, Australia. *Geology* **31:** 981–984.

Edwards, D.S., Summons, R.E., Kennard, J.M., Nicoll, R.S., Bradshaw, J., Bradshaw, M., Foster C.B., O'Brien, G.W., and Zumberge, J.E. (1997). Geochemical characterisation of Palaeozoic petroleum systems in northwestern Australia. *Austral. Petrol. Production Explorationists Assoc. J.* **37:** 351–379.

Evitt, W.R. (1963). A discussion and proposals concerning fossil dinoflagellates, hystrichospheres, and acritarchs: 2. *Proc. Nat. Acad. Sci., U S A* **49:** 298–302.

Farrimond, P., Eglinton, G., and Brassell, S.C. (1986). Alkenones in Cretaceous black shales, Blake-Bahama Basin, western North Atlantic. *Org. Geochem.* **10:** 897–903.

Falkowski, P.G., Katz, M.E., Knoll, A.H., Quigg, A., Raven, J.A., Schofield, O., and Taylor, F.J.R. (2004). The evolution of modern eukaryotic phytoplankton. *Science* **305:** 354–360.

Fennel, K., Follows, M., and Falkowski, P.G. (2005). The co-evolution of the nitrogen, carbon and oxygen cycles in the Proterozoic ocean. *Am. J. Sci.* **305:** 526–545.

Fike, D.A., Grotiznger, J.P., Pratt, L.M., and Summons, R.E. (2006). Oxidation of the Ediacaran Ocean. *Nature* **444:** 744–747.

Foster, C.B., and Afonin, S.A. (2006). *Syndesmorion* gen. nov. A coenobial alga of Chlorococcalean affinity from the continental Permian-Triassic deposits of Dalongkou *section, Xinjiang Province, China. Rev. Palaeobot. Palynol.* **138:** 1–8.

Gelin, F., Boogers, I., Noordeloos, A.A.M., Sinninghe Damsté, J.S., Hatcher, P.G., and de Leeuw, J.W. (1996). Novel, resistant microalgal polyethers: an important sink of organic carbon in the marine environment? *Geochim. Cosmochim. Acta* **60:** 1275–1280.

Gelin, F., Boogers, I., Noordeloos, A.A.M., Sinninghe Damsté, J.S., Riegman, R., and de Leeuw, J.W. (1997). Resistant biomacromolecules in marine microalgae of the classes Eustigmatophyceae and Chlorophyceae: geochemical implications. *Org. Geochem.* **26:** 659–675.

Gelin, F., Volkman, J.K., Largeau, C., Derenne, S., Sinninghe Damsté, J.S., and de Leeuw, J. W. (1999). Distribution of aliphatic, nonhydrolyzable biopolymers in marine microalgae. *Org. Geochem.* **30:** 147–159.

Gellatly, A.M., and Lyons, T.M. (2005). Trace sulfate in mid-Proterozoic carbonates and the sulfur isotope record of biospheric evolution. *Geochim. Cosmochim. Acta* **69:** 3813–3829.

Golubic, S., and Seong-Joo, L. (1999). Early cyanobacterial fossil record: preservation, palaeoenvironments and identification *Eur. J. Phycol.* **34:** 339–348.

Grantham, P.J. (1986). The occurrence of unusual C_{27} and C_{29} sterane predominances in two types of Oman crude oil. *Org. Geochem.* **9:** 1–10.

Grantham, P.J., Lijmbach, G.W.M., Posthuma, J., Hughes Clarke, M.W., and Willink R.J. (1987). Origin of crude oils in Oman. *J. Petroleum Geol.* **11:** 61–80.

Grantham, P.J., and Wakefield, L.L. (1988). Variations in the sterane carbon number distributions of marine source rock derived crude oils through geological time. *Org. Geochem.* **12:** 61–73.

Grice, K., Cao, C., Love, G.D., Bottcher, M.E., Twitchett, R.J., Grosjean, E., Summons, R.E., Turgeon, S.C., Dunning, W., and Jin, Y. (2005). Photic zone euxinia during the Permian-Triassic superanoxic event. *Science* **307:** 706–709.

Grosjean, E., Stalvies, C., Love, G.D., Lewis, A.N., Hebting, Y., Fike, D.A., Taylor, P.N., Newall, M.J., Grotzinger, J.P., Farrimond, P., and Summons, R.E. (2005). New oil-source correlations in the South Oman Salt Basin. *Organic Geochemistry: Challenges for the 21st Century*. 22 IMOG Seville, Spain, Abstract OOS-1.

Grotzinger, J.P., and Knoll, A.H. (1999). Proterozoic stromatolites: evolutionary mileposts or environmental dipsticks? *Ann. Rev. Earth Planet. Sci.* **27:** 313–358.

Hayes, J.M., Summons, R.E., Strauss, H., Des Marais, D.J., and Lambert, I.B. (1992). Proterozoic biogeochemistry. *The Proterozoic Biosphere: A Multidisciplinary Study*. J.W. Schopf and C. Klein, eds. Cambridge, UK, Cambridge University Press, pp. 81–133.

Hebting, Y., Schaeffer, P., Behrens, A., Adam, P., Schmitt, G., Schneckenburger, P., Bernasconi, S.M., and Albrecht, P. (2006). Biomarker evidence for a major preservation pathway of sedimentary organic carbon. *Science* **312:** 1627–1631.

Hedges, J.I., and Keil, R.G. (1995). Sedimentary organic matter preservation: an assessment and speculative synthesis. *Mar. Chem.* **49:** 81–115.

Herman, N. (1990). *Organic World One Billion Years Ago*. Nauka, Leningrad.

Hofmann, H.J., Grey, K., Hickman, A.H., and Thorpe, R.I. (1999). Origin of 3.45 Ga coniform stromatolites in Warrawoona Group, Western Australia. *Geol. Soc. Am. Bull.* **111:** 1256–1262.

Holba, A.G., Dzou L.I.P., Masterson, W.D., Hughes, W.B., Huizinga, B.J., Singletary, M.S., Moldowan, J.M., Mello, M.R., and Tegelaar, E. (1998a). Application of 24-norcholestanes for constraining source age of petroleum. *Org. Geochem.* **29:** 1269–1283.

Holba, A.G., Tegelaar, E.W., Huizinga, B.J., Moldowan, J.M., Singletary, M.S., McCaffrey, M.A., and Dzou, L.I.P. (1998b). 24-norcholestanes as age-sensitive molecular fossils. *Geology* **26:** 783–786.

Höld, I.M., Schouten, S., Jellema, J., and Sinninghe Damsté, J.S. (1999). Origin of free and bound mid-chain methyl alkanes in oils, bitumens and kerogens of the marine, Infracambrian Huqf Formation (Oman). *Org. Geochem.* **30:** 1411–1428.

Holland, H.D. (2006). The oxygenation of the atmosphere and oceans. *Phil. Trans. R. Soc. B.* **361:** 903–915.

Huntley, J.W., Xiao, S.H., and Kowalewski, M. (2006). 1.3 Billion years of acritarch history: an empirical morphospace approach. *Precambrian Res.* **144:** 52–68.

Javaux, E.J., Knoll A.H., and Walter, M.R. (2004). TEM evidence for eukaryotic diversity in mid-Proterozoic oceans. *Geobiology* **2:** 121–132.

Jones, C.E., and Jenkyns, H.C. (2001). Seawater strontium isotopes, oceanic anoxic events, and seafloor hydrothermal activity in the Jurassic and Cretaceous. *Am. J. Sci.* **301:** 112–149.

Katz, M.E., Finkel, Z.V., Grzebyk, D., Falkowski, P.G., and Knoll, A.H. (2004). Evolutionary trajectories and biogeochemical impacts of marine eukaryotic phytoplankton. *Ann. Rev. Ecol. Syst.* **35:** 523–556.

Kaufman, A.J., Knoll, A.H., and Awramik, S.M. (1992). Bio- and chemostratigraphic correlation of Neoproterozoic sedimentary successions: the upper Tindir Group, northwestern Canada as a test case. *Geology* **20:** 181–185.

Kharecha, P., Kasting, J., and Siefert, J. (2005). A coupled atmosphere-ecosystem model of the early Archean Earth. *Geobiology* **3:** 53–76.

Kleemann, G., Poralla, K., Englert, G., Kjøsen, H., Liaaen-Jensen, S., Neunlist, S. and Rohmer, M. (1990). Tetrahymanol from the phototrophic bacterium *Rhodopseudomonas palustris*: first report of a gammacerane triterpene from a prokaryote. *J. Gen. Microbiol.* **136:** 2551–2553.

Klein, C., Beukes, N.J., and Schopf, J.W. (1987). Filamentous microfossils in the early Proterozoic Transvaal Supergroup—their morphology, significance, and paleoenvironmental setting. *Precambrian Res.* **36:** 81–94.

Knoll, A.H. (1989). Evolution and extinction in marine realm: some constraints imposed by microplankton. *Phil. Trans. R. Soc. B* **325:** 279–290.

Knoll, A.H. (1994). Proterozoic and Early Cambrian protists: evidence for accelerating evolutionary tempo. *Proc. Nat. Acad. Sci. U S A* **91:** 6743–6750.

Knoll, A.H. (2003a). The geological consequences of evolution. *Geobiology* **1:** 3–14.

Knoll, A.H. (2003b). *Life on a Young Planet*. Princeton, NJ, Princeton University Press.

Knoll, A.H. (2003c). Biomineralization and evolutionary history. *Rev. Mineral. Geochem.* **54:** 329–356.

Knoll, A.H., and Canfield, D.E. (1998). Isotopic inferences on early ecosystems. *Paleontol. Soc. Pap.* **4:** 212–243.

Knoll, A.H., and Golubic, S. (1992). Living and Proterozoic cyanobacteria. *Early Organic Evolution: Implications for Mineral Energy Resources*. M. Schidlowski S. Golubic, M.M. Kimberley, D.M. McKirdy, and P.A. Trudinger, eds. Berlin, Springer-Verlag, pp. 450–462.

Knoll, A.H., Javaux, E.J., Hewitt, D., and Cohen, P. (2006). Eukaryotic organisms in Proterozoic oceans. *Phil. Trans. R. Soc. B* **361:** 1023–1038.

Knoll, A.H., and Swett, K. (1987). Micropaleontology across the Precambrian-Cambrian boundary in Spitsbergen. *J. Paleontol.* **61:** 898–926.

Knoll, A.H., and Swett. K. (1990). Carbonate deposition during the late Proterozoic era: an example from Spitsbergen. *Am. J. Sci.* **290-A:** 104–132.

Knoll, A.H., Swett, K., and Mark. J. (1991). The Draken Conglomerate Formation: paleobiology of a Proterozoic tidal flat complex. *J. Paleontol.* **65:** 531–569.

Kohnen, M.E.L., Sinninghe Damsté. J.S., Baas, M., Kock-van Dalen, A.C., and de Leeuw, J.W. (1993). Sulphur-bound steroid and phytane carbon skeletons in geomacromolecules: implications for the mechanism of incorporation of sulphur into organic matter. *Geochim. Cosmochim. Acta* **57:** 2515–2528.

Kohnen, M.E.L., Sinninghe Damsté, J.S., and de Leeuw, JW. (1991). Biases from natural sulphurization in palaeoenvironmental reconstruction based on hydrocarbon biomarker distributions. *Nature* **349:** 775–778.

Kooistra, W.H.C.F., Gersonde, R., Medlin, L.K., and Mann, D.G. (2006). The origin and evolution of the diatoms: their adaptation to a planktonic existence. *Evolution of Aquatic Photosutotrophs*. P. Falkowski and A.H. Knoll, eds. London, Academic Press, pp. xxx–xxx.   [AU11]

Koopmans, M.P., Van Kaam-Peters, H.M.E., Schouten, S., de Leeuw, J.W., Sinninghe Damsté, J.S., Koster, J., Kenig, F., and Hartgers, W.A. (1996). Diagenetic and catagenetic products of isorenieratene: molecular indicators for photic zone anoxia: *Geochim. Cosmochim. Acta* **60:** 4467–4496.

Kopp, R.E., Kirschvink, J.L., Hilburn, I.A., and Nash, C.Z. (2005). The Paleoproterozoic snowball Earth: a climate disaster triggered by the evolution of oxygenic photosynthesis. *Proc. Nat. Acad. Sci. U S A* **102:** 11131–11136.

Kuypers, M.M.M., Lourens, L.J., Rijpstra, W.I.C., Pancost, R.D., Nijenhuis, I.A., and Sinninghe Damsté, J.S. (2004a). Orbital forcing of organic carbon burial in the proto-North Atlantic during oceanic anoxic event 2. *Earth Planet. Sci. Lett.* **228:** 465–482.

Kuypers, M.M.M., van Breugel, Y., Schouten, S., Erba, E., Sinninghe Damsté, J.S. (2004b). N_2-fixing cyanobacteria supplied nutrient N for Cretaceous oceanic anoxic events. *Geology* **32:** 853–856.

Lanier, W.P. (1986). Approximate growth rates of Early Proterozoic microstromatolites as deduced by biomass productivity. *Palaios* **1:** 525–542.

Logan G. A., Hayes J. M., Hieshima G. B., and Summons R. E. (1995). Terminal Proterozoic reorganisation of biogeochemical cycles. *Nature* **376:** 53–56.

Love G.D., Snape C.E., Carr A.D., and Houghton R. C. (1995). Release of covalently-bound alkane biomarkers in high yields from kerogen via catalytic hydropyrolysis. *Org. Geochem.* **23:** 981–986.

Maliva, R., Knoll, A.H., and Siever, R. (1989). Secular change in chert distribution: a reflection of evolving biological participation in the silica cycle. *Palaios* **4:** 519–532.

Marlowe, I.T., Green, J.C., Neal, A.C., Brassell, S.C., Eglinton, G., and Course, P.A. (1984). Long chain (*n*-C37-C39) alkenones in the Prymnesiophyceae. Distribution of alkenones and other lipids and their taxonomic significance. *Br. Phycol. J.* **19:** 203–216.

Marshall, C.P., Javaux, E.J., Knoll, A.H., and Walter, M.R. (2005). Combined micro-Fourier transform infrared (FTIR) spectroscopy and Micro-Raman spectroscopy of Proterozoic acritarchs: a new approach to palaeobiology. *Precambrian Res.* **138:** 208–224.

Martin, J.H., Knauer, G.A., Karl, D.M., and Broenkow, W.W. (1987). VERTEX: carbon cycling in the northeast Pacific. *Deep-Sea Res*. **34:** 267–285.

McCollom, T.M., and Seewald, J.S. (2006). Carbon isotope composition of organic compounds produced by abiotic synthesis under hydrothermal conditions. *Earth Planet. Sci. Lett*. **243:** 74–84.

McKirdy, D.M., Webster, L.J., Arouri, K.R., Grey, K., and Gostin, V.A. (2006). Contrasting sterane signatures in Neoproterozoic marine rocks of Australia before and after the Acraman asteroid impact. *Org. Geochem*. **37:** 189–207.

Mendelson, C.V., and Schopf, J.W. (1992). Proterozoic and selected Early Cambrian microfossils and microfossil-like objects. *The Proterozoic Biosphere: A Multidisciplinary Study*. J.W. Schopf and C. Klein, eds. Cambridge, UK, Cambridge University Press, pp. 867–951.

Miller, S.L. (1953). A production of amino acids under possible primitive Earth conditions. *Science* **117:** 527–528

Moczydlowska, M. (1991). Acritarch biostratigraphy of the Lower Cambrian and the Precambrian-Cambrian boundary in southeast Poland. *Fossils Strata* **29:** 1–127.

Moldowan, J.M. (1984). C30-steranes, novel markers for marine petroleums and sedimentary rocks. *Geochim. Cosmochim. Acta* **48:** 2767–2768.

Moldowan, J.M., Dahl, J.E.P., Huizinga, B.J., Fago, F.J., Hickey, L.J., Peakman, T.M., and Taylor, D.W. (1994). The molecular fossil record of oleanane and its relation to angiosperms. *Science* **265:** 768–771.

Moldowan, J.M., Lee, C.Y., Watt, D.S., Jeganathan, A., Slougui, N.E., and Gallegos, E.J. (1991). Analysis and occurrence of C_{26}-steranes in petroleum and source rocks. *Geochim. Cosmochim. Acta* **55:** 1065–1081.

Moldowan, J.M., and Talyzina, N.M. (1998). Biogeochemical evidence for dinoflagellate ancestors in the early Cambrian. *Science* **281:** 1168–1170.

Molyneux, S.G., Le Hérissé, A., and Wicander, R. (1996). Paleozoic phytoplankton. *Palynology: Principles and Applications*. J. Jansonius and D.C. McGregor, eds. Tulsa, OK, American Association of Stratigraphic Palynologists Press, pp. 493–529.

Noffke, N., Eriksson, K.A., Hazen, R.M., and Simpson, E.L. (2006). A new window into Early Archean life: microbial mats in Earth's oldest siliciclastic tidal deposits (3.2 Ga Moodies Group, South Africa). *Geology* **34:** 253–256.

Peters, K.E., Walters, C.C., and Moldowan, J.M. (2005) *The Biomarker Guide,* 2nd ed. Cambridge, UK, Cambridge University Press.

Peterson, K.J., and Butterfield, N.J. (2005). Origin of the Eumetazoa: testing ecological predictions of molecular clocks against the Proterozoic fossil record. *Proc. Nat. Acad. Sci. U S A* **102:** 9547–9552.

Porter, S.M, Meisterfeld, R., and Knoll, A.H. (2003). Vase-shaped microfossils from the Neoproterozoic Chuar Group, Grand Canyon: a classification guided by modern testate amoebae. *J. Paleontol*. **77:** 409–429.

Prahl, F.G., de Lange, G.J., Lyle, M., and Sparrow, M.A. (1989). Postdepositional stability of long-chain alkenones under contrasting redox conditions. *Nature* **341:** 434–437.

Rampen, S.W., Schouten, S., Abbas, B., Panoto, F.E., Muyzer, G., Campbell, C.N., Fehling, J., and Sinninghe Damsté, J.S. (2005). The origin of 24-norcholestanes and their use as age-diagnostic biomarkers. *Organic Geochemistry: Challenges for the 21st Century*. 22 IMOG Seville, Spain, Abstract PB1–10.

Revill A.T., Volkman J.K., O'Leary T., Summons R.E., Boreham C.J., Banks M.R., and Denwer K. (1994). Depositional setting, hydrocarbon biomarkers and thermal maturity of tasmanite oil shales from Tasmania, Australia. *Geochim. Cosmochim. Acta* **58:** 3803–3822.

Robinson, N., Eglinton, G., and Brassell S.C. (1984). Dinoflagellate origin for sedimentary 4α-methylsteroids and 5α(H)-stanols. *Nature* **308:** 439–442.

Rohmer, M., Bisseret, P., and Neunlist, S. (1992). The hopanoids: prokaryotic triterpenoids and precursors of ubiquitous molecular fossils. Biological Markers in Sediments and Petroleum. J.M. Moldowan, P. Albrecht, and R.P. Philp, eds. New York, Prentice Hall, pp. 1–17.

Rohmer, M., Bouvier-Nave, P., and Ourisson, G. (1984). Distribution of hopanoid triterpenes in prokaryotes. *J. Gen. Microbiol*. **130:** 1137–1150.

Rosing, M.T., and Frei, R. (2004). U-rich Archaean seafloor sediments from Greenland—indications of >3700 Ma oxygenic photosynthesis. *Earth Planet. Sci. Lett*. **217:** 237–244.

Sanchez-Baracaldo, P., Hayes, P.K., and Blank, C.E. (2005). Morphological and habitat evolution in the Cyanobacteria using a compartmentalization approach. *Geobiology* **3:** 145–165.

Schopf, J.W. (1968). Microflora of the Bitter Springs Formation, Late Precambrian, central Australia. *J. Paleontol*. **42:** 651–688.

Schopf, J.W. (1993). Microfossils of the early Archean Apex chert—new evidence of the antiquity of life. *Science* **260:** 640–646.

Schopf, J.W. (2006). Fossil evidence of Archaean life. *Phil. Trans. R. Soc. B* **361:** 869–885.

Schopf, J.W., Kudryavtsev, A.B., Agresti, D.G., Wdowiak, T.J., and Czaja, A.D. (2002a). Laser-Raman imagery of Earth's earliest fossils. *Nature* **416:** 73–76.

Schopf, J.W., Kudryavtsev, A.B., Agresti, D.G., Wdowiak, T.J., and Czaja, A.D. (2002b). Laser-Raman spectroscopy: images of the Earth's earliest fossils? Reply. *Nature* **420:** 477.

Sergeev, V.N., Gerasimenko, L.M., and Zavarzin, G.A. (2002). The Proterozoic history and present state of cyanobacteria. *Microbiology* **71:** 623–637.

Sergeev, V.N., Knoll, A.H., and Grotzinger, J.P. (1995). Paleobiology of the Mesoproterozoic Billyakh Group, northern Siberia. *Paleontol. Soc. Mem*. **39:** 1–37.

Shen, Y., Knoll, A.H., and Walter, M.R. (2003). Evidence for low sulphate and deep water anoxia in a mid-Proterozoic marine basin. *Nature* **423:** 632–635.

Sinninghe Damsté, J.S., Muyzer, G., Abbas, B., Rampen, S.W., Masse, G., Allard, W.G., Belt, S.T., Robert, J.M., Rowland, S.J., Moldowan, J.M., Barbanti, S.M., Fago, F.J., Denisevich, P., Dahl, J., Trindade, L.A.F., and Schouten, S. (2004). The rise of the rhizosolenid diatoms. *Science* **304:** 584–587.

Sinninghe Damsté, J.S., Rampen, S., Rijpstra, W.I.C., Abbas, B., Muyzer, G., and Schouten, S. (2003). A diatomaceous origin for long-chain diols and mid-chain hydroxy methyl alkanoates widely occurring in Quaternary marine sediments: Indicators for high-nutrient conditions. *Geochim. Cosmochim. Acta* **67:** 1339–1348.

Sinninghe Damsté, J.S., Rijpstra, W.I.C., Schouten, S., Peletier, H., van der Maarel, M.J., and Gieskes, W.W.C. (1999a). A C_{25} highly branched isoprenoid alkene and C_{25} and C_{27} n-polyenes in the marine diatom *Rhizosolenia setigera. Org. Geochem.* **30:** 95–100.

Sinninghe Damsté, J.S., Schouten, S., Rijpstra, W.I.C., Hopmans, E.C., Peletier, H., Gieskes, W.W.C., and Geenevasen, J.A.J. (1999b). Structural identification of the C25 highly branched isoprenoid pentaene in the marine diatom *Rhizosolenia setigera. Org. Geochem.* **30:** 1581–1583.

Subroto, E.A., Alexander, R., and Kagi, R.I. (1991). 30-Norhopanes: their occurrence in sediments and crude oils. *Chem. Geol.* **93:** 179–192.

Summons, R.E., Bradley, A.S., Jahnke, L.L., and Waldbauer, J.R. (2006). Steroids, triterpenoids and molecular oxygen. *Phil. Trans. R. Soc. B* **361:** 951–968

Summons, R.E., Brassell, S.C., Eglinton, G., Evans, E., Horodyski, R.J., Robinson, N., and Ward, D.M. (1988b). Distinctive hydrocarbon biomarkers from fossiliferous sediments of the Late Proterozoic Walcott Member, Chuar Group, Grand Canyon, Arizona. *Geochim. Cosmochim. Acta* **52:** 2625–2637.

Summons, R.E., and Capon, R.J. (1991). Identification and significance of 3-ethyl steranes in sediments and petroleum. *Geochim. Cosmochim. Acta* **55:** 2391–2395.

Summons, R.E., Jahnke, L.L., Hope, J.M., and Logan, G.A. (1999). 2-Methylhopanoids as biomarkers for cyanobacterial oxygenic photosynthesis. *Nature* **400:** 554–557.

Summons, R.E., and Powell, T.G. (1987) Identification of aryl isoprenoids in source rocks and crude oils: biological markers for the green sulphur bacteria. *Geochim. Cosmochim. Acta* **51:** 557–566.

Summons, R.E., and Powell T.G. (1992). Hydrocarbon composition of the Late Proterozoic oils of the Siberian Platform: implications for the depositional environment of the source rocks. *Early Organic Evolution: Implications for Mineral and Energy Resources.* M. Schidlowski, S. Golubic, M.M. Kimberley, D.M. McKirdy, and P.A. Trudinger, eds. Berlin, Springer-Verlag, pp. 296–507.

Summons, R.E., Powell, T.G. and Boreham, C.J. (1988a). Petroleum geology and geochemistry of the Middle Proterozoic McArthur Basin, Northern Australia: III. Composition of extractable hydrocarbons. *Geochim. Cosmochim. Acta* **52:** 1747–1763.

Summons, R.E., Taylor D., and Boreham, C.J. (1994). Geochemical tools for evaluating petroleum generation in Middle Proterozoic sediments of the McArthur Basin, Northern Territory, Australia. *Austral. Petroleum Explor. Assoc. J.* **34:** 692–706.

Summons, R.E., Thomas, J., Maxwell, J.R., and Boreham, C. J. (1992). Secular and environmental constraints on the occurrence of dinosterane in sediments. *Geochim. Cosmochim. Acta* **56:** 2437–2444.

Summons, R.E., Volkman, J.K., and Boreham, C.J. (1987). Dinosterane and other steroidal hydrocarbons of dinoflagellate origin in sediments and petroleum. *Geochim. Cosmochim. Acta* **51:** 3075–3082.

Summons, R.E., and Walter M.R. (1990). Molecular fossils and microfossils of prokaryotes and protists from Proterozoic sediments. *Am. J. Sci.* **290-A:** 212–244.

Suzuki, N., Yasuo, N., Nakajo, T., and Shine, H. (2005). Possible origin of 24-norcholesterol in marine environment. *Organic Geochemistry: Challenges for the 21st Century.* 22 IMOG Seville, Spain, Abstract OB2-2.

Talyzina, N.M. (2000). Ultrastructure and morphology of *Chuaria circularis* (Walcott, 1899) Vidal and Ford (1985) from the Neoproterozoic Visingso Group, Sweden. *Precambrian Res.* **102:** 123–134.

Talyzina, N.M., Moldowan, J.M., Johannsson, A., and Fago, F.J. (2000). Affinities of Early Cambrian acritarchs studied by using microscopy, fluorescence flow cytometry and biomarkers. *Rev. Palaeobot. Palynol.* **108:** 37–53.

Tappan, H. (1980). *The Paleobiology of Plant Protists.* San Francisco, Freeman.

Ten Haven, H.L., Rohmer, M., Rullkotter, J., and Bisseret, P. (1989). Tetrahymanol, the most likely precursor of gammacerane, occurs ubiquitously in marine sediments. *Geochim. Cosmochim. Acta* **53:** 3073–3079.

Tice, M.M., and Lowe, D.R. (2004). Photosynthetic microbial mats in the 3,416-Myr-old ocean. *Nature* **431:** 549–552.

Tice, M.M., and Lowe, D.R. (2006). Hydrogen-based carbon fixation in the earliest known photosynthetic organisms. *Geology* **34:** 37–40.

Tomitani, A., Knoll, A.H., Cavanaugh, C.M., and Ohno, T. (2006). The evolutionary diversification of cyanobacteria: molecular phylogenetic and paleontological perspectives. *Proc. Nat. Acad. Sci. U S A* **103:** 5442–5447.

Treibs, A. (1936). Chlorophyll and hemin derivatives in organic mineral substances. *Angew. Chem.* **49:** 682–686.

van Breugel, Y., Schouten, S., Paetzel, M., Ossebaar, J., Sinninghe Damsté, J.S. (2005). Reconstruction of $\delta^{13}C$ of chemocline CO2 (aq) in past oceans and lakes using the $\delta^{13}C$ of fossil isorenieratene. *Earth Planet. Sci. Lett.* **235:** 421–434.

van Kaam-Peters, H.M.E., Köster, J., van der Gaast, S.J., Dekker, M., de Leeuw, J.W., and Sinninghe Damsté, J.S. (1998). The effect of clay minerals on diasterane/ [AU12] sterane ratios. *Geochim. Cosmochim. Acta* **62:** 2923–2929.

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

Vidal, G., and Moczydlowska, M. (1997). Biodiversity, speciation, and extinction trends of Proterozoic and Cambrian phytoplankton. *Paleobiology* **23:** 230–246.

Volkman, J.K. (2003). Sterols in microorganisms. *Appl. Microbiol. Biotechnol.* **60:** 496–506.

Volkman, J.K., Barrett, S.M., and Dunstan, G.A. (1994). C_{25} and C_{30} highly branched isoprenoid alkanes in laboratory cultures of two marine diatoms. *Org. Geochem.* **21:** 407–413.

Volkman, J.K., Eglinton, G., Corner, E.D.S., and Sargent, J.R. (1980). Novel unsaturated straight-chain C_{37}-C_{39} methyl and ethyl ketones in marine sediments and a coccolithophore *Emiliania huxleyi*. *Advances in Organic Geochemistry 1979*. A.G. Douglas and J.R. Maxwell, eds. London, Pergamon, pp. 219–227.

Volkova, N.G., Kirjanov, V.V., Piscun, L.V., Paškeviciene, L.T., and Jankauskas, T.V. (1983). Plant microfossils. *Upper Precambrian and Cambrian Palaeontology of the East European Platform*. A. Urbanek and A.Y. Rozanov, eds. Warsaw, Wydawnictwa Geologiczne, pp. 7–46.

Wignall, P.B., and Twitchett, R.J. (2002). Extent, duration and nature of the Permian-Triassic superanoxic event. *Geol. Soc. Am. Spec. Paper* **356:** 395–413.

Wray, J.L. (1977). *Calcareous Algae*. Amsterdam, Elsevier, Amsterdam.

Xiao, S., Knoll, A.H., Yuan, X., and Pueschel, C.M. (2004). Phosphatized multicellular algae in the Neoproterozoic Doushantuo Formation, China, and the early evolution of florideophyte red algae. *Am. J. Bot.* **91:** 214–227.

Xiao, S., Yuan, X., Steiner, M., and Knoll, A.H. (2002). Macroscopic carbonaceous compressions in a terminal Proterozoic shale: a systematic reassessment of the Miaohe biota, South China. *J. Paleontol.* **76:** 345–374.

Yoon, H.S., Hackett, J.D., Ciniglia, C., Pinto, G., and Bhattacharya, D. (2004). A molecular timeline for the origin of photosynthetic eukaryotes. *Mol. Biol. Evol.* **21:** 809–818.

Zhang, Y. (1981). Proterozoic stromatolite microfloras of the Gaoyuzhuang Formation (Early Sinian, Riphean), Hebei, China. *J. Paleontol.* **55:** 485–506.

Zumberge, J.E. (1987). Prediction of source rock characteristics based on terpane biomarkers in crude oils: a multivariate statistical approach. *Geochim. Cosmochim. Acta* **51:** 1625–1637.

Zundel, M., and Rohmer, M. (1985a). Hopanoids of the methylotrophic bacteria Methylococcus capsulatus and Methylomonas sp. as possible precursors of C_{29} and C_{30} hopanoid chemical fossils. *FEMS Microbiol. Lett.* **28:** 61–64.

Zundel, M., and Rohmer, M. (1985b). Prokaryotic triterpenoids 3. The biosynthesis of 2ß-methylhopanoids and 3ß-methylhopanoids of *Methylobacterium organophilum* and *Acetobacter pasteurianus* ssp. *pasteurianus. Eur. J. Biochem.* **150:** 35–39.

Zundel, M., and Rohmer, M. (1985c). Prokaryotic triterpenoids. 1. 3β-Methylhopanoids from Acetobacter sp. and Methylococcus capsulatus. *Eur. J. Biochem.* **150:** 23–27.

Zumberge, J.E., Russell, J.A., and Reid, S.A. (2005). Charging of Elk Hills reservoirs as determined by oil geochemistry. *AAPG Bull.* **89:** 1347–1371.

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