

## AN ATMOSPHERIC STIMULUS FOR CYANOBACTERIAL-BIOINDUCED CALCIFICATION CA. 350 MILLION YEARS AGO?

ROBERT RIDING

*University of Tennessee, Department of Earth and Planetary Sciences, Knoxville, Tennessee 37996-1410, USA  
e-mail: riding@cardiff.ac.uk*

### ABSTRACT

Cyanobacterial calcification is promoted by CO<sub>2</sub>-concentrating mechanisms (CCMs) developed in response to photosynthetic carbon limitation. Changes in atmospheric composition (CO<sub>2</sub> fall, O<sub>2</sub> rise) near the Devonian–Mississippian transition (ca. 360 Ma) were sufficiently large to induce CCMs in cyanobacteria. Cyanobacterial sheath calcification significantly increased during the Mississippian, ca. 325–355 Ma. It is proposed that these atmospheric changes triggered cyanobacteria to induce CCMs—previously developed during a large CO<sub>2</sub> decline in the Proterozoic—and that this promoted their calcification. CCMs in phytoplankton stimulate primary productivity by increasing photosynthetic efficiency and ameliorating carbon limitation. Phytoplankton community restructuring in favor of groups that possessed effective CCMs but had poor body-fossil records, such as picoplanktic cyanobacteria, could account for Late Devonian acritarch decline and the subsequent apparent scarcity of phytoplankton in the late Paleozoic (the so-called phytoplankton blackout). This is supported by biomarkers indicating an increase in cyanobacteria at the Devonian–Mississippian transition and by carbon isotope values and black shale deposition that, despite acritarch decline, reflect increased primary productivity. The Mississippian episode of cyanobacterial calcification was relatively short lived. Calcification declined ca. 325 Ma, before the end of the Mississippian, as a continued decline in CO<sub>2</sub> lowered seawater carbonate saturation. The induction of cyanobacterial CCMs, triggered by Late Devonian change to a relatively low CO<sub>2</sub> and high O<sub>2</sub> atmosphere, has probably persisted to the present day, but well-developed calcification in marine cyanobacteria has been restricted to intervals of elevated carbonate saturation state.

### INTRODUCTION

Many algae and invertebrates exert strong control at the cellular level over biocalcification processes in order to consistently produce skeletons that are crucial for their survival (Weiner and Dove, 2003), but in some organisms calcification is only weakly regulated. This latter process has been described as bioinduced rather than controlled calcification (Lowenstam, 1981), and it is much more prone to external influence. This susceptibility adds a level of complexity to the fossil record of bioinduced calcifiers but also enhances opportunities for their paleoenvironmental interpretation (Stanley and Hardie, 1998).

Cyanobacteria are photosynthetic bacteria possessing a long Precambrian–Phanerozoic record as both uncalcified and calcified fossils. Their calcification is strongly bioinduced; it is not obligate and is mediated by environmental factors as well as biological processes (Golubic, 1973; Pentecost and Riding, 1986). Key external influences on cyanobacterial calcification include carbonate saturation state (Kempe and Kaźmierczak, 1994) and the availability of dissolved inorganic carbon (DIC) (Thompson and Ferris, 1990; Merz, 1992). As a result, marine calcified cyanobacteria have a distinctly episodic pattern of abundance through time, ranging from rock-forming ability to virtual

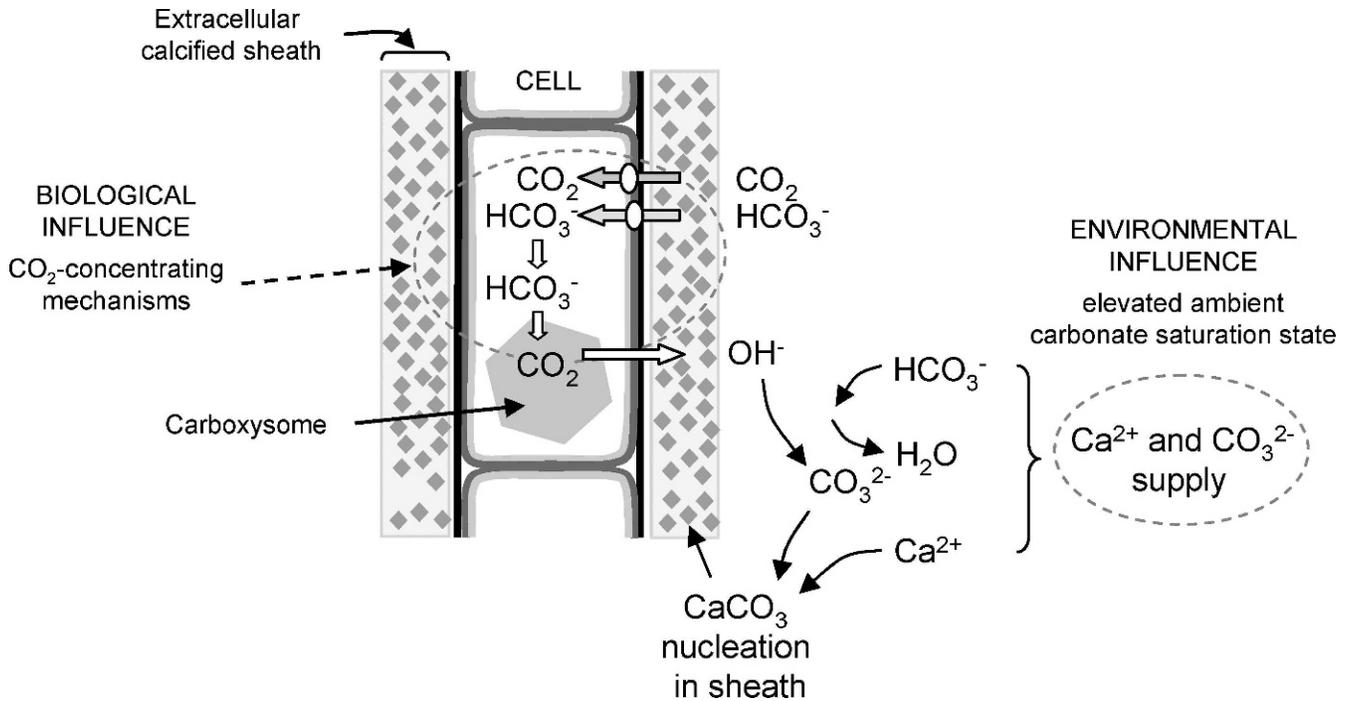
absence, and this can be related to environmental influences on their calcification (Riding, 1992, 2006; Arp et al., 2001).

Late Devonian–Early Mississippian changes in atmospheric composition, specifically CO<sub>2</sub> decline and O<sub>2</sub> increase, were among the largest and most abrupt of the Phanerozoic (Berner, 2006). They are likely to have significantly affected photosynthetic organisms and are expected to have put pressure on cyanobacteria to improve photosynthetic efficiency by actively importing bicarbonate (Badger et al., 2002). A side effect of bicarbonate import and its conversion to CO<sub>2</sub> by carbonic anhydrase is the promotion of cyanobacterial calcification (Thompson and Ferris, 1990; Merz, 1992). Marine cyanobacteria show increased calcification during the Mississippian (Arp et al., 2001). Here I explore the possibility that this episode of cyanobacterial calcification was a direct response to changes in atmospheric composition that commenced in the Late Devonian and directly affected photosynthesis. The same effects could also help to account for significant coeval changes observed in marine phytoplankton communities (Riding, 2008).

### CO<sub>2</sub>-CONCENTRATING MECHANISMS

The starting point for these considerations is the ability of cyanobacteria to increase photosynthetic efficiency by actively importing inorganic carbon (as CO<sub>2</sub> or HCO<sub>3</sub><sup>-</sup>) into their cells. These CO<sub>2</sub>-concentrating mechanisms (CCMs) help overcome limitations in low DIC availability that result from levels of present-day atmospheric CO<sub>2</sub> that geologically are extremely low. CCMs are widely present among photosynthetic organisms (Giordano et al., 2005) and are particularly well developed in cyanobacteria (Badger and Price, 2003). Badger et al. (2002, p. 169) suggested that late Paleozoic changes in atmospheric composition “would have placed significant pressures on both cyanobacterial and algal photosynthesis.” This reasoning centers on the attributes of ribulose bisphosphate carboxylase oxygenase (RuBisCO), the primary carbon-fixing enzyme on Earth. RuBisCO has a relatively low affinity for CO<sub>2</sub> and at the same time is able to fix oxygen as well as carbon (Bowes et al., 1971). Under present-day conditions of low CO<sub>2</sub> and high O<sub>2</sub>, these qualities in RuBisCO are deficiencies that limit photosynthesis by promoting both carbon limitation and oxygenase activity. A plausible explanation is that RuBisCO developed under Archean conditions of CO<sub>2</sub> abundance and O<sub>2</sub> scarcity (Raven, 1997a). To overcome these obstacles and increase photosynthetic rates under today’s reversed conditions, many algae and cyanobacteria, as well as higher plants, possess the cellular mechanisms—generally termed CCMs—that use energy to increase CO<sub>2</sub> concentrations in the vicinity of RuBisCO (Giordano et al., 2005).

The RuBisCOs in cyanobacteria have the lowest CO<sub>2</sub> affinity and lowest CO<sub>2</sub>/O<sub>2</sub> selectivity of any RuBisCO in oxygen-producing organisms, with the probable exception of the Form II RuBisCO of peridinin-containing dinoflagellates (Tcherkez et al., 2006; J.A. Raven, personal communication, 2009). Such RuBisCOs have their highest specific reaction rates at saturating CO<sub>2</sub> concentrations, so they perform well under high CO<sub>2</sub> regardless of the O<sub>2</sub> concentration. It is therefore not surprising that CCMs are particularly well developed in



**FIGURE 1**—Inferred model of sheath calcification in a filamentous cyanobacterium driven by photosynthesis and enhanced by  $\text{CO}_2$ -concentrating mechanisms (CCMs) (based on Riding, 2006). CCMs actively import  $\text{CO}_2$  and  $\text{HCO}_3^-$  into the cell for carbon fixation, which liberates  $\text{OH}^-$  ions from the cell, raising external pH. This can stimulate  $\text{CaCO}_3$  precipitation if ambient carbonate saturation is high, and the cyanobacterial sheath can provide a nucleation site. Key influences on cyanobacterial calcification, biological CCMs and environmental saturation state are circled. Sheath calcification can produce durable calcified microfossils such as *Girvanella* (see Fig. 5).

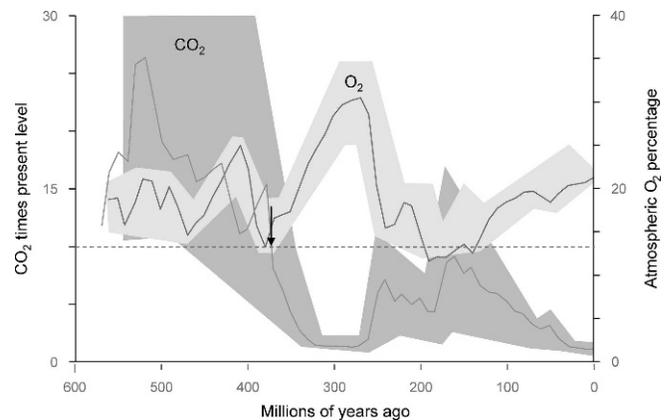
cyanobacteria where they include active bicarbonate uptake (Kaplan et al., 1980; Badger and Price, 2003) coupled with the use of carbonic anhydrase to convert bicarbonate to  $\text{CO}_2$  for delivery to the site of RuBisCO (Badger, 2003). Active bicarbonate transport and carbonic anhydrase conversion are thus distinctive aspects of cyanobacterial CCMs (Fig. 1).

Thresholds for CCM development are not closely constrained, but in the presence of oxygen, cyanobacterial CCMs are induced at  $\text{CO}_2$  levels below  $\sim 10$  times the present level (Badger et al., 2002). In addition to low  $\text{CO}_2$ , elevated  $\text{O}_2$  is also thought to promote CCM induction, although this effect is less well understood (Vance and Spalding, 2005; Woodger et al., 2005), since oxygen competitively inhibits  $\text{CO}_2$  fixation by RuBisCO and promotes photorespiration, the light-dependent release of  $\text{CO}_2$  by photosynthetic organisms (Bowes et al., 1971). The expectation, therefore, is that times in the geological past when there was both a substantial decrease in  $\text{CO}_2$  and increase in  $\text{O}_2$  would have presented a challenge to photosynthetic organisms that increased selective pressure for CCMs (Raven, 1997a).

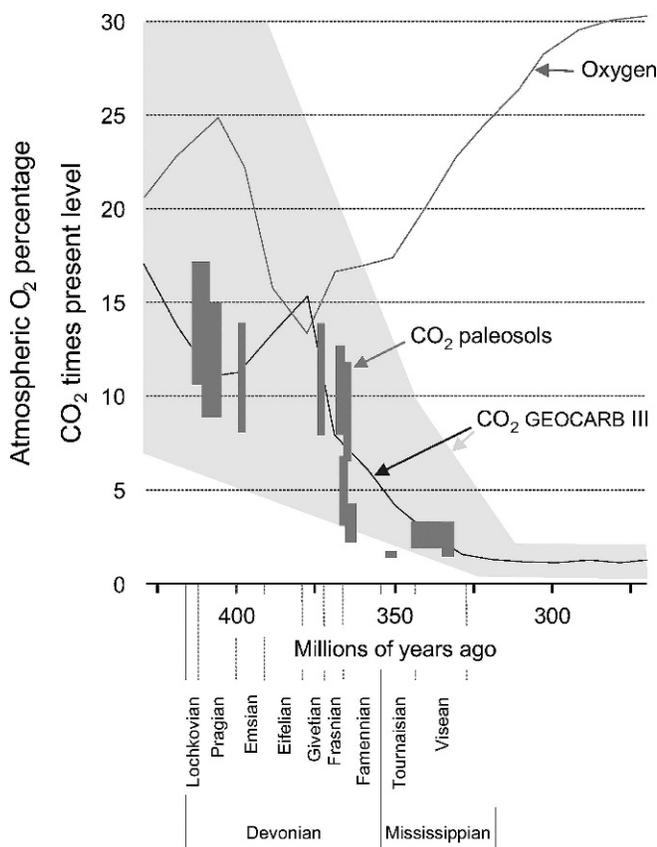
#### LATE DEVONIAN CHANGES IN ATMOSPHERIC COMPOSITION

Badger et al. (2002, fig. 5) drew attention to a period in the late Paleozoic when  $\text{CO}_2$ -limitation and  $\text{O}_2$  increase may have initiated the development of CCMs in aquatic photosynthetic organisms. These inferred changes in atmospheric composition are based on biogeochemical models of the global carbon and sulfur cycles (Fig. 2). Berner and Kothavala (2001) modeled Phanerozoic variation in atmospheric  $\text{CO}_2$  based on the processes that variously release  $\text{CO}_2$  to the atmosphere and remove and sequester it in rocks as carbonate and organic carbon. Oxygen models have been based on the weathering and burial of organic carbon and pyrite sulfur (Berner, 2006, fig. 20). Berner and Kothavala's (2001) estimates show large fluctuations in atmo-

spheric  $\text{CO}_2$  from present-day atmospheric levels (PAL) to up to  $>25$  times PAL in the late Cambrian. One of the episodes of largest change in atmospheric composition commenced in the Late Devonian, ca. 370 Ma, as  $\text{CO}_2$  levels declined and  $\text{O}_2$  increased (Fig. 2). The modeled estimates for  $\text{CO}_2$  at this time are supported by proxy records such as paleosol analyses and leaf stomatal indices (Royer, 2006, fig. 1). Paleosol data indicate abrupt decline in  $\text{CO}_2$  from  $>10$  PAL to  $<5$  PAL in the Famennian, ca. 365 Ma (Driese et al., 2000, fig. 8; Royer, 2006, fig. 3a; Fig. 3). This reduction below 10 PAL  $\text{CO}_2$  could be expected to induce CCMs in cyanobacteria, as suggested by Badger et al. (2002).



**FIGURE 2**—Modeled Phanerozoic values of atmospheric  $\text{CO}_2$  (Berner and Kothavala, 2001) and  $\text{O}_2$  (Berner, 2006). Shaded areas show estimated errors. According to the estimate of  $\text{CO}_2$ , levels fell to  $<10$  PAL in the Late Devonian (ca. 370 Ma; arrow) and continued to decline for 50 myr, while  $\text{O}_2$  increased. Changes on these scales promote  $\text{CO}_2$ -concentrating mechanisms (CCMs) in algae and cyanobacteria (Badger and Price, 2003).



**FIGURE 3**—Atmospheric CO<sub>2</sub> and O<sub>2</sub> estimates for the Devonian–Mississippian transition. Carbon dioxide estimates from paleosol data (Driese et al., 2000) and modeled levels (GEOCARB III, Berner and Kothavala, 2001). Grey area is error estimate for GEOCARB III values; O<sub>2</sub> estimates from Berner (2006). Timescale from Haq and Van Eysinga (1998). Paleosol data suggest that CO<sub>2</sub> levels fell from >10 to <5× present-atmospheric level (PAL) in early Famennian (ca. 360–365 Ma) as O<sub>2</sub> levels began to rise.

## CYANOBACTERIAL CALCIFICATION

### Role of CO<sub>2</sub>-Concentrating Mechanisms

Cyanobacterial calcification is based in general on photosynthetic uptake of DIC and specifically upon CCMs (Thompson and Ferris, 1990; Merz, 1992). RuBisCO requires CO<sub>2</sub>, and CO<sub>2</sub> can diffuse into the cell whereas bicarbonate does not (Giordano et al., 2005). The greater abundance of bicarbonate in seawater makes it a valuable carbon source, however, even though energy is required to pump it into the cell and convert it to CO<sub>2</sub> (Fig. 1). CCMs have therefore been developed for this task where DIC is scarce, and cyanobacterial CCMs can include active CO<sub>2</sub> and HCO<sub>3</sub><sup>-</sup> import into the cell (Price et al., 2008). The CCMs are cellularly regulated and respond to ecological influences on growth, such as carbon-limiting conditions that can develop in microbial mats and in plankton blooms (Rost et al., 2003; Price et al., 2008), but the primary control on inorganic carbon availability is the overall atmospheric level of CO<sub>2</sub>. It is postulated that passive CO<sub>2</sub> diffusion into the cell has little effect on the external pH, whereas intracellular conversion of HCO<sub>3</sub><sup>-</sup> to CO<sub>2</sub> by carbonic anhydrase has a large effect because this process releases OH<sup>-</sup> ions, stimulating pH increase in the immediate external cellular environment (Miller and Colman, 1980). Where ambient waters are sufficiently saturated for CaCO<sub>3</sub> minerals, this can result in calcification and CaCO<sub>3</sub> crystallites nucleate on or near the cell surface (Thompson and Ferris, 1990) or in the enveloping mucilaginous sheath (Merz, 1992).

Under conditions of carbon limitation, cyanobacterial CCMs function to maximize carbon uptake and its delivery as CO<sub>2</sub> to

RuBisCO, since only CO<sub>2</sub> can serve as the substrate for RuBisCO (Price et al., 2008). Both CO<sub>2</sub> and HCO<sub>3</sub><sup>-</sup> may actively be taken up by the cells, but there is preferential accumulation of HCO<sub>3</sub><sup>-</sup> since CO<sub>2</sub> can be lost by leakage. Bicarbonate ions are delivered to the carboxysome, the site of RuBisCO, where carbonic anhydrase is used to convert them to CO<sub>2</sub>. This conversion releases OH<sup>-</sup>, which is removed from the cell, raising external pH levels. Biological functions that contribute directly to cyanobacterial calcification are therefore active bicarbonate uptake and its conversion to CO<sub>2</sub> by carbonic anhydrase with the release of OH<sup>-</sup>; and these are key components of cyanobacterial CCMs. Calcification can be further facilitated and localized by the presence of cell surface layers and external, protective mucilaginous sheaths that can provide diffusion-limited sites and/or calcium-adsorption potential (Pentecost and Bauld, 1988; Schultze-Lam and Beveridge, 1994). In addition, elevated carbonate saturation state of the external medium is essential for precipitation (see below); otherwise, the pH generated by CCMs may be insufficient to result in nucleation of CaCO<sub>3</sub> minerals. Thus, cyanobacterial calcification is promoted by the combined influences of CCMs, elevated ambient saturation state, and extracellular organic sites for nucleation (Fig. 1).

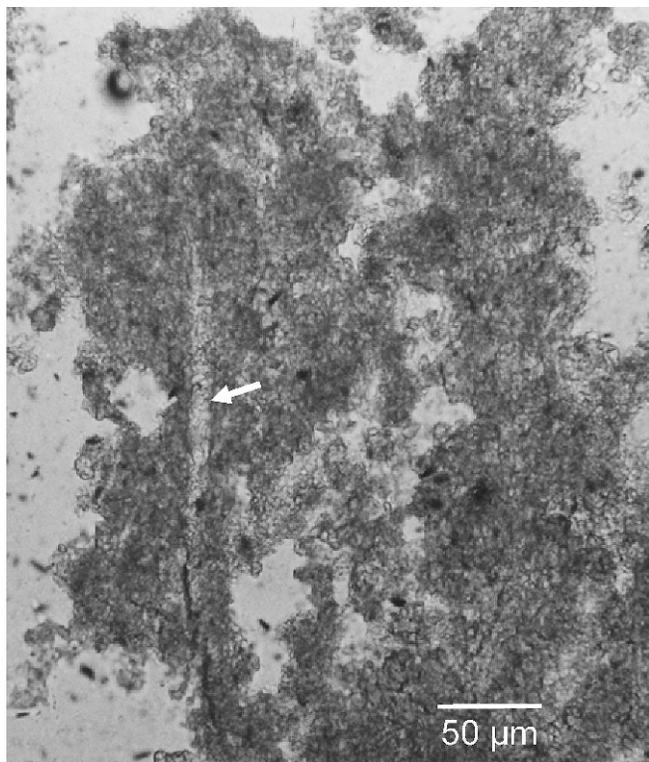
### Carbonate Saturation State

Calcification will not occur unless ambient carbonate saturation state is already relatively elevated (Riding, 1993; Kempe and Kazmierczak, 1994; Merz-Preiß and Riding, 1999; Arp et al., 2001); as with inorganic carbon availability, the primary control on saturation state is environmental. Riding and Liang (2005) calculated Phanerozoic variation in surface seawater-saturation ratio for CaCO<sub>3</sub> minerals (aragonite and calcite) using (1) estimates of past seawater ionic composition (Hardie, 1996; Stanley and Hardie, 1998); (2) atmospheric CO<sub>2</sub> levels (Berner and Kothavala, 2001); and (3) detrended temperature based on δ<sub>18</sub>O values (Veizer et al., 2000). They estimated DIC using the correlation established for pCO<sub>2</sub> and HCO<sub>3</sub><sup>-</sup> for the last 100 myr in the revised BLAG data (Lasaga et al., 1985; BLAG = Berner, Lasaga, and Garrels) and extrapolated to earlier periods from Berner and Kothavala's (2001) pCO<sub>2</sub> data; pH was calculated from HCO<sub>3</sub><sup>-</sup> and pCO<sub>2</sub>. With this input, Riding and Liang (2005) calculated Ω<sub>aragonite</sub> and Ω<sub>calcite</sub> using a stoichiometric equilibrium, aquatic-geochemistry approach (PHREEQC code, version 2, Parkhurst and Appelo, 1999). The dissociation constants for aqueous species were taken from the PHREEQC database, and the activity coefficients were estimated using the Davies' equation incorporated in the PHREEQC program. Comparison using PHRQPITZ (Plummer et al., 1988) showed these results to be within <6% of Pitzer models.

### Sheath-Calcified Cyanobacteria

The fossil record of calcified cyanobacteria is generated by calcification of the protective mucilaginous sheath (Pentecost and Riding, 1986; Fig. 1). So far, this process is only known in filamentous cyanobacteria. It leaves interior cellular strands (trichomes) uncalcified as it transforms sheaths into distinctive and durable tubiform and dendritic shrublike microfossils (Riding, 1991; Figs. 4–5).

Paleoproterozoic evidence for uncalcified cyanobacteria is provided by ca. 2500 Ma isotopic values and biomarkers (Anbar et al., 2007) and ca. 2000 Ma body fossils (Hofmann, 1976). Sheath-calcified fossils occur by ca. 1200 Ma (Kah and Riding, 2007) and retained a presence, sometimes abundant, in shallow-marine carbonates until the Mesozoic, yet similar fossils are vanishingly scarce in Cenozoic sediments (Riding, 1992; Arp et al., 2001). Present-day uncalcified cyanobacteria are common in marine and freshwater environments (Whitton, 2008), and calcified forms are almost unknown in the sea; in freshwater they are only conspicuous in calcareous streams and lakes (Pentecost, 2005). In addition to calcified sheaths, a variety of problematic microfossils have commonly been



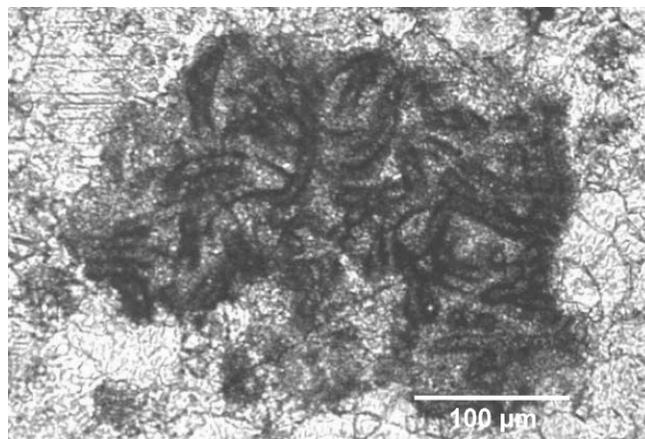
**FIGURE 4**—Present-day calcified shrublike sheath, probably from oscillatoriacean *Schizothrix calcicola*. Internal tube (arrowed) was occupied by uncalcified strand of cells (trichome); Squaw Island, Canandaigua Lake, New York State.

considered as calcified cyanobacteria (Riding, 1991). To avoid these difficulties in compiling Phanerozoic abundance data, Arp et al. (2001, fig. 3d) considered only “microfossils that can be assigned to micrite-impregnated cyanobacterial sheaths” such as *Girvanella*, *Ortonella*, and similar forms (Arp et al., 2001, supplemental table 4, <http://www.sciencemag.org/cgi/content/full/sci;292/5522/1701/DC1>).

These data of Arp et al. (2001; Fig. 6) show that during the Paleozoic, marine calcified cyanobacterial abundance ranged from 0 to up to 75 reports per 10 myr interval. This trend is patterned by peaks at ca. 500, ca. 425, and ca. 370 Ma that were relatively short lived, with durations  $\leq 12$  myr. These peaks broadly correspond with times of elevated seawater saturation state (Riding and Liang, 2005, fig. 5). A subsequent peak in the Mississippian, ca. 340 Ma, is different in that it continued longer ( $\sim 27$  myr, during the Tournaisian and Viséan) but at a time when saturation state, although still relatively high, was declining. What stimulated this relatively prolonged Mississippian phase of calcification during a period when saturation state was undergoing decline?

#### Mississippian Calcification

The following interpretation is considered here. Late Devonian  $\text{CO}_2$  decline and  $\text{O}_2$  increase induced CCMs in cyanobacteria, stimulating calcification in the Early Mississippian while saturation state was still relatively high. Reduction in saturation state led to rapid decline in calcification before the end of the Mississippian, although CCM induction may well have continued to the present day. It is also suggested that cyanobacteria induced preexisting CCMs. Cyanobacteria probably developed CCMs during substantial decline in atmospheric  $\text{CO}_2$  in the Proterozoic (ca. 1200 Ma; Riding, 2006; Kah and Riding, 2007). Carbon dioxide levels subsequently increased in the early to mid-Paleozoic before again declining substantially in the Late Devonian as  $\text{O}_2$  levels rose (Fig. 7). These late Paleozoic changes in atmospheric



**FIGURE 5**—*Girvanella* calcified cyanobacterial sheath, Late Devonian (Frasnian), Wuzhishang Formation, Yangdi, Guangxi, China. Photograph courtesy of Qi Feng.

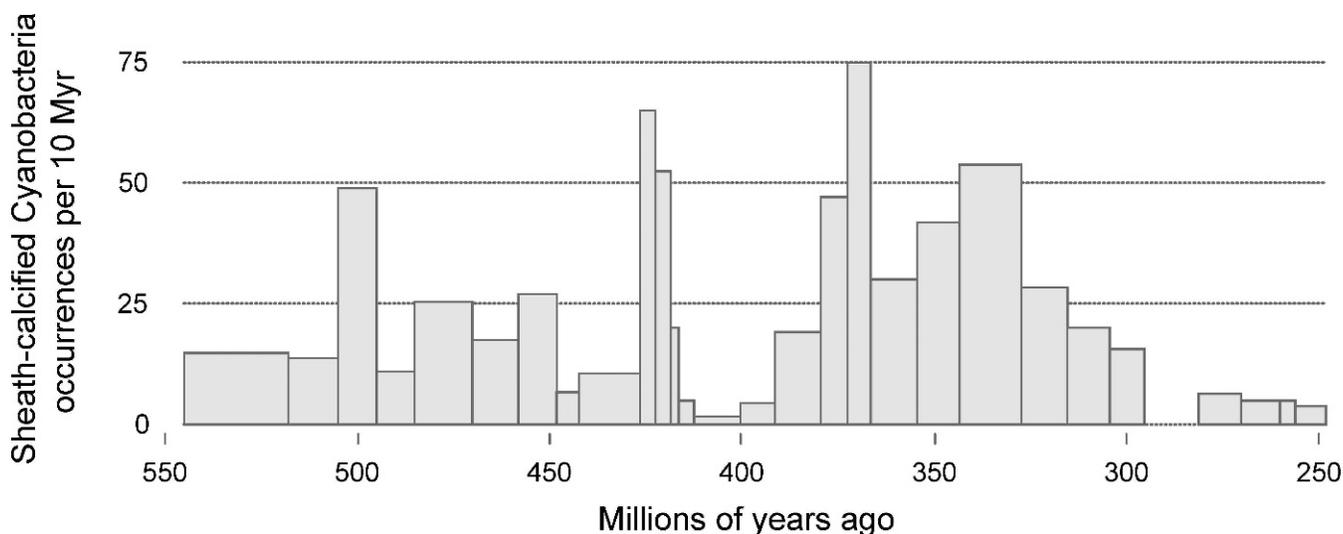
composition were sufficiently large to increase selectivity for CCMs in cyanobacteria (Raven, 1997a; Badger et al., 2002), and it is proposed that they resulted in the increase in calcification observed in the Tournaisian–Viséan.

#### DISCUSSION

The inferences concerning global conditions during the Devonian–Mississippian transition are based on published data that are brought together here for the first time. They include estimates of atmospheric composition, seawater carbonate saturation, and calcified cyanobacterial microfossil abundance. These considerations and comparisons shed light on events that at first sight might appear to be unrelated. In addition to the central question of controls on cyanobacterial calcification and its significance in the Mississippian aftermath of atmospheric change, these events include geological recognition and timing of CCM development-induction in cyanobacteria and algae, the role of atmospheric change and CCMs in secular patterns of phytoplankton diversity and abundance, and the broad significance of bioinduced calcification for paleoenvironmental interpretation.

#### Carbon Concentrating Mechanisms in Geological History

Raven (1997a, p. 331) suggested that the increase in oxygen in the late Neoproterozoic (650–550 Ma), combined with a decrease in  $\text{CO}_2$ , would have increased selective pressures for the development of CCMs in eukaryotes. He suggested that these pressures were no doubt present throughout the Phanerozoic to varying degrees but were probably strongest in the high- $\text{O}_2$ , low- $\text{CO}_2$  atmosphere of the upper Carboniferous. Because they had no unequivocal records of changes in  $\text{O}_2$  and  $\text{CO}_2$  prior to ca. 600 Ma, Badger et al. (2002, p. 169) concentrated on the possibility that cyanobacterial and algal CCMs may have been initiated in the latter part of the Paleozoic. There was a large decline in  $\text{CO}_2$  levels ca. 400 Ma, while the  $\text{O}_2$  concentration almost doubled, and it could be argued that this was the first time major pressure was applied to photosynthetic organisms to develop CCMs (Badger et al., 2002). Von Caemmerer and Furbank (1999) estimated an  $\text{O}_2:\text{CO}_2$  ratio of 100 as the selection-pressure threshold for CCM development in  $\text{C}_4$  plants. On this basis Behrenfeld et al. (2008, fig. 8) expected that CCM evolution could have occurred ca. 350–260 Ma and again  $< 100$  Ma. They found no direct evidence for phytoplankton or vascular plants having evolved CCMs during the Carboniferous but postulated that the late Eocene increase in  $^{13}\text{C}_{\text{org}}$  (Falkowski et al., 2005, fig. 1) represented reduced photosynthetic discrimination and was consistent with the functioning of CCMs (Behrenfeld et al., 2008).



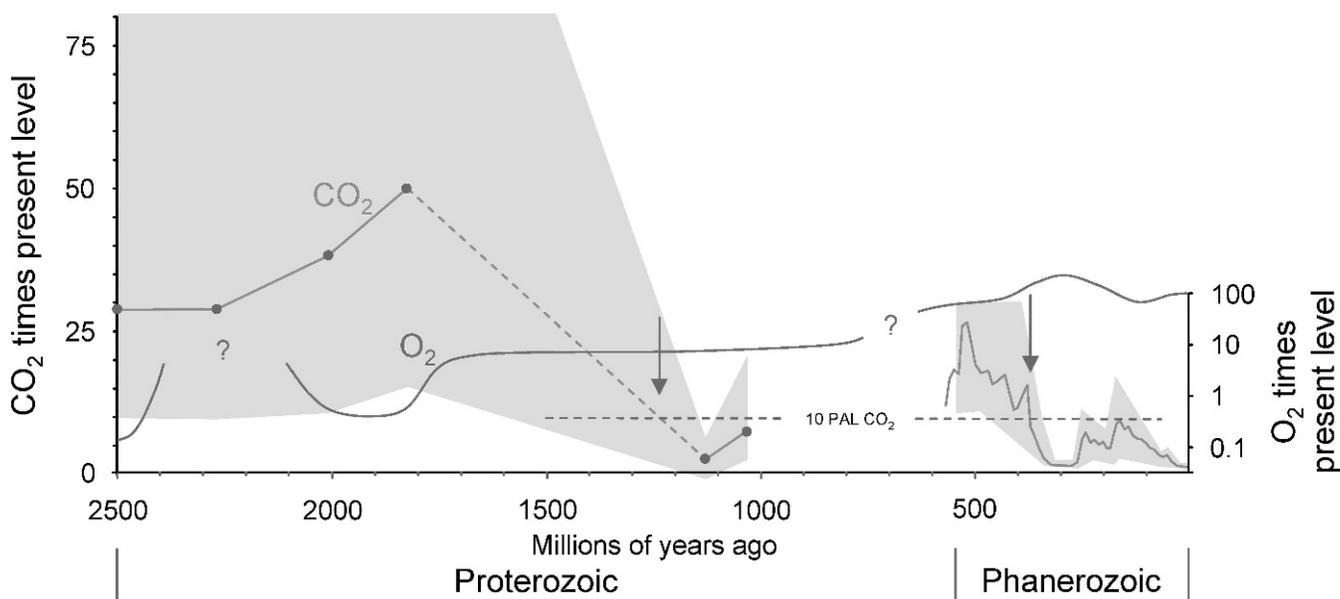
**FIGURE 6**—Paleozoic abundance of marine sheath-calcified cyanobacteria from Arp et al. (2001, fig. 3d). Timescale from Haq and Van Eysinga (1998). Peaks at ca. 500, ca. 425, and ca. 370 Ma are attributed to elevated carbonate saturation (Fig. 9C–D) (Riding and Liang, 2005); ca. 340 Ma peak is attributed to CCM induction in response to a fall in  $\text{CO}_2$  below  $\sim 10\times$  PAL in the Famennian. Subsequent decline after ca. 340 Ma peak is attributed to Late Mississippian decline in seawater saturation state (Fig. 9D).

Raven (1997a) and Badger et al. (2002) did not consider cyanobacterial calcification as a possible indicator of CCM acquisition. Subsequent work has linked Proterozoic sheath-calcified microfossils to declines in atmospheric  $\text{CO}_2$  (Riding, 2006; Fig. 6), supporting a relatively early origin ( $\geq 1200$  Ma, Kah and Riding, 2007) for carbon-dioxide concentrating mechanisms, a possibility foreseen by Raven (1997a, 2003). Thus, although Mississippian calcified cyanobacteria support the view of Badger et al. (2002) that atmospheric changes around the Devonian–Mississippian transition (ca. 360 Ma) could have induced CCMs, this has to be seen in the context of much earlier exposure of cyanobacteria to similarly low atmospheric  $\text{CO}_2$  levels in the Mesoproterozoic. This interpretation has several implications.

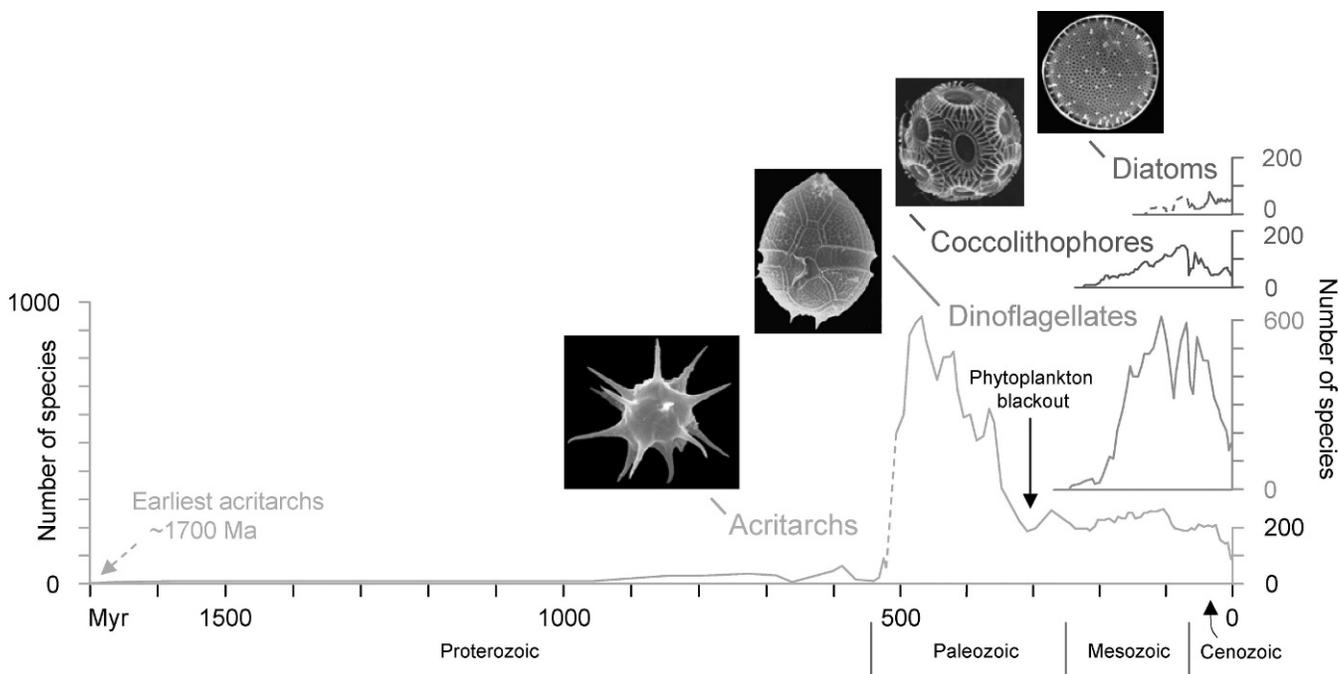
1. During the Paleozoic, cyanobacteria already possessed CCMs that they could induce whenever they encountered carbon limitation, e.g., in benthic microbial mats and planktic blooms. This would account for

the presence of calcified cyanobacteria (Fig. 6) in the early–mid-Paleozoic, when atmospheric  $\text{CO}_2$  levels were probably substantially  $>10\times$  PAL (Fig. 2). Possession of developed CCMs also permitted cyanobacteria to induce them when atmospheric conditions changed in the Late Devonian.

2. On the assumption that  $\text{CO}_2$  limitation did not promote algal and cyanobacterial CCM development until the Phanerozoic, Badger et al. (2002) inferred that the cyanobacteria involved in the original primary endosymbiotic event(s) did not have CCMs. For this reason, the original members of the Chlorophyta (green algae) and Rhodophyta (red algae) would not have had any CCM genetic elements in common with cyanobacteria. They therefore argued that chlorophytes and rhodophytes, along with secondary and tertiary endosymbiont algae that evolved during the  $\text{CO}_2$  limitation of the Phanerozoic, must have developed independent strategies for adapting to low  $\text{CO}_2$  (Lee and



**FIGURE 7**—Atmospheric  $\text{CO}_2$  and  $\text{O}_2$  estimates for the past 2500 myr. Proterozoic  $\text{CO}_2$  from paleosols (Sheldon, 2006). Phanerozoic  $\text{CO}_2$  modeled (GEOCARB III, Berner and Kothavala, 2001). Shaded areas show estimated errors. Atmospheric  $\text{O}_2$  estimates (log scale) from Canfield (2005, fig. 6). Arrows indicate times when  $\text{CO}_2$  level may have fallen below 10 PAL in the Mesoproterozoic (ca. 1200 Ma) and Late Devonian (ca. 370 Ma). Decline ca. 370 Ma coincided with substantial  $\text{O}_2$  increase.



**FIGURE 8**—Algal phytoplankton species diversity over the past 1700 myr (data from Katz et al., 2004) with Cenozoic diatom trend from Rabosky and Sorhannus (2009). Dashed line near 500 Ma links separate acritarch compilations. Earlier dashed part of diatom trend shows genus diversity. Photograph credits: Ludovic Stricanne (acritarch), Jeremy Young (cocolithophore), Fiona Scott (Australian Antarctic Division) (diatom), Susan Carty (dinoflagellate). Acritarch decline ca. 350 Ma initiated a prolonged interval of low diversity (arrow; Riegel, 2008) that persisted for remainder of Paleozoic. Building on Strother's suggestion (2008), this could in part reflect competition from poorly preserved picoplankton able to induce CCMs. Estimates (Berner and Kothavala, 2001) suggest that atmospheric  $\text{CO}_2$  remained low until ca. 260–250 Ma (Fig. 2), probably maintaining the importance of phytoplankton with CCMs until very late in the Paleozoic.

Kugrens, 2000; Badger et al., 2002). Raven (2003) pointed out that an earlier origin for  $\text{CO}_2$ -concentrating mechanisms would make it easier to account for aspects of algal development, such as cyanelles in glaucocystophytes.

Thus, a relatively early ( $\geq 1200$  Ma, Kah and Riding, 2007) origin for cyanobacterial CCMs might have facilitated transmission of these adaptations to algae. Molecular clock estimates, however, suggest an earlier date (1.38–1.54 Ga) for the primary endosymbiotic event, i.e., when eukaryotes first acquired cyanobacteria as plastids (Hackett et al., 2007), and definite eukaryote microfossils appeared by 1850–1650 Ma (Knoll et al., 2006). It remains to be seen whether earlier evidence for CCMs, in the form of sheath-calcified cyanobacteria, might be found and have a bearing on Proterozoic algal development.

3. There is evidence that  $\text{O}_2$  increased to  $\sim 5\%$  PAL in the late Paleoproterozoic (ca. 1800 Ma) and remained near that level to the early Neoproterozoic (1000 Ma; Canfield, 2005). During the same period,  $\text{CO}_2$  underwent substantial decline, possibly from  $\sim 50$  PAL to  $< 10$  PAL (Sheldon, 2006; Fig. 7). Details of these trends are not known, and there has not been a methodical search for sheath-calcified microfossils, making any suggestions tentative. Nonetheless, appearance of sheath-calcified cyanobacteria at ca. 1200 Ma is consistent with reduction in  $\text{CO}_2$  below 10 PAL at that time (Kah and Riding, 2007), the threshold sufficient to induce CCMs (Badger et al., 2002). Oxygen levels may not have risen above 10% PAL until the late Neoproterozoic (Canfield, 2005), so it is possible that large  $\text{CO}_2$  decline may on its own have been sufficient to promote cyanobacterial CCM development. These sheath-calcified cyanobacteria formed in aquatic microbial mats (Turner et al., 1993; Kah and Riding, 2007), however, and it is therefore possible that in this microenvironment they were subject not only to carbon limitation (Raven, 1997b) but also to localized  $\text{O}_2$  increase (from oxygenic photosynthesis) that increased oxygenase activity.

4. Growing evidence from the geological record (Riding, 2006; Kah and Riding, 2007) supports inferences based on extant organisms (Raven, 1997b; Badger et al., 2002; Raven et al., 2008) that the

evolution of inorganic carbon-concentrating mechanisms in cyanobacteria can be related to long-term changes in atmospheric composition. Cyanobacteria may be unique, given their long geological range, in providing evidence of both CCM development (in the Proterozoic) and its subsequent widespread induction (at the Devonian–Mississippian transition).

#### Phytoplankton

Conditions promoting CCM induction could help account for important changes in algal phytoplankton ca. 360 Ma that have challenged explanation (Strother, 2008). The acritarch cysts that dominate the record of Cambrian–Devonian phytoplankton underwent a marked Late Devonian decline in abundance (Tappan, 1968; Knoll et al., 2007; Fig. 8), and the ensuing low-diversity interval has been termed a phytoplankton blackout (Riegel, 2008). Nonetheless, organic carbon stable isotope values (Saltzman, 2005) and widespread black-shale deposition (Ulmishek and Klemme, 1990) suggest an overall Devonian–Mississippian increase in phytoplankton productivity, which is supported by the abundance of suspension feeders and bioturbators (Martin, 2003). Martin (2003) proposed that acritarch diversity declined due to either a nutrient increase that reduced encystment or, as Strother (1996) suggested, the rise of non-encysting algae. Thus, rather than overall phytoplankton decline (Riegel, 2008), there may instead have been a major reorganization of phytoplankton, with acritarchs being replaced by other groups (Riding, 2008). Strother (2008) suggested that acritarchs evolved under relatively high  $\text{CO}_2$  and low nutrient conditions and were eventually replaced by algae that were more successful at heterotrophic nutrient uptake, as well as being better able to use  $\text{HCO}_3^-$  as a carbon source for photosynthesis.

Small coccoid cells (picoplankton) are major components of present-day phytoplankton, but due to their small size, commonly  $< 3 \mu\text{m}$ , they often went unnoticed until relatively recently (Iturriaga and Mitchell,

1986; Bryant, 2003). It is now recognized that they include very abundant cyanobacteria and prasinophyte green algae (Diez et al., 2001; Falkowski et al., 2004; O'Kelly, 2007). No body fossils of marine picoplanktic cyanobacteria have been reported, although it is likely that they were no less important throughout the Phanerozoic than they are today. In contrast to cyanobacteria, some prasinophytes produce cystlike phycocysts that record their presence throughout the Paleozoic particularly during black shale events (Tappan, 1980). This could reflect their ability to effectively utilize reduced nitrogen (Prauss, 2007). Present-day picoplanktic cyanobacteria possess well-developed CCMs (Badger and Price, 2003), and there is evidence that prasinophytes also do (Parker et al., 2008; Peers and Niyogi, 2008). It has been noted that cyanobacteria increased in the Mississippian (Tappan, 1968), and this may have balanced the loss of eukaryotic phytoplankton (Riegel, 2008). Prasinophytes also survived the Late Devonian extinctions (Tappan, 1980). Biomarkers support Devonian–Mississippian increase in both cyanobacteria (Knoll et al., 2007, fig. 5b) and prasinophytes (Schwark and Empt, 2006).

It is therefore possible that the Late Devonian acritarch decline reflects major restructuring of phytoplankton communities in favor of small cells with effective CCMs, such as cyanobacteria and prasinophytes. Despite increased energetic costs, CCMs assist phytoplankton to overcome carbon limitation that can arise, e.g., under bloom conditions (Rost et al., 2003), thereby enhancing productivity (Kaplan and Reinhold, 1999); they also provide critical advantages where competitors lack CCMs (Derelle et al., 2006). The late Paleozoic phytoplankton blackout would therefore be more apparent than real, reflecting rise to dominance of relatively invisible picophytoplankton triggered by changing atmospheric composition. This development can still be viewed essentially as a change in nutrient availability, since inorganic carbon is the preeminent nutrient resource for carbon fixation. Furthermore, it does not preclude additional nutritional effects that have been suggested (e.g., Riegel, 2008). Cyanobacteria compete well with algae under low-nutrient conditions where not only carbon but also nitrogen is limiting (Lindell et al., 1998), e.g., during water-column stratification (Lindell and Post, 1995) and anoxia (e.g., Kuypers et al., 2004), both of which have been widely inferred in epeiric seas during the Devonian–Mississippian transition (Wilde and Berry, 1984; McGhee, 1996).

Devonian–Mississippian changes in phytoplankton communities were accompanied by significant increases in suspension-feeding echinoderms. Echinoderms became important sediment producers in the Famennian (Peterhänsel and Pratt, 2001) and Mississippian (Kammer and Ausich, 2006). Blastoids (Waters et al., 2003) and crinoids (Kammer and Ausich, 2006) both show diversity peaks in the Mississippian, the so-called Age of Crinoids (Easton, 1960). Blastoids, characterized by delicate brachials with narrow food grooves, were most diverse during the late Famennian, Tournaisian, and Visean (Waters et al., 2003). Among crinoids, the largest expansion in generic richness is shown by camerates and advanced cladids during the Tournaisian–Visean (Kammer and Ausich, 2006, fig. 1). These groups possessed pinnulate arms with narrow food grooves (Kammer and Ausich, 2006). Present-day comatulid (feather-star) crinoids with similar pinnulation select food particles according to food-groove size (La Touche and West, 1980; Liddell, 1982). These changes in morphology and abundance in Famennian–Mississippian suspension-feeding echinoderms suggest both a shift and increase in food supply toward smaller particles, such as picoplankton or the microplankton that feed on them.

Prasinophytes may have appeared by 1500 Ma, under low-oxygen conditions, which could account for their ability to use reduced nitrogen (Litchman, 2007). This time of origin would also have allowed them, along with cyanobacteria, to have experienced mid-Proterozoic CO<sub>2</sub> decline that promoted CCM development. In the Devonian, prior possession of CCMs would have allowed immediate response to changing conditions. It is difficult to assess the extent to which Devonian

acritarchs may have possessed CCMs. Acritarchs are by definition of unknown affinity and are also highly heterogeneous. They are known by ca. 1700 Ma (Zhang, 1986; Yan and Liu, 1993; Javaux et al., 2004) but show low diversity until ca. 800–900 Ma, followed by order-of-magnitude Cambrian–Ordovician species increase (Huntley et al., 2006; Knoll et al., 2006; Fig. 8). Cambrian–Devonian CO<sub>2</sub> levels are thought to have been >10 PAL, and generally much higher (Fig. 2), so it is possible that many Late Devonian acritarch groups had not been exposed to conditions requiring CCMs (Strother, 2008). Picophytoplankton with well-developed CCMs, such as cyanobacteria and prasinophytes, could have expanded rapidly at the expense of acritarchs lacking CCMs as the atmosphere changed near the end of the Devonian. This would have transformed phytoplankton communities, stimulated productivity, increased blooms, and radically altered the food supply to suspension-feeding invertebrates.

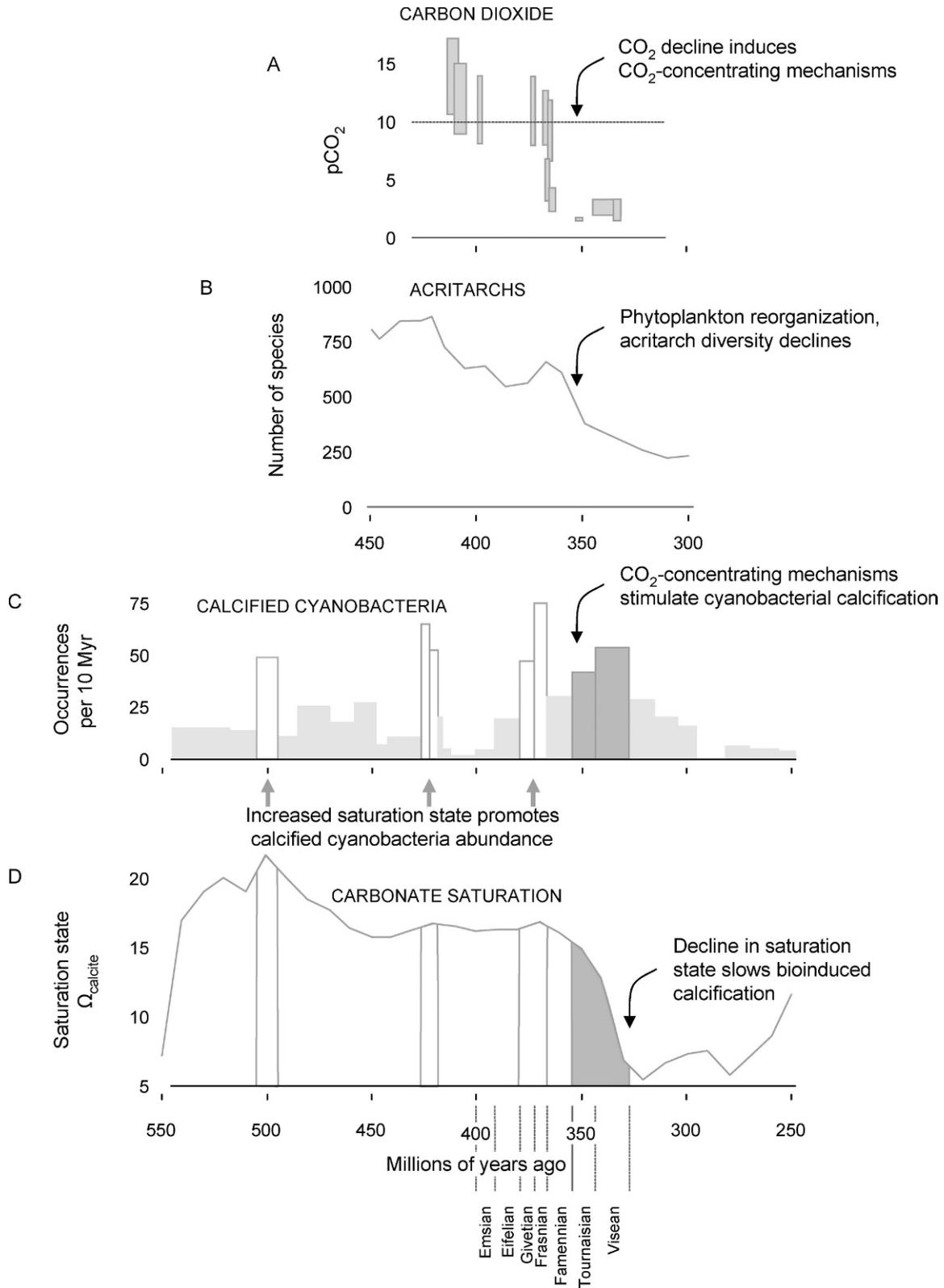
### Bioinduced Calcification

Distinctions between biologically induced (Lowenstam, 1981) and controlled (Mann, 1983), and also between enzymatic and nonenzymatic biomineralization are not clear cut (Weiner and Dove, 2003), but remain useful generalizations (Stanley and Hardie, 1998; Schlager, 2003). The terms bioinduced and nonenzymatic are commonly used to describe calcification in microbial carbonates (Chafetz and Buczynski, 1992; Webb, 1996, 2001), cold seeps, hydrothermal vents (Schlager, 2003, fig. 2), some cave carbonates (Cacchio et al., 2004), and whittings (Robbins and Blackwelder, 1992).

In comparison with biologically controlled calcification, relatively few examples of bioinduced calcification produce readily recognizable fossils. Bioinduced calcifiers with a good fossil record include calcified cyanobacteria (Arp et al., 2001) and green algae such as charophytes, halimedaecans, and dasycladaleans (Lowenstam and Weiner, 1983; Stanley and Hardie, 1998). Their dependence on environmental factors to assist calcification is reflected in their present-day spatial distribution, and in their secular distribution over geological timescales. Marine calcified green algae such as dasycladaleans show marked fluctuation in abundance and diversity through time (Aguirre and Riding, 2005), but to a lesser degree than calcified cyanobacteria. They are restricted today to warm shallow seas (Berger and Kaefer, 1992) and can show reduced calcification near the limits of their ranges (Marin and Ros, 1992). Cyanobacterial calcification is even more environmentally dependent than that of green algae, as reflected by its strongly nonobligate character, extreme scarcity in present-day seas, and highly episodic secular distribution that includes intervals of apparent complete absence (Arp et al., 2001). Arguably, cyanobacteria exhibit the most strongly bioinduced calcification to have produced a clear long-term fossil record. Their dependence on carbonate saturation state and CO<sub>2</sub> availability for calcification makes them potentially significant indicators of changes in past conditions. Work is required to add detail to their secular distribution (e.g., Arp et al., 2001) and refine understanding of thresholds that determine their calcification (e.g., Riding and Liang, 2005; Riding, 2006).

### Atmospheric Change

Proxy (paleosol) data and modeling (Berner and Kothavala, 2001; Berner, 2006) suggest that the Late Devonian–Early Mississippian interval experienced the largest (>10 PAL) abrupt decline in CO<sub>2</sub> of the Phanerozoic (Fig. 2). Mid-Proterozoic decline was probably much larger (>40 PAL), but its timing and speed are poorly constrained (Kasting, 1987; Sheldon, 2006; Fig. 7). Both declines are likely to have significantly affected photosynthetic organisms (Badger et al., 2002; Riding, 2006), and in turn can be expected to have increased productivity and contributed to black shale deposition. Carbon dioxide reduction also results in global cooling, as well as a drop in carbonate



**FIGURE 9**—Interpretive summary of Late Devonian–Early Mississippian events. A) Late Devonian atmospheric CO<sub>2</sub> declines to levels <math><10</math> PAL, inducing CO<sub>2</sub>-concentrating mechanisms (CCM) in cyanobacteria. B) Decline in acritarch phytoplankton diversity could reflect competition from cyanobacteria under carbon-limiting conditions. C) CCM induction promotes sheath-calcification in cyanobacteria, and this is supported by sufficiently elevated carbonate saturation (see D). D) Episode of abundant sheath-calcification is maintained until carbonate saturation declines in Late Mississippian. Marine carbonate saturation trend from Riding and Liang (2005).

concentration, and both of these lower seawater saturation for CaCO<sub>3</sub> minerals. It is therefore possible to invoke large-scale decline in CO<sub>2</sub> to account for both the inception and termination of the Mississippian cyanobacterial calcification episode. Its inception could reflect a decline in CO<sub>2</sub> below 10× PAL, which promoted calcification by inducing CCMs. Its termination could result from reduction in calcification as further CO<sub>2</sub> decline lowered the saturation state (Fig. 9d).

The decline of CO<sub>2</sub> and increase in O<sub>2</sub> that commenced near the end of the Devonian have been linked in particular to the evolution and spread of vascular plants (Algeo et al., 1995). It has been proposed that the evolution of vascular land plants impacted terrestrial weathering (Knoll and James, 1987) by increasing nutrient flux to shallow seas and drawing down atmospheric CO<sub>2</sub> (Algeo et al., 1995; Berner and Kothavala, 2001), as well as by burial of recalcitrant organic carbon (especially lignin) that leaves photosynthetically liberated O<sub>2</sub> in the atmosphere (Berner et al., 2007). Berner et al. (2007) suggested how fluctuations in oxygen may have affected organisms during the course of the Phanerozoic, and they related rising oxygen levels in the Mississippian–Pennsylvanian to increases in the abundance and size of terrestrial arthropods and vertebrates. Raven (1997a) and Badger et al. (2002) recognized that late Paleozoic changes in CO<sub>2</sub> and O<sub>2</sub> levels could be expected to have increased selective pressure for CCMs in marine algae and cyanobacteria. It is now possible to infer that both terrestrial and marine biotas were impacted by the changes in CO<sub>2</sub> and O<sub>2</sub> levels that land-plant evolution helped to generate. If this is correct, then the rise of terrestrial vegetation increased carbon limitation in aquatic plants.

One of the unforeseen results of these events is the possibility that the evolution of trees led to increased calcification in cyanobacteria. In addition, decline in acritarchs and increase in phytoplankton with CCMs, such as cyanobacteria, foreshadowed further adaptive responses in the Mesozoic that gave rise to phytoplankton groups such as dinoflagellates and coccolithophorids (Fig. 8). During the course of the past 400 myr, increasing ocean oxygenation shifted the availability of trace metals essential for cell biochemistry in favor of the red algal plastids acquired by these groups and also subsequently by diatoms (Falkowski et al., 2004). At the same time, reduced availability of CO<sub>2</sub> maintained selection pressure for CCMs because, despite Mesozoic increases, CO<sub>2</sub> levels may have remained <10 PAL throughout the past 350 myr (Fig. 2). It is not surprising, therefore, that algal phytoplankton groups that appeared in the Mesozoic, including dinoflagellates (Berman-Frank et al., 1995), coccolithophores (Nimer and Merrett, 1996), and diatoms (Tortell and Morel, 2002), now all possess CCMs. These long-term developments underline the importance not only of oxygen and its effects on aquatic trace-metal availability (Anbar and Knoll, 2002; Morel and Price, 2003; Quigg et al., 2003; Falkowski et al., 2004) but also of CO<sub>2</sub> availability (Raven, 1997b; Badger et al., 2002) on phytoplankton evolution. In cyanobacteria too, CCM induction probably persisted from the Late Devonian to the present day, with calcification developing in marine forms whenever carbonate saturation was sufficiently high. This supports the view that the secular pattern of cyanobacterial sheath calcification has been jointly mediated by seawater saturation state and CCM induction (Riding, 2006, fig. 5), as calcification will only occur where both CCMs are induced and saturation state is sufficiently elevated.

## CONCLUSIONS

Badger et al.'s (2002) suggestion that the Devonian–Mississippian decline in atmospheric CO<sub>2</sub> and increase in O<sub>2</sub> could have induced CO<sub>2</sub>-concentrating mechanisms (CCMs) in cyanobacteria is supported by the geological record of developments in the marine realm. These include: (1) Mississippian increase in cyanobacterial calcification, with CCM induction inferred to be linked both to calcification and to changes in atmospheric composition that increased carbon limitation;

and (2) restructuring of marine phytoplankton communities and diversification of suspension-feeding echinoderms with narrow food grooves. Acritarch diversity declined, but overall phytoplankton productivity rose, reflected in black shale deposition and positive carbon isotope excursions, and biomarkers show increases in both cyanobacteria and prasinophyte algae.

The following links and timings are envisaged: atmospheric CO<sub>2</sub> decrease and O<sub>2</sub> increase commenced in the Famennian (Late Devonian), creating carbon limitation that exerted selective pressure for CCMs in marine algae and cyanobacteria. Cyanobacteria and possibly also prasinophytes had developed CCMs during the equally large or larger Proterozoic CO<sub>2</sub> decline. They therefore possessed well-developed CCMs, and their ability to induce these as the atmosphere changed conferred competitive superiority over phytoplankton lacking CCMs, which may have included most acritarchs. As a result, cyanobacteria and prasinophytes increased and acritarchs declined. In this view the so-called Mississippian–Permian phytoplankton blackout may be an artifact of the poor preservation potential of picophytoplankton whose presence is nonetheless reflected by biomarkers, carbon isotope values, and black shale abundance. Atmospheric conditions continued to favor CCM development in marine algae and cyanobacteria during the remainder of the Paleozoic and probably to the present day. Before the end of the Mississippian, however, cyanobacterial calcification was reduced as carbonate-saturation state, which had been elevated during much of the early–mid-Paleozoic, declined. As a result, the Mississippian peak of calcified cyanobacterial abundance did not extend beyond the end of the Visean (ca. 325 Ma; Fig. 9).

The fossil record of bioinduced calcification can provide information concerning significant environmental factors whose effects might otherwise be difficult to distinguish. This study suggests previously unforeseen links between biocalcification, marine photosynthesis, phytoplankton, and atmosphere-ocean composition during the Devonian–Mississippian transition. These links help to account for patterns of cyanobacterial calcification and for large late Paleozoic changes in marine phytoplankton that have challenged explanation. They draw attention to the effects of large-scale sustained decline in CO<sub>2</sub> on photosynthetic organisms and connect Devonian–Mississippian changes in the terrestrial and marine biotic realms. These links may also shed light on the timing of CCM acquisition among cyanobacteria and algae over longer timescales. All these insights deserve further scrutiny. They are likely to complement rather than preclude the effects of other influences that have been invoked to account for significant ecologic and evolutionary changes during the Paleozoic from the Late Devonian onward.

## ACKNOWLEDGMENTS

John Raven advised on CO<sub>2</sub>-concentrating mechanisms and read the preliminary manuscript. Colin D. Sumrall and Johnny A. Waters gave guidance on echinoderms. Many perceptive suggestions by PALAIOS reviewers J. Fred Read and Gregory Webb improved the final version. The editors provided timely and encouraging support. For all this help, I am most grateful.

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ACCEPTED JUNE 30, 2009