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

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ABSTRACT
Cyanobacterial calcification is promoted by CO₂-concentrating mechanisms (CCMs) developed in response to photosynthetic carbon limitation. Changes in atmospheric composition (CO₂ fall, O₂ 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 CO₂ 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 picoplanktonic cyanobacteria, could account for Late Devonian acritarch decline and the subsequent apparent scarcity of phytolithophyta in the late Paleozoic (the so-called phytolithophyta 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 CO₂ lowered seawater carbonate saturation. The induction of cyanobacterial CCMs, triggered by Late Devonian change to a relatively low CO₂ and high O₂ 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 (Kemp and Kaczmierczak, 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 CO₂ decline and O₂ 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 CO₂ 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).

CO₂-CONCENTRATING MECHANISMS
The starting point for these considerations is the ability of cyanobacteria to increase photosynthetic efficiency by actively importing inorganic carbon (as CO₂ or HCO₃⁻) into their cells. These CO₂-concentrating mechanisms (CCMs) help overcome limitations in low DIC availability that result from levels of present-day atmospheric CO₂ 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 CO₂ and at the same time is able to fix oxygen as well as carbon (Bowes et al., 1971). Under present-day conditions of low CO₂ and high O₂, 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 CO₂ abundance and O₂ 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 CO₂ concentrations in the vicinity of RuBisCO (Giordano et al., 2005).

The RuBisCOs in cyanobacteria have the lowest CO₂ affinity and lowest CO₂/O₂ selectivity of any RuBisCO in oxygen-producing organisms, with the probable exception of the Form II RuBisCO of peridinin-containing dinoflagellates (Tchernov et al., 2006; J.A. Raven, personal communication, 2009). Such RuBisCOs have their highest specific reaction rates at saturating CO₂ concentrations, so they perform well under high CO₂ regardless of the O₂ concentration. It is therefore not surprising that CCMs are particularly well developed in...