Mesoproterozoic carbon dioxide levels inferred from calcified cyanobacteria

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ABSTRACT

Filamentous and shrub-like carbonate fabrics produced by in vivo cyanobacterial sheath calcification in stromatolites of the ca. 1200 Ma Society Cliffs Formation, Baffin and Bylot Islands, Arctic Canada, are 400 m.y. older than previously reported examples. In vivo sheath calcification is promoted by carbon dioxide concentrating mechanisms (CCMs) and is a direct ecophysiological link to atmospheric CO_2 concentration. CCMs are induced in present-day cyanobacteria under experimental conditions when pCO_2 is below ~0.36% (~10 times present atmospheric level, PAL). Society Cliffs calcified cyanobacteria consequently imply pCO_2 levels of <0.36% at ca. 1200 Ma. This inference is consistent with marine carbon isotope modeling that suggests pCO_2 of 7–10 PAL in the late Mesoproterozoic. Combined, petrographic, experimental, and modeling results therefore suggest that Mesoproterozoic pCO_2 concentrations were not substantially different from Phanerozoic values and were significantly less than previous estimates of up to 200 PAL. Assuming 10% lower solar luminosity in the late Mesoproterozoic, pCO_2 levels of 10 PAL or less require the presence of additional greenhouse gases for maintenance of an ice-free Earth. At 10 PAL pCO_2, methane concentrations of 100–200 ppm would have been sufficient to sustain warm Earth surface conditions. The low atmospheric oxygen and limited marine sulfate concentrations required to sustain atmospheric methane provide additional support for sulfur isotope models that suggest protracted oxygenation of Earth's Proterozoic biosphere.

Keywords: Proterozoic, cyanobacteria, photosynthesis, calcification, carbon dioxide.

INTRODUCTION

In the presence of a faint young sun, Earth's early atmosphere must have contained greenhouse gases sufficient to overcome lower temperatures driven by decreased solar luminosity (Sagan and Mullen, 1972). Traditionally, carbon dioxide and water vapor have been assumed to have been the principal greenhouse gases (Owen et al., 1979), and theoretical models require pCO_2 concentrations of 50–900 times present atmospheric level (PAL) 2.5 b.y. ago, and 10–400 PAL 1.5 b.y. ago, to avoid prolonged global glaciation (Kasting, 1987). Empirical estimates based on paleosols and weathering rinds, however, suggest pCO_2 levels in or below the lower part of this modeled range from the late Archean (Hessler et al., 2004) to the Mesoproterozoic (Rye et al., 1995; Sheldon, 2006). These relatively low estimates of pCO_2 imply the presence of additional greenhouse gases, such as methane, for maintenance of nonfreezing surface conditions (Pavlov et al., 2003; Kasting, 2005). Biological production and photochemical survival of methane would have been enhanced in low-oxygen environments of the Archean and early Proterozoic (Kasting et al., 1983; Goldblatt et al., 2006), and models suggest that methane values could readily have reached ~400 ppm (Pavlov et al., 2001). Furthermore, at high atmospheric concentrations, methane acts as an effective barrier to solar input (methane haze), which could trigger episodes of global cooling consistent with "snowball" glaciations in the early and late Proterozoic (Pavlov et al., 2001; Schrag et al., 2002; Pavlov et al., 2003).

Methane flux, however, is strongly dependent upon atmospheric pO_2 and marine sulfate concentration, both of which may have changed dramatically after ca. 2.2 Ga (Canfield, 1998; Farquhar et al., 2000). Because methane levels cannot currently be constrained from the geologic record, empirical measurements of pCO_2 remain critical to understanding the long-term evolution of Earth's atmosphere. Few estimates of Proterozoic pCO_2 levels have been based on fossils. Comparisons of carbon isotope composition of Mesoproterozoic (1.4 Ga) acritarchs with specific photosynthetic carbon-fixation pathways restrict pCO_2 levels only within a wide range, from >10 to 200 PAL (Kaufman and Xiao, 2003). Here, we use in vivo cyanobacterial calcification as a barometer for paleo-pCO_2 and infer late Mesoproterozoic (ca. 1.2 Ga) pCO_2 levels to have been ≤0.36% (~10 PAL). This value supports results from Fe-silicate equilibria models and models based on constitutive mass balance of paleosols, which indicate pCO_2 levels of <5–25 PAL from 3.2 to 1.0 Ga (Hessler et al., 2004; Sheldon, 2006), which is within the range of Phanerozoic pCO_2 values derived from the GEOCARB III model (Berner and Kothavala, 2001).

MICROBIAL FABRICS OF THE SOCIETY CLIFFS FORMATION

The ca. 1.2 Ga Society Cliffs Formation (Kah et al., 2001), northernmost Baffin and Bylot Islands, Arctic Canada, consists of >600 m of peritidal dolostone deposited on a stable platform. Eastern and northeastern portions of the basin represent sedimentary deposition in intertidal to supratidal, low-energy, evaporative tidal-flat environments. Tidal-flat environments are characterized by low-diversity microbial populations that occur in discrete layers within low-relief mounds (<1 m in diameter), interlaminated with thin accumulations of detrital micrite and seafloor precipitates that encrust topographic surfaces. Penecontemporaneous silicification results in excellent preservation of primary microbial and precipitate fabrics and facilitates interpretation of otherwise dolomitized microfabrics (Kah and Knoll, 1996). Silicified mat fabrics consist primarily of coccoidal cyanobacteria (*Eoentophysalis* sp.) or monotypic filament mats (*Siphonophycus* sp.) that construct vertically oriented tufts, <0.5 mm to >10 mm in height, that are preserved through a combination of early lithification, burial by detrital micrite, and encrustation by carbonate precipitates (Kah and Knoll, 1996).

In addition to silicified mat fabrics, the Society Cliffs Formation locally preserves calcified microbial filaments and shrubs (Fig. 1), which occur interlaminated with seafloor precipitates and detrital micrite and adjacent to silicified mats. Calcified filaments occur as subvertical unbranched curved tubes, 15 μm wide, in dense micrite. The tubes have relatively constant diameter, and uniform thickness micritic walls are locally visible where filaments cross (Fig. 1A). Uniformity of wall thickness and absence of filament degradation, which would occur during postmortem calcification, indicate sheath impregnation produced by in vivo calcification. In vivo cyanobacterial calcification is localized in the protective mucilaginous sheath surrounding cyanobacterial cells; Pentecost and Riding, 1986; Merz-Preiß, 2000). The size and shape of Society Cliffs calcified filaments closely resemble *Girvanella*, which has present-day analogs in in vivo $CaCO_3$-impregnated sheaths of the scytonematacean cyanobacterium *Plectonema* (Riding, 1977).

Microbial shrubs are composed of fine microspar; they are 200–600 μm high and up to 200 μm wide and have irregular margins (Fig. 1B). They generally broaden upward and are digitate in their upper regions. On

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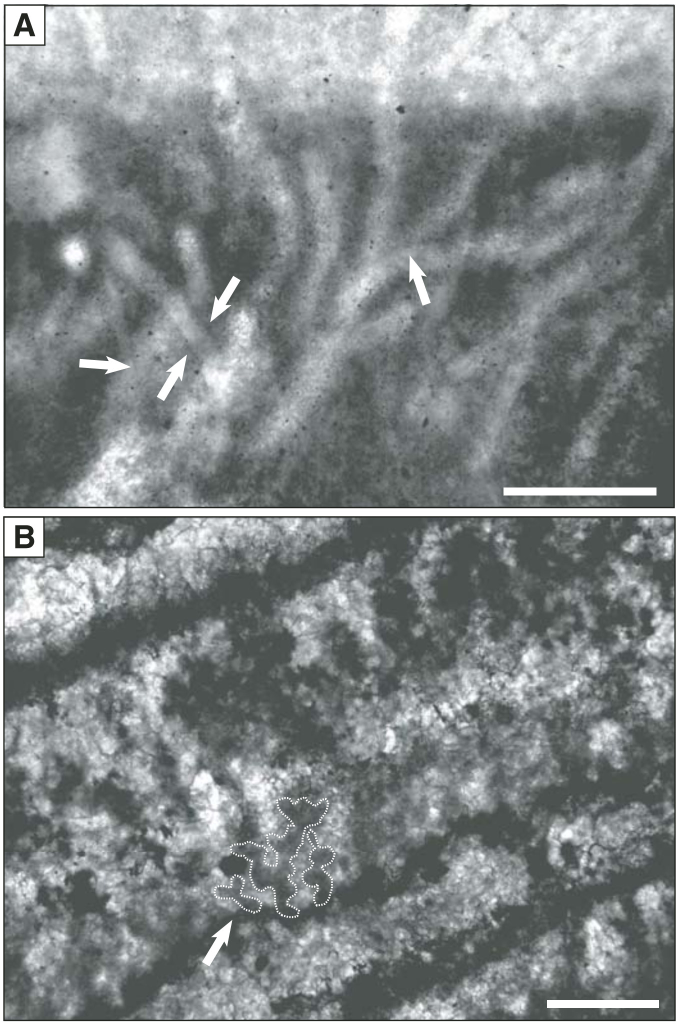

Figure 1. Society Cliffs Formation calcified cyanobacteria. A: Filament molds are 15 μm in diameter and up to 1.2 mm in length. Uniform thickness walls (arrows) are typical of in vivo sheath calcification. Scale bar is 125 μm. B: Calcified shrubs composed of dolomicrospar are ~200 μm wide, 200–600 μm high, and have irregular digitate margins (outlined). Structures of similar size, spacing, and orientation preserved in early diagenetic chert consist of vertically oriented microbial filament tufts. Scale bar is 500 μm.

curved stromatolite surfaces, consistent vertical orientation of the shrubs suggests a phototactic growth response. In size and morphology, shrubs closely resemble *Angusticellularia* (= *Angulocellularia*), a modern oscillatoriacean cyanobacteria that calcifies by micritic impregnation of thick irregular sheaths (Riding and Voronova, 1982). A filamentous origin for the Society Cliffs shrubs is further supported by the presence of filamentous tufts of *Siphonophycus* sp. in silicified regions adjacent to shrub carbonate.

CYANOBACTERIAL CALCIFICATION AND PALEO-PCO$_2$ ESTIMATES

Cyanobacterial calcification is primarily dependent on ambient carbonate saturation state (Kempe and Kazmierczak, 1994) and on pH changes in the microbial sheath resulting from photosynthetic uptake of CO$_2$ and HCO$_3^-$ (Golubic, 1973; Arp et al., 2001). This latter effect is greatly enhanced by carbon concentrating mechanisms (CCMs), which include active HCO$_3^-$ transport into the cells, its conversion to CO$_2$, and concomitant release of OH$^-$ ions that further raises sheath pH, promoting CaCO$_3$ nucleation (Fig. 2; Merz, 1992). Laboratory experiments show that present-day cyanobacteria and algae induce CCMs in response to atmospheric CO$_2$ below 0.36% (Badger et al., 2002, and references therein). It is reasoned, therefore, that the inception of cyanobacterial sheath calcification in the Proterozoic reflects reduction of atmospheric CO$_2$ to this critical threshold (Riding, 2006).

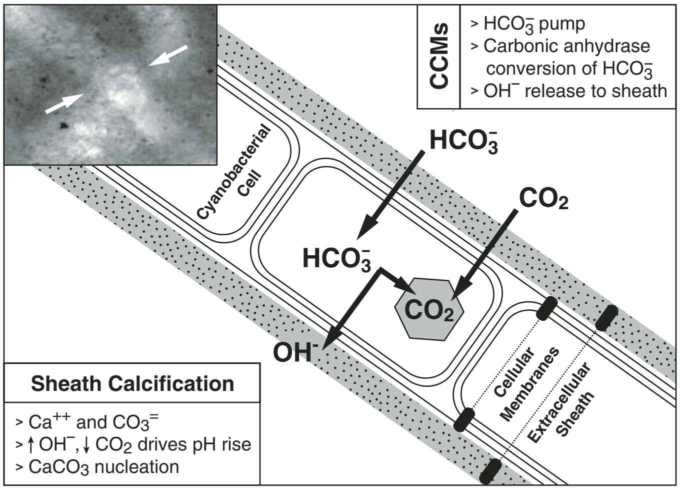

Figure 2. Inferred mechanism of in vivo calcification in response to carbon-concentrating mechanism (CCM) induction. Sheath is preserved via nucleation and impregnation by finely crystalline CaCO$_3$ as pH rises in response to OH$^-$ release due to active HCO$_3^-$ uptake (after Riding, 2006).

Photosynthetic carbon uptake within robust and highly productive benthic mats can result in microenvironmental CO$_2$ concentrations well below equilibrium levels. In these environments, CCM induction could occur even when atmospheric CO$_2$ exceeds 0.36%. In the Society Cliffs examples, however, calcified cyanobacteria occur as thin, submillimeter layers that are overlain by micritic drapes or precipitates that encrust microbial topography, suggesting that tufts maintained contact with seawater throughout growth. Under these circumstances, we infer that CCM induction occurred under equilibrium conditions, which indicates atmospheric CO$_2$ levels close to or below 0.36%. Prior to discovery of Society Cliffs calcified cyanobacteria, the oldest reports of in vivo sheath calcification included *Girvanella* in the 750–700 Ma Draken Group of Spitzbergen (Knoll et al., 1993) and similar structures in the ca. 800 Ma Little Dal Group of northwest Canada (Turner et al., 1993). Calcified cyanobacteria in the Society Cliffs Formation predate these Neoproterozoic occurrences by at least 400 m.y.

DISCUSSION

The presence of calcified cyanobacteria in the Society Cliffs Formation indicates atmospheric pCO$_2$ levels ≤0.36% (~10 PAL) at 1.2 Ga. Assuming solar luminosity 90% of the present-day levels in the late Mesoproterozoic (Gough, 1981), a one-dimensional climate model (Kasting, 1987) indicates that CO$_2$ concentrations of ~10 PAL would result in average global surface temperatures of ~7 °C. However, the absence of convincing glacial deposits (Williams and Schmidt, 1996; Young, 1998) suggests that Mesoproterozoic temperatures were likely closer to 15–20 °C (Kasting, 1987), thereby requiring the presence of additional greenhouse gases. Climate models based on addition of methane to an atmosphere with present-day CO$_2$ levels show that a 100 ppm increase in methane would result in an increase in global surface temperature of <12° (Pavlov et al., 2003). Thus, we suggest that methane concentrations in the late Mesoproterozoic may have reached 100–200 ppm, which would have required at least a tenfold increase in methane flux.

Sustaining elevated methane is problematic in an oxygenated Earth system that favors both lower methane production via competition of sulfate-reducing bacteria with methanogens for organic matter and increased removal of methane via chemical oxidation, consumption by aerobic methanotrophs (Ren et al., 1997), and anaerobic decomposition (Boetius et al., 2000). Alternatively, biospheric oxygen, and consequently marine sulfate concentrations (Habicht et al., 2002), may have remained low throughout much of the Proterozoic. Based on microbial physiology, Canfield and Teske (1996) proposed that disproportionating sulfur-oxidizing bacteria would not have evolved until pO_2 reached 5%–15% PAL. Discrimination of sulfur disproportionation via $\Delta^{33}S$ analysis suggests that these levels were first reached at ca. 1.3 Ga (Johnston et al., 2005), which supports arguments that the relatively restricted S-isotope range observed in pyrite prior to ca. 750 Ma likely resulted from marine sulfate concentrations so low as to limit the isotopic expression of bacterial sulfur cycling (Kah et al., 2001). Rate-dependent modeling of S-isotope change recorded in carbonate-associated sulfate further suggests that marine sulfate concentrations remained <15% of modern values until at least 1.2 Ga and may not have risen substantially until the mid-Neoproterozoic (Kah et al., 2004). Together, these lines of reasoning support low atmospheric oxygen and potentially elevated methane levels throughout the Mesoproterozoic.

These paleo-pCO_2 estimates of ≤10 PAL for the ca. 1.2 Ga Society Cliffs calcified cyanobacteria (Fig. 2) are considerably lower than >10–200 PAL estimates based on the isotopic composition of ca. 1.4 Ga acritarchs (Kaufman and Xiao, 2003). Nonetheless, Society Cliffs values are similar to those obtained by constitutive mass balance calculations (Sheldon, 2006) of ca. 1.1 Ga Sturgeon Falls (Zbinden et al., 1988) and 0.98 Ga Sheigra (Retallack and Mindszenty, 1994) paleosols (Fig. 3). Society Cliffs pCO_2 estimates are also consistent with both textural evidence from marine carbonates and model calculations that suggest a decrease in the size of the marine dissolved inorganic carbon (DIC) reservoir through the Mesoproterozoic (Bartley and Kah, 2004). In this model, DIC reservoir size affects the sensitivity of the marine carbon isotopic system to biogeochemical perturbation: a DIC reservoir >10× present effectively buffers the ocean against isotopic change, whereas a DIC reservoir <10× present provides an insufficient buffer against isotopic change. By calculating DIC reservoir size from rates of isotopic response and recovery, Kah and Bartley (2004) suggested that marine DIC, and thus atmospheric pCO_2, was likely to be >10× present prior to ca. 1.3 Ga, 7–10× present in the late Mesoproterozoic, and 2× present in the latest Neoproterozoic (Fig. 3). Prior to ca. 1.3 Ga, elevated DIC resulted in limited isotopic change, which hinders utilization of the C-isotopic record for accurate determination of DIC reservoir size. Nonetheless, geologically rapid isotopic shifts in the latest Paleoproterozoic (Melezhik et al., 1999) suggest that Archean marine DIC may not have significantly exceeded 10× present, and may have been as low as 2× present (Hessler et al., 2004).

Emerging views of the Proterozoic global carbon cycle suggest that atmospheric pCO_2 may not have differed substantially from that estimated for the Phanerozoic (Fig. 3). Because in vivo cyanobacterial calcification is significantly influenced by pCO_2-driven changes in carbonate saturation state (Riding, 2006), we suggest calcified cyanobacteria may have been more widespread in the Precambrian than currently recognized and may have played a critical role in constraining trends in pCO_2. For example, current estimates suggest that pCO_2 may have been >10 PAL at 1.4 Ga, but they do not constrain maximum pCO_2 (Kaufman and Xiao, 2003; Bartley and Kah, 2004). Discovery of sheath calcified cyanobacteria of this age would constrain pCO_2 to ≤10 PAL. Similarly, elevated pCO_2 estimates for the Paleoproterozoic (Rye et al., 1995; Sheldon, 2006) suggest that cyanobacterial sheath calcification may have been absent at this time, whereas lower pCO_2 estimates for the Archean (Hessler et al., 2004) would have permitted CCM-induced sheath calcification.

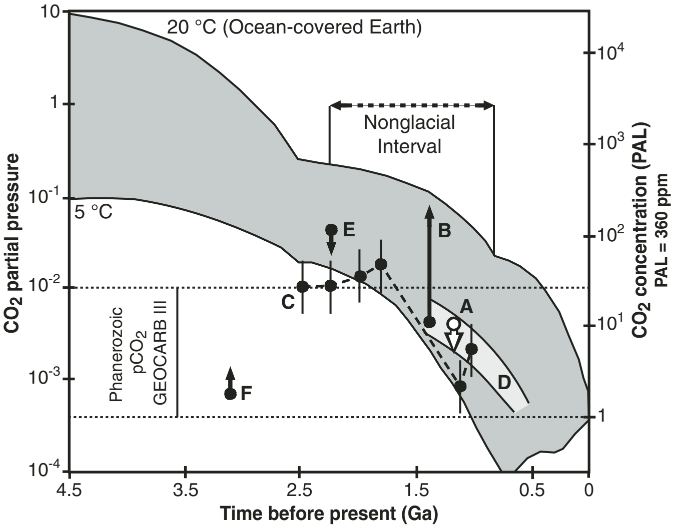

Figure 3. Estimates of Proterozoic pCO_2. Shaded region represents model pCO_2 estimates from Kasting (1987), wherein upper and lower boundaries reflect average surface temperatures for an ice-free (20 °C) and ice-covered (5 °C) Earth. Limits of Phanerozoic pCO_2 from GEOCARB III model (Berner and Kothavala, 2001) are denoted by dashed lines. Cyanobacterial calcification (A; present study) indicates Mesoproterozoic (1.6–1.0 Ga) pCO_2 <10 present atmospheric level (PAL), similar to minimum estimates based on acritarch isotopic composition (B; Kaufman and Xiao, 2003), estimates derived from paleosol mass balances (C; Sheldon, 2006), and model estimates derived from C-isotope reservoir modeling (D; Kah and Bartley, 2004). These estimates, together with those for Paleoproterozoic (2.5–1.6 Ga) (E; Rye et al., 1995) and Archean (3.8–2.5 Ga) (F; Hessler et al., 2004), suggest that pCO_2 may never have been substantially higher than Phanerozoic levels, which would have required additional greenhouse gases to compensate for decreased solar luminosity, particularly during ice-free intervals.

CONCLUSIONS

The induction of CO_2-concentrating mechanisms during photosynthesis, and resultant in vivo calcification of cyanobacterial sheaths, provides an ecophysiological link to atmospheric pCO_2. Calcified sheaths from the Society Cliffs Formation represent the first known occurrence of in vivo calcification, and they indicate pCO_2 levels ≤10 PAL in the late Mesoproterozoic. Estimates are similar to those inferred from Mesoproterozoic paleosols and are consistent with estimates of 7–10 PAL from time-dependent models of marine carbon isotope change. Relatively low concentrations of atmospheric CO_2 would require addition of other greenhouses gases, e.g., 100–200 ppm methane, to counteract the effects of lower solar luminosity on Earth surface temperature. Such atmospheric methane concentrations are consistent with estimates of low pO_2 and marine sulfate concentration that reflect protracted oxygenation of the Proterozoic biosphere. The potential importance of methane on early Earth requires critical evaluation of paleo-pCO_2. Recent models (Fig. 3) suggest that pCO_2 in the Precambrian may not have differed significantly from Phanerozoic values, yet evidence for cyanobacterial calcification has not been confidently recognized in the Paleoproterozoic or Archean. Because in vivo cyanobacterial calcification provides an empirical indication of pCO_2 levels ≤10 PAL, discovery of these distinctive microfossils in rocks older than 1.2 Ga could provide critical constraints on the evolution of Earth's early atmosphere.

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