Geobiology (2006), **4**, 299–316 DOI: 10.1111/j.1472-4669.2006.00087.x

Cyanobacterial calcification, carbon dioxide concentrating mechanisms, and Proterozoic–Cambrian changes in atmospheric composition

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ABSTRACT

Photosynthetic uptake of inorganic carbon can raise the pH adjacent to cyanobacterial cells, promoting $CaCO_3$ precipitation. This effect is enhanced by CO_2 concentrating mechanisms that actively transport HCO_3^- into cells for carbon fixation. CO_2 concentrating mechanisms presumably developed in response to atmospheric decrease in CO_2 and increase in O_2 over geological timescales. In present-day cyanobacteria, CO_2 concentrating mechanisms are induced when the atmospheric partial pressure of CO_2 (p_{CO2}) falls below ~0.4%. Reduction in p_{CO2} during the Proterozoic may have had two successive effects on cyanobacterial calcification. First, fall in p_{CO2} below ~1% (33 times present atmospheric level, PAL) resulted in lower dissolved inorganic carbon (DIC) concentrations that reduced pH buffering sufficiently for isolated $CaCO_3$ crystals to begin to nucleate adjacent to cyanobacterial cells. As a result, blooms of planktic cyanobacteria induced precipitated 'whitings' of carbonate mud in the water column whose sedimentary accumulation began to dominate carbonate platforms ~1400–1300 Ma. Second, fall in p_{CO2} below ~0.4% (10 PAL) induced CO_2-concentrating mechanisms that further increased pH rise adjacent to cells and promoted *in vivo* cyanobacterial sheath calcification. Crossing of this second threshold is indicated in the fossil record by the appearance of *Girvanella* 750–700 Ma. Coeval acquisition of CO_2 concentrating mechanisms by planktic cyanobacteria further stimulated whiting production. These inferences, that p_{CO2} fell below ~1% ~1400–1300 Ma and below ~0.4% 750–700 Ma, are consistent with empirical and modelled palaeo-atmosphere estimates. Development of CO_2 concentrating mechanisms was probably temporarily slowed by global cooling ~700–570 Ma that favoured diffusive entry of CO_2 into cells. Lower levels of temperature and DIC at this time would have reduced seawater carbonate saturation state, also hindering cyanobacterial calcification. It is suggested that as Earth emerged from 'Snowball' glaciations in the late Neoproterozoic, global warming and O_2 rise reactivated the development of CO_2 concentrating mechanisms. At the same time, rising levels of temperature, calcium ions and DIC increased seawater carbonate saturation state, stimulating widespread cyanobacterial *in vivo* sheath calcification in the Early Cambrian. This biocalcification event promoted rapid widespread development of calcified cyanobacterial reefs and transformed benthic microbial carbonate fabrics.

Received 21 April 2006; accepted 21 September 2006

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INTRODUCTION

Silicified cyanobacteria are locally common in Proterozoic sediments (Schopf & Klein, 1992), yet calcified cyanobacteria were scarce or absent until the Neoproterozoic (Swett & Knoll, 1985; Knoll *et al.*, 1993; Turner *et al.*, 1993, 2000a,b) and did not become widespread until the advent of the Palaeozoic at 542 Ma (Riding, 1994). If seawater saturation state with respect to $CaCO_3$ minerals was high during much of the Proterozoic, as seems likely (Knoll *et al.*, 1993), then why was cyanobacterial calcification so poorly developed in comparison to the Palaeozoic? Attempts to account for this paradox, dubbed the 'Precambrian Enigma' (Riding, 1994), have emphasized changes in seawater chemistry (Riding, 1982; Knoll *et al.*, 1993; Arp *et al.*, 2001). In addition to reduced pH buffering (Arp *et al.*, 2001) and elevated saturation state (Kempe & Kazmierczak, 1994), cyanobacterial sheath calcification is also enhanced by a key set of biological adaptations, CO_2 concentrating mechanisms (CCMs) (Merz, 1992). It is proposed here that cyanobacterial CCMs developed

in the Proterozoic in response to falling p_{CO2} and rising p_{O2} levels, and that CCM development is reflected by the appearance in the geological record of *in vivo* calcified sheaths of benthic filamentous cyanobacteria. Currently, the earliest known definite occurrence of such calcified sheaths is *Girvanella* 750–700 Ma (Swett & Knoll, 1985). This is more than 300 Myr earlier than the previously suggested origin of cyanobacterial CCMs (Badger *et al.*, 2002). At the same time that benthic cyanobacteria developed CCMs, they would also have been developed by planktic cyanobacteria, especially under bloom conditions where inorganic carbon was a limiting resource. This is likely to have stimulated the extensive precipitation of small $CaCO_3$ crystals in the water column as 'whitings'. Deposition of this whiting carbonate mud significantly changed Proterozoic patterns of carbonate sedimentation.

GEOLOGICAL RECORD OF CALCIFIED CYANOBACTERIA

Palaeoproterozoic and Mesoproterozoic (2500–1000 Myr) records of calcified cyanobacteria are equivocal (Riding, 1994). The earliest confirmed occurrence of sheath calcified cyanobacteria is in columnar stromatolites of the Draken Conglomerate Group/Draken Formation of north-eastern Spitsbergen (Swett & Knoll, 1985; Fairchild, 1991; fig. 6(a); Knoll *et al.*, 1993; fig. 8) whose age, from biostratigraphic and chemostratigraphic data, is 750–700 Myr (Knoll *et al.*, 1991). Swett & Knoll (1985; fig. 13) interpreted the loosely intertwined nonseptate cylindrical micritic filaments 2–6 μm in diameter as 'extracellular sheaths of oscillatoriacean cyanobacteria'. The illustrations do not clearly show tubular morphology, but Knoll *et al.* (1993; p. 516) emphasized that the 'filaments are defined by a dark cylinder of finely crystalline dolomite that is hollow in the best preserved specimens'. These features allow the Draken microfossils to be identified as *Girvanella*.

A less well-preserved 'tubule-thread microfossil, analogous to the calcimicrobe *Girvanella*', is reported from reefs of the Little Dal Group in the Mackenzie Mountains of north-west Canada (Turner *et al.*, 1993; fig. 3). The age of the Little Dal Group is currently poorly constrained at <1083 to >779 Ma (Turner *et al.*, 1993, 2000a,b), but chemostratigraphic correlation with the Bitter Springs Formation of Australia, if confirmed, would indicate a date of ~835 Myr (Batten *et al.*, 2004; p. 250). These Little Dal filamentous microfossils include unbranched and slightly curved thin-walled tubes with external diameter ranging from 7–13 μm. Turner *et al.* (1993; p. 260) compared them with calcified oscillatoriacean sheaths and noted their similarity to *Girvanella*, but pointed out that the Little Dal tubes are unusually long, up to 500 μm. These fossils therefore resemble *Girvanella* (Turner *et al.*, 2000b; fig. 4b, p. 97) but are not definitely identified.

Sturtian Glaciation, the first of two or more Neoproterozoic glaciations, commenced at ~700 Ma (Walter *et al.*, 2000). Draken *Girvanella* thus predates commencement of the interval of

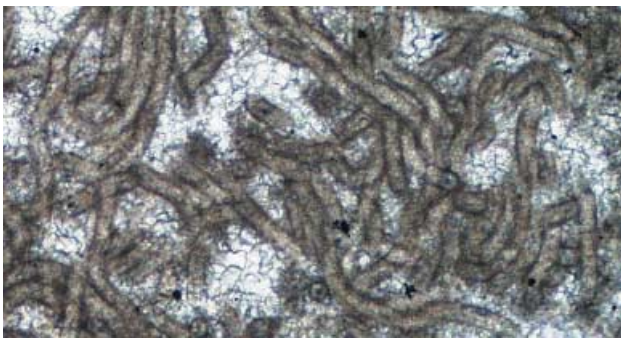

Fig. 1. *Girvanella*, early Mid-Ordovician, Lunnan, Tarim, China. The tubes represent $CaCO_3$-impregnated cyanobacterial sheaths. Note the regular tube width and wall thickness. Width of view 1 mm.

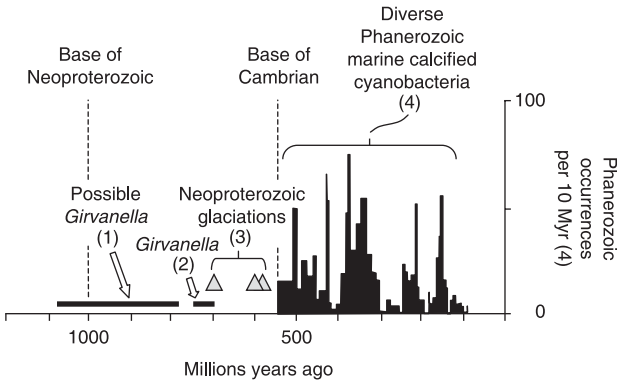

Fig. 2. Neoproterozoic–Phanerozoic record of marine calcified cyanobacteria. (1) 'Possible *Girvanella*' refers to thin-walled Little Dal tubules (Turner *et al.*, 1993, 2000a,b), the age of which is only broadly constrained but may be ~835 Myr (Batten *et al.*, 2004; p. 250); (2) Draken *Girvanella* (Swett & Knoll, 1985; Knoll *et al.*, 1993); (3) Neoproterozoic glaciations (Walter *et al.*, 2000); (4) Phanerozoic calcified cyanobacteria, reported occurrences per 10 Myr (Arp *et al.*, 2001).

'Snowball' glaciations by up to 50 Myr, and Little Dal's possible *Girvanella* predates this interval by 79–383 Myr. Younger Neoproterozoic records of calcified cyanobacteria are scarce or lacking. Well-preserved microbial carbonates occur in the Noonday Dolomite of Death Valley, a postglacial cap carbonate that may be linked to Sturtian (~700 Myr) or Marinoan (~600 Myr) glaciation (Corsetti & Grotzinger, 2005). The Noonday contains fabrics reminiscent of *Epiphyton* and *Renalcis*, but lacks definite examples of these fossils (Corsetti & Grotzinger, 2005), and *Girvanella* is not recorded. This suggests that the palaeogeographical distribution of calcified cyanobacteria was very limited during the period of 'Snowball' glaciations and its aftermath up until the Cambrian, when calcified cyanobacteria became widespread (Riding, 1994). The first record of a diverse calcified cyanobacterial flora is in the earliest Cambrian Nemakit–Daldynian Stage (Riding & Voronova, 1984). Subsequently, *Girvanella* (Fig. 1) and other calcified cyanobacteria were components of Cambrian reefs (Rowland & Shapiro, 2002) and of shallow marine carbonate sediments throughout much of the Palaeozoic–Mesozoic (Riding, 2000; Arp *et al.*, 2001) (Fig. 2).

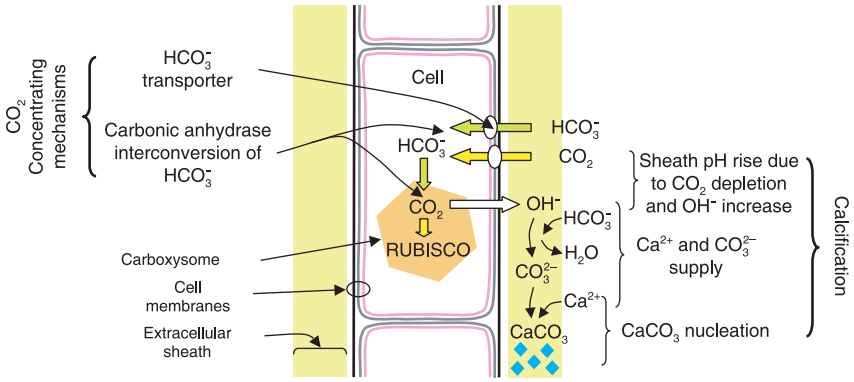

Fig. 3. Integrated model of *in vivo* cyanobacterial sheath calcification driven by CCM-enhanced photosynthesis (based on synthesis of information from Miller & Colman, 1980; Thompson & Ferris, 1990; Merz, 1992; Price *et al.*, 1998; Kaplan & Reinhold, 1999; Badger & Price, 2003), showing an idealized filamentous cyanobacterium. CCMs involve carbon import by uptake of CO_2 and active transport of HCO_3^- into the cell where carbonic anhydrase enzymes convert CO_2 into HCO_3 that diffuses into the carboxysome. In the carboxysome, carbonic anhydrase again converts HCO_3^- into CO_2. This liberates OH- ions that are released from the cell. Calcification is stimulated by this photosynthetic uptake of CO_2 and HCO_3^- and OH^- release which elevates sheath pH. At this raised pH, extracellular HCO_3^- converts into CO_3^{2-}, increasing saturation state with respect to $CaCO_3$ minerals and favouring $CaCO_3$ nucleation in the sheath.

CO_2 CONCENTRATING MECHANISMS IN CYANOBACTERIA

Two factors of central importance for photosynthesis in aquatic organisms are the availability of dissolved inorganic carbon (DIC) and the mechanism of the primary carbon-fixing enzyme, ribulose-1.5 biphosphate carboxylase-oxygenase (RUBISCO). CCMs are processes, widely present in photosynthetic organisms including cyanobacteria, that concentrate CO_2 in cells to stimulate carbon fixation (Berry *et al.*, 1976; Kaplan *et al.*, 1980; Raven, 1997a; Miyachi *et al.*, 2003; Ogawa & Kaplan, 2003). It seems likely that the need for CCMs arises from inefficiency of RUBISCO (Kaplan *et al.*, 1980; Badger, 1987) and its ability to bind O_2 as well as CO_2 at the same site. When this occurs, oxygenase activity competitively inhibits carbon fixation, resulting in loss of CO_2 from the cell by photorespiration. Oxygenase activity increases with O_2 and temperature, and carbon fixation slows as a consequence. CCMs help to overcome RUBISCO's low affinity for CO_2 and also to depress its oxygenase activity by concentrating CO_2 at the site of RUBISCO in the cell (e.g. Kaplan *et al.*, 1980, 1994; Raven, 1997a; Kaplan & Reinhold, 1999; Ghoshal & Goyal, 2001; Omata *et al.*, 2001; Miyachi *et al.*, 2003; Ogawa & Kaplan, 2003). CO_2 diffuses much more slowly in aqueous solution than in air, limiting its availability for photosynthesis. Consequently, in aquatic organisms, CCMs do not only overcome RUBISCO's deficiencies with regard to carbon fixation, but also permit acclimation to conditions where DIC levels are limiting (Kaplan & Reinhold, 1999), such as in benthic microbial mats and planktic blooms.

CCMs differ widely among organisms from bacteria to vascular plants. In cyanobacteria they involve active carbon transport into the cell (Kaplan & Reinhold, 1999), and the ability to concentrate CO_2 by up to 1000 times the extracellular carbon concentration (Kaplan *et al.*, 1980; Badger & Price, 2003). As a result, cyanobacteria have the most effective CCMs known (Badger, 2003). The site of RUBISCO in the cyanobacterial cell is a polyhedral compartment termed the carboxysome (Shively *et al.*, 1973). In cyanobacteria, active HCO_3^- transport accumulates HCO_3^- in the cell, where it diffuses into the carboxysome and is converted into CO_2 (Beer *et al.*, 1992; Price *et al.*, 1998; Kaplan & Reinhold, 1999; Badger & Price, 2003). Interconversion of CO_2 and HCO_3^- is accelerated by carbonic anhydrase (CA) enzymes (Badger, 2003). CA converts CO_2 into HCO_3^- outside the carboxysome, and then converts HCO_3^- into CO_2 inside the carboxysome, delivering CO_2 to the active site of RUBISCO. HCO_3^- transport and subsequent carbonic anhydrase interconversions thus constitute CCMs in cyanobacteria (Fig. 3).

Based on the types of carboxysome and RUBISCO present, Badger *et al.* (2002) recognized α-cyanobacteria and β-cyanobacteria. Many β-cyanobacteria have well-developed CCMs, and this could in part reflect their preferential occurrence in microbial mats where population densities are high, nutrients are abundant, and DIC can be a limiting resource (Badger & Price, 2003). In β-cyanobacteria, increased HCO_3^- conversion to CO_2 by carbonic anhydrase activity, an early phase of CCM development, is likely to have required p_{CO2} below ~0.36% (10 times present atmospheric level (PAL)) (Badger *et al.*, 2002; p. 169). Based on this estimate, aqueous CO_2 levels in equilibrium with <0.4% CO_2 in the atmosphere is here taken as an arguable approximate threshold for predicting when the development of a CCM in cyanobacteria may have started. Possibly this condition initially occurred in microbial mat microenvironments of low DIC availability.

CYANOBACTERIAL CALCIFICATION

Several observations suggest that cyanobacterial calcification is related to photosynthetic carbon uptake (Gleason, 1972;

Golubic, 1973; Pentecost & Riding, 1986). These include increased $\delta^{13}C$ isotope values in the precipitated $CaCO_3$ (Pentecost & Spiro, 1990; Merz, 1992; Andrews *et al.*, 1997); decrease in calcification when dichlorophenyl-dimethyurea, an inhibitor that suppresses electron transport in photosystem II (Badger & Andrews, 1982), is added (Merz, 1992; fig. 5); pH rise in the vicinity of calcifying cells (Thompson & Ferris, 1990; Lee *et al.*, 2004); and restriction of precipitation to illuminated cells (Thompson, 2000; p. 253). Efficient cyanobacterial CCMs that include active HCO_3^- transporters (Kaplan & Reinhold, 1999; Badger & Price, 2003) should promote calcification (Merz, 1992). This is supported by the observation in a study by Merz (1992, fig. 6) that calcification in *Schizothrix* and *Scytonema* decreased when ethoxyzolamide, an inhibitor of the carbonic anhydrase CCM, was added.

Inference of a relationship between CCM-stimulated photosynthesis and calcification (Merz, 1992) suggests the following integrated sequential model for cyanobacterial calcification, based on observed and inferred CCMs (Miller & Colman, 1980; Badger & Price, 2003) and calcification (Thompson & Ferris, 1990; Merz, 1992) processes (Fig. 3): (i) carbon import is enhanced by CO_2 uptake and active transport of HCO_3^- into the cell; (ii) carbonic anhydrase (CA) enzymes convert CO_2 into HCO_3; (iii) HCO_3^- diffuses into the carboxysome; (iv) CA enzymes convert HCO_3^- into CO_2; (v) OH ions liberated by conversion of HCO_3^- into CO_2 are released from the cell; (vi) CO_2 uptake and OH^- release both lead to increased pH in the sheath; and (vii) at increased pH, HCO_3^- converts into CO_3^{2-}, raising saturation state with respect to $CaCO_3$ minerals, and $CaCO_3$ nucleates within the sheath, provided that initial ambient saturation is sufficiently high. It has been suggested that protons and CO_2 generated by calcification are used in photosynthesis (McConnaughey & Whelan, 1997); if this is correct, then the process of calcification could itself be regarded as a CCM.

Differences in degree of cyanobacterial calcification within the same environment (Golubic, 1973) have been attributed to differences in sheath composition and structure that influence calcium-absorption, -binding, and -diffusion (Pentecost & Bauld, 1988; Merz, 1992). It is proposed here that differences in CCM development are also important and that calcified cyanobacteria operate efficient CCMs that elevate sheath pH sufficiently to induce calcification, as for example in some varieties of the unicellular cyanobacterium *Synechococcus* (Thompson & Ferris, 1990; Lee *et al.*, 2004). Research on cyanobacterial CCMs needs to be extended to filamentous forms such as *Phormidium*, *Rivularia* and similar varieties that show intense calcification in hardwater lakes and streams at the present-day.

TIMING OF CCM DEVELOPMENT

If CCMs contribute significantly to cyanobacterial calcification (Merz, 1992) and atmospheric levels of $CO_2 < 0.4\%$ trigger CCM development (Badger *et al.*, 2002), then questions arise when this threshold was crossed and whether it coincided with the appearance of sheath calcified cyanobacteria (*Girvanella*) at 750–700 Ma? Four lines of evidence permit estimation of Proterozoic atmospheric CO_2. First, palaeosol iron silicates constrain CO_2 levels to less than ~100 PAL near the Archaean–Proterozoic transition 2750–2200 Ma (Rye *et al.*, 1995; Holland, 1999), and acritarch carbon isotope values indicate that CO_2 could have been as high as 200 PAL or nearly as low as 10 PAL, 1400 Ma (Kaufman & Xiao, 2003). The limits set by these empirical estimates are very broad but nonetheless are consistent with CO_2 levels having been within the lower parts of modelled estimates (Kasting, 1993). Second, the sedimentary carbon isotope record provides support for the view that CO_2 levels were relatively low when calcified cyanobacteria appeared. Neoproterozoic sedimentary $\delta^{13}C$ average values are relatively high and are associated with large isotopic excursions (Kaufman & Knoll, 1995). These could reflect both increased decoupling of C_{org} and C_{carb} between shelf and basin environments together with relatively low CO_2 and a small DIC reservoir 'perhaps approaching modern levels' (Bartley & Kah, 2004). Third, CO_2 drawdown due to enhanced silicate weathering is among the factors inferred to have contributed to major mid-late Neoproterozoic glaciations (Walter *et al.*, 2000; Hoffman & Schrag, 2002). Walter *et al.* (2000) recognized major glaciations at ~700 Ma (Sturtian) and ~600 Ma (Marinoan), and possibly a third minor glaciation at 570 Ma. Recent U-Pb geochronology indicates an age of 635 Myr for the Marinoan (Bodiselitsch *et al.*, 2005). Immediately prior to Sturtian Glaciation, weathering effects could have reduced CO_2 by 0.13% (Donnadieu *et al.*, 2004) and simulations suggest that CO_2 levels may have fallen to 0.0859% (Ridgwell *et al.*, 2003) or even ~0.013% (Hyde *et al.*, 2000). Fourth, modelled estimates that p_{CO2} was 12 PAL (= 0.43%) ~550 Ma, on a rising trend (Berner & Kothavala, 2001; fig. 13), imply that latest Neoproterozoic p_{CO2} levels were below this. Overall, these estimates suggest that p_{CO2} fell below 0.4% between 1250 and 750 Ma (Fig. 4).

DISCUSSION

CCM development

It is reasonable to speculate that at some point following the appearance of RUBISCO in the Archaean, declining atmospheric CO_2 and increasing O_2 levels led photoautotrophs to develop CCMs (Raven, 1997a; Badger & Price, 2003). There could have been selective pressures for CCMs as early as 2300 Ma in benthic microbial mats where DIC removal and O_2 accumulation were localized (Giordano *et al.*, 2005; p. 118). Raven (1997a) suggested that these selective pressures on eukaryotes intensified 650–550 Myr and especially 300 Ma ago. Adopting this approach, Badger *et al.* (2002; p. 169) proposed that cyanobacterial CCMs developed during the Late

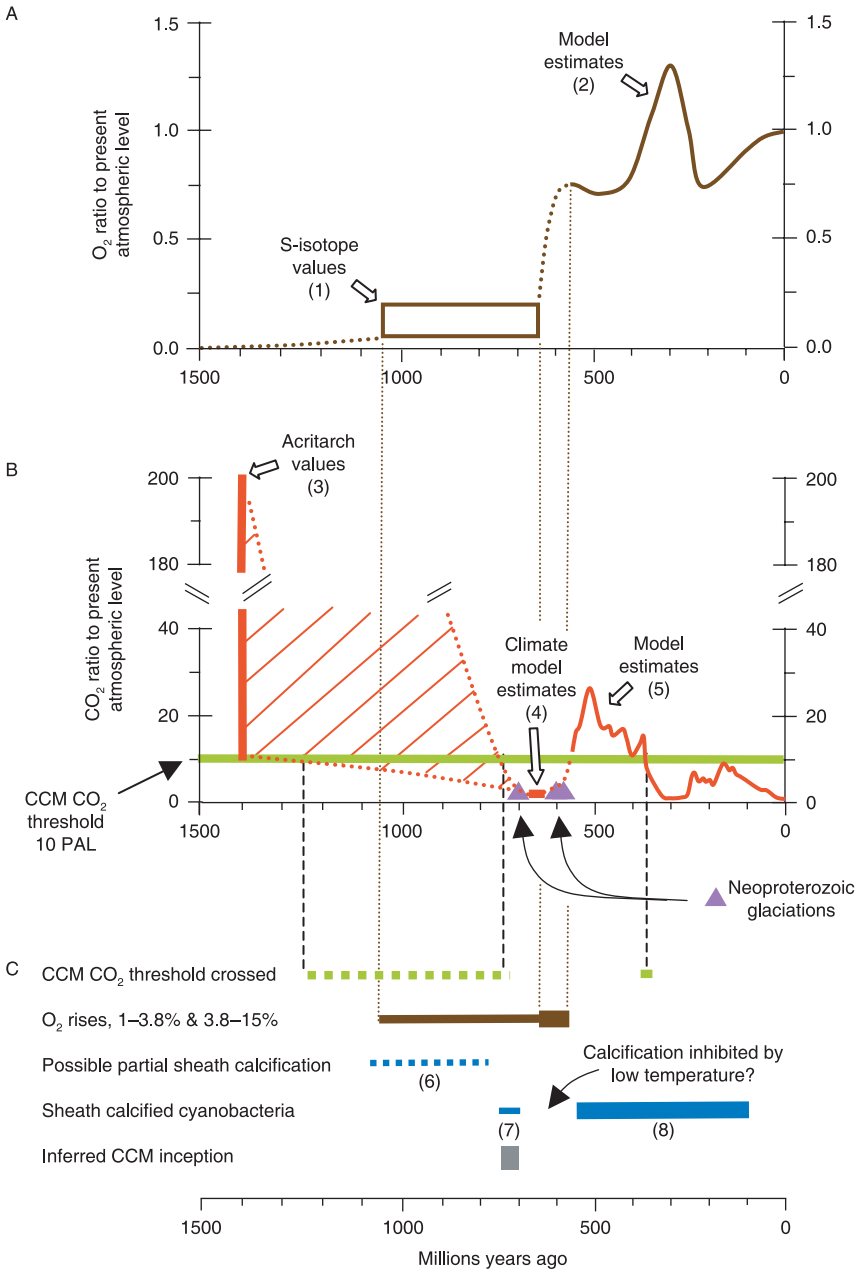

Fig. 4. Mesoproterozoic–Phanerozoic atmospheric trends related to cyanobacterial calcification and CCM inception. (A) O_2, continuous trend lines based on published estimates: (1) Canfield & Teske (1996); (2) Berner (2001; fig. 9). Dotted trend lines are inferred trends. Increase from less to greater than 5–18% PAL O_2 (~1–3.8%) between 1050 and 640 Ma is likely to have increased the selective pressure for CCMs. (B) CO_2, continuous trend lines based on published estimates: (3) Kaufman & Xiao (2003); (4) Hyde *et al*. (2000), Ridgwell *et al*. (2003); (5) Berner & Kothavala (2001). Dotted trend lines are inferred. Based on these estimates, reduction in CO_2 below the ~0.4% threshold to induce CCMs could have occurred during the interval 1250–750 Ma. Neoproterozoic glaciations (~700–570 Ma) could be linked to CO_2 decline. (C) Secular distribution of calcified marine cyanobacteria: (6) possible occurrence of *in vivo* calcified cyanobacteria (Turner *et al*., 1993, 2000a,b), although these may represent post-mortem calcification (see Discussion: 'Calcification in *Girvanella*') (7) definite occurrence of *in vivo* sheath impregnated cyanobacteria (Swett & Knoll, 1985; Knoll *et al*., 1993) (8) definite occurrences of marine sheath calcified cyanobacteria (Riding, 1982, 1994; Arp *et al*., 2001). It is proposed that the first confirmed appearance of sheath calcified cyanobacteria (*Girvanella* ~750–700 Ma, Swett & Knoll, 1985) reflects CCM acquisition in response to O_2 increase and CO_2 decline, specifically p_{CO2} = 0.4%. This timing is consistent with estimated initial O_2 rise 1050–640 Ma (A). In comparison with published p_{CO2} estimates that the 0.4% (10 PAL) threshold may have been crossed during the 1250–750 Myr interval (B), the first known occurrence of *Girvanella* suggests that this point was reached relatively late (750–700 Ma), shortly prior to Sturtian glaciation.

Devonian–Late Permian interval (~380–265 Ma) in response to marked fall in CO_2 (Berner & Kothavala, 2001) and rise in O_2 (Berner, 2001). However, it is suggested here that equally large reduction in CO_2 level very likely occurred at least 300 Myr prior to this, during the Proterozoic, when estimates indicate that CO_2 fell below the ~0.4% CCM threshold 1250–750 Ma ago (Fig. 4). Occurrence of *Girvanella* in the 750–700-Myr-old Draken Conglomerate Group (Swett & Knoll, 1985; Knoll *et al*., 1993) is consistent with this timing of CO_2 decline, suggesting that CCMs sufficient to induce sheath calcification had developed by ~750 Ma.

In the case of pO_2, increase from less than 0.05–0.18 PAL (~1–3.8%) to greater than this level is inferred for the interval 1050–640 Ma from sulphur-isotope records that could reflect evolutionary radiation of sulphide-oxidizing bacteria (Canfield & Teske, 1996). Organic carbon burial suggested by positive $\delta^{13}C$ excursions in marine carbonates would indicate further oxygenation both before (Walter *et al*., 2000) and after (Kaufman *et al*., 1997) Marinoan/Varanger Glaciation, 635 Ma. Carbon and sulphur isotope mass balance modelling suggests that pO_2 was ~15% ~550 Ma (Berner, 2001). Overall, these estimates indicate that pO_2 rose from ~1–3.8% to ~15% between 1050 and 550 Ma, with the greater part of this increase occurring 640–550 Ma. The size of this O_2 rise therefore rivals that estimated for the Carboniferous (Berner, 2001) (Fig. 4). Although oxygen may not be a major signal to switch on

CCMs at the present day (J. Raven, pers. comm., 2006), it does supplement the inorganic carbon signal in at least one cyanobacterium (Woodger *et al.*, 2005), and would have further increased selective pressure on cyanobacteria to develop CCMs to counter photorespiration.

'The Precambrian Enigma'

If seawater saturation state favoured $CaCO_3$ precipitation during much of the Proterozoic (Knoll *et al.*, 1993; Kah & Knoll, 1996), particularly in the earlier part of this eon (Bartley & Kah, 2004), why was cyanobacterial calcification generally so poorly developed (Riding, 1994)? In a resourceful attempt to account for this paradox, Knoll *et al.* (1993; p. 522) proposed that cyanobacterial calcification was inhibited during the Proterozoic by very high supersaturation state that resulted in abundant micrite precipitation. They suggested that these small (= 4 μM) $CaCO_3$ particles acted as preferred nuclei for further precipitation, and that cyanobacteria were unable to calcify when these 'competing crystallites' were 'in the immediate microenvironment'. Knoll *et al.* (1993) inferred that skeletal biomineralization at the commencement of the Cambrian lowered saturation state, reducing micrite production and permitting cyanobacterial calcification 'where competing crystallites were absent'.

There are several difficulties with this. First, the view that micrite hindered cyanobacterial calcification is not consistent with the intimate association of calcified cyanobacteria and micrite in Cambrian reefs where, on average, two-thirds of reef volume is micrite (Kiessling, 2002; fig. 26). Second, Early Palaeozoic micrite may have been produced by disaggregation of calcified cyanobacteria such as *Girvanella* (Pratt, 2001), also indicating that sheath calcification was not hindered by micrite proximity. Third, widespread heavily calcified cyanobacteria appeared early in the Cambrian, in the Nemakit–Daldynian (Riding & Voronova, 1984), whereas radiation of volumetrically significant shelly faunas, such as reefal archaeocyath sponges, required by the suggestion of Knoll *et al.* (1993) to reduce saturation state, is concentrated in younger Early Cambrian stages (Sepkoski, 1992).

An alternative possibility to account for 'the Precambrian Enigma' is that prior to the Neoproterozoic, cyanobacterial sheath calcification was inhibited by the pH buffering of seawater produced by elevated p_{CO2}. Cyanobacterial calcification depends on pH rise resulting from photosynthetic carbon uptake (Thompson & Ferris, 1990; Merz, 1992), and the degree of pH change is also a function of water chemistry (Fairchild, 1991). In an important contribution, Arp *et al.* (2001) suggested that, in addition to elevated environmental saturation state (Kempe & Kazmierczak, 1994), cyanobacterial sheath calcification results from further localized photosynthetically induced rise in calcite supersaturation (ΔSI_{Cc} of 0.2) in the sheath, and they argued that as long as p_{CO2} exceeded 10^{-2} atm (33 PAL), high DIC concentrations would have prevented ΔSI_{Cc} exceeding 0.2. Arp *et al.* (2001) accordingly proposed that early mid-Proterozoic scarcity of calcified cyanobacterial sheaths reflects p_{CO2} > 33 PAL and that '700- to 750-million-year-old calcified cyanobacteria (Knoll *et al.*, 1993) that unequivocally resulted from micritic sheath impregnation would set an upper limit of the p_{CO2} at 10^{-2} atm'.

This innovative suggestion is generally consistent with the appearance of sheath calcification and with palaeo-atmosphere estimates of declining p_{CO2} levels, and represents a significant research advance. But it also raises questions. First, Draken *Girvanella* occurs 750–700 Ma, but estimates suggest that p_{CO2} was already below 33 PAL ~850 Ma, and may have reached this level much earlier (Fig. 4). If p_{CO2} 33 PAL is the threshold for sheath calcification then the Little Dal fossils, in the interval 1083–779 Myr, have an age that is more consistent with Arp *et al.*'s (2001) suggestion, yet their nature as well as their precise age remain uncertain. Second, although Arp *et al.* (2001) based their calculations on present-day cyanobacteria, they did not take into account the effect of CCMs. p_{CO2} 33 PAL substantially exceeds the 10 PAL level of p_{CO2} at which CCMs are induced. It is therefore likely that during the Proterozoic, so long as p_{CO2} exceeded 10 PAL, cyanobacteria would not have possessed CCMs and would not have developed intense sheath calcification.

The interpretation proposed here builds on and develops that of Arp *et al.* (2001), as follows. Reduction in atmospheric p_{CO2} below ~1% (33 PAL) permitted partial sheath calcification, but intense sheath calcification only occurred when CCMs were induced as p_{CO2} levels fell below ~0.4% (10 PAL). In this view, the irregular Little Dal tubules (Turner *et al.*, 2000b; fig. 4b) may reflect incipient *in vivo* calcification at p_{CO2} 33 PAL, and the better defined cylinders of the 750–700 Myr Draken *Girvanella* (Knoll *et al.*, 1993; p. 516) reflect fully developed sheath impregnation when p_{CO2} levels fell below 10 PAL. It is therefore proposed that the appearance of *in vivo* sheath impregnation, 750–700 Ma, reflects CCM development at p_{CO2} < 10 PAL, rather than the effect of DIC reduction at p_{CO2} 33 PAL suggested by Arp *et al.* (2001). Further work is required to establish whether fully impregnated calcified sheaths occur in, or predate, the Little Dal specimens. If they do, it would suggest that the p_{CO2} 10 PAL threshold required to induce CCMs was reached at a date prior to 750–700 Ma.

CCMs differ in their uptake and transport systems for CO_2 and HCO_3^- and in the carbonic anhydrases that interconvert CO_2 and HCO_3^-, and CCM acquisition is thought to have occurred in stages (Badger & Price, 2003). The observed pattern of incipient sheath calcification (Little Dal), followed by well-defined sheath calcification in *Girvanella* (Draken), and then by Early Cambrian sheath calcification among more diverse cyanobacteria, is consistent with stepwise CCM acquisition leading to increasing CCM expression as global levels of CO_2, O_2 and temperature changed. Once CCMs had been acquired, DIC would only have limited calcification in normal

marine environments at p_{CO2} > 33 PAL (Arp *et al.*, 2001). Current estimates suggest that this level has not been reached during the past 850 Myr (Fig. 4). Thus, whereas high DIC limits present-day cyanobacterial calcification in highly alkaline waters such as soda lakes (Arp *et al.*, 2001), key long-term controls on cyanobacterial calcification in normal seawater throughout the Phanerozoic are more likely to have been overall seawater carbonate saturation state (Riding & Liang, 2005a,b) and CCM expression (Riding, 2006) (see 'Role of carbon dioxide' section).

More accurate information concerning p_{CO2} levels and the time of origination of calcified cyanobacterial sheaths in the Proterozoic is required to elucidate these possibilities. Apparent scarcity of calcified cyanobacteria could be due to recrystallization and other alteration processes. It is also possible that calcified cyanobacteria in early Proterozoic sediments have been overlooked. Clarification of the age and nature of the Little Dal microfossils is also important. Confirmation of the presence of *Girvanella*, or other well-defined sheath calcified cyanobacteria, in the Little Dal would indicate that sheath impregnation, used here to calibrate CCM induction and infer p_{CO2} = 0.4%, occurred prior to 750–700 Ma. Given the available <1083 to >779 Myr limits on the age of the Little Dal, this would remain consistent with current published estimates of p_{CO2}, suggesting that the 10 PAL threshold was crossed 1250–750 Ma (Fig. 4), but would indicate a more gradual p_{CO2} decline than is inferred from taking Draken *Girvanella* to reflect inception of CCMs. If *in vivo* sheath calcification older than the Little Dal is recognized then this could constrain p_{CO2} estimates earlier in the Proterozoic. The extent to which CCM induction has influenced cyanobacterial calcification in younger time periods, for example at times of lowered CO_2 levels in the Late Palaeozoic (Riding, 2006), remains to be explored.

Calcification in *Girvanella*

In filamentous cyanobacteria, strands (trichomes) of cells are commonly surrounded by a protective mucilaginous sheath composed of extracellular polymeric substances secreted by the cells (e.g. Merz-Preiß, 2000). During photosynthesis, CO_2 and HCO_3^- enter the cells and hydroxyl ions are excreted, raising sheath pH (Fig. 3). If ambient saturation state for $CaCO_3$ minerals is sufficiently high, nucleation of $CaCO_3$ crystals within the sheath can result. Continuation of this process impregnates the sheath with $CaCO_3$, yielding a calcified replica that preserves sheath outline and dimensions (Riding, 1977; Pentecost & Riding, 1986; Merz, 1992; Merz *et al.*, 1995). Trichomes are not calcified and are removed by decay. The potential calcified microfossil produced by this process is therefore the sheath. Where the sheath is relatively thin it may be tubular in form, as in *Girvanella* (Riding, 1977). Where it is thicker it may have a shrub-like form and the sites of trichomes may be preserved as thin cylindrical moulds within it, as in *Angulocellularia* (*Angusticellularia*) (Riding & Voronova, 1982).

This *in vivo* photosynthetic sheath impregnation contrasts with post-mortem sheath calcification that results from decay. It is likely that antibacterial substances inhibit heterotrophic bacteria in living cyanobacteria (Merz-Preiß, 2000), but dead filaments are prone to bacterial attack (Chafetz & Buczynski, 1992) and the sheath is progressively distorted and transformed as it undergoes decomposition and degradation (Bartley, 1996). Some bacterial decay processes, such as fermentation, may not result in calcification but others, such as those involving sulphate reducing bacteria, can raise pH and, provided that ambient conditions are suitable, can result in carbonate precipitation (Krumbein, 1979). Such degradative calcification is not known to result in the faithful sheath preservation typically observed in present-day and fossil cyanobacteria that were calcified during life. In ensheathed filaments, degradative calcification results in patchy and irregular crusts of variable thickness and continuity (Chafetz & Buczynski, 1992). This uneven encrustation suggests the absence of post-mortem mechanisms that promote restricted sheath impregnation. In addition, decaying sheaths rapidly tend to lose their original shape. Even though sheaths are more resistant than cellular material, experiments show that they undergo changes in shape and size over periods of 125 days, and after that they can exhibit rupturing and loss of tubular morphology (Bartley, 1996). Thus, *in vivo* calcification tends to result in impregnation that preserves original sheath morphology and dimensions (Riding, 1977; Merz-Preiß, 2000), and may record photosynthetic C-isotope values in the carbonate (Pentecost & Spiro, 1990). In contrast, post-mortem degradative sheath calcification is likely to result in distorted filaments variably permeated and veneered by carbonate (Turner *et al.*, 2000b).

Recognition of *Girvanella* as a sheath impregnated by $CaCO_3$ during the life of the cyanobacterium is central to Arp *et al.*'s (2001) interpretation and to the modification of that interpretation proposed here. *Girvanella* has a distinct hollow interior (the site of the trichome(s)) and is not to be confused with solid filaments (*cf* Pratt, 1995; fig. 1). It shows constancy, within individual filaments, in both tube diameter and wall thickness (Riding, 1977) (Fig. 1). This is consistent with the sheath having undergone carbonate impregnation, without either prior organic degradation or subsequent irregular carbonate encrustation. Close morphologic similarities between present-day calcified cyanobacteria and marine microfossils such as *Angusticellularia*, *Botomaella* and *Cayeuxia*, as well as *Girvanella* (Riding, 1977; Riding & Voronova, 1984; Riding, 1991), suggest that these are cyanobacterial sheaths that calcified during life and therefore in response to photosynthetic carbon uptake (see 'Cyanobacterial Calcification' section).

Pratt (2001) suggested that calcification in *Girvanella* might be 'induced by specific chemical changes in the sheath that arose during heterotrophic bacterial and chemical degradation'. Arp *et al.* (2002) acknowledged that 'micrite can be

derived from loosely calcified cyanobacterial sheaths' but added 'we question the formation of *Girvanella* tubes by post-mortem bacterial calcification' and pointed out that such effects are unlikely to maintain the tube structure. In response, Pratt (2002) stated that precipitation does have 'the potential to replicate' decaying sheaths in examples shown by Sprachta *et al.* (2001). However, the degraded and decaying sheaths of *Phormidium* illustrated by Sprachta *et al.* (2001; figs 14 and 15) show irregular crystal crusts that incompletely and unevenly surround collapsed sheaths. These are typical of post-mortem calcification and differ from the impregnated (as opposed to encrusted) tubular sheaths of *Girvanella*. Pratt (2002) acknowledged that 'Arp *et al.* may well be correct that *Girvanella* formed by *in vivo* calcification of sheaths, and I can accept this for tubular specimens exhibiting finely calcified walls. It is therefore important, in searching for fossil evidence of sheath impregnated cyanobacterial fossils such as *Girvanella* to ensure that these are not confused with degraded filaments. None of the filaments so far reported from the Little Dal Group has confidently been recognized as *Girvanella* (Turner *et al.*, 2000b; p. 97) and most of them appear to represent post-mortem rather than *in vivo* calcification. The range of preservation shown by these Little Dal filamentous fossils is documented in detail by Turner *et al.* (2000b; figs 4 and 5). They recognized progression from 'tubules to thread-like filaments, to grumeaux, grumulous clumps, and diffuse micritic streaks with ghosts of filaments' (Turner *et al.*, 2000b; p. 90). These largely appear to represent calcified degraded sheaths and associated extracellular polymeric substances. Tubular filaments are scarce in the Little Dal, and 'most of the filamentous microfossils are of the thread-like variety', which Turner *et al.* (2000b; pp. 90, 108) attribute to variations in the timing and extent of calcification and 'invasion by heterotrophic bacteria'.

While it therefore remains possible that *in vivo* calcified sheaths formed during Little Dal time, and may be represented by thin-walled tubules in the Little Dal Group (see Turner *et al.*, 2000b; fig. 4b), this still requires confirmation. It is therefore accepted here that the earliest, currently known, example of a cyanobacterium that very likely represents *in vivo* sheath calcification, is *Girvanella* from the 750–700 Myr Draken Formation.

Cyanobacterial calcification and the Proterozoic–Cambrian transition

Following onset of the period of glaciations ~700 Ma, it appears that sheath-calcified cyanobacteria were scarce for the remainder of the Neoproterozoic (Riding, 1994). This could reflect reduction in both CCM development and in seawater saturation state with respect to $CaCO_3$ minerals. Global cooling favours diffusive entry of CO_2 into the cell (see Raven *et al.*, 2002), that may have reduced CCM development. Combination of low temperatures and relatively low p_{CO2} would also have lowered seawater saturation state, limiting cyanobacterial calcification. Nonetheless, sheath-calcified cyanobacteria could be expected during warmer episodes that intervened between major glaciations. Extensive glaciation would have hindered terrestrial weathering of silicate minerals that reduces build-up of CO_2 in the atmosphere. This would have led to an increasingly CO_2-rich atmosphere and global warming that would ultimately have terminated glaciations. Hoffman & Schrag (2002) attributed Neoproterozoic post-glacial cap carbonates to rapid thaw that exposed land surfaces to weathering that flushed calcium and bicarbonate into the oceans, raising seawater saturation state with respect to carbonate minerals. In this view, rising seas flooded shelves with these alkaline waters, rapidly precipitating the carbonate sediments that cap glacial tillites on several continents. However, so far as I am aware, there are no reports of sheath-calcified cyanobacteria from cap carbonates (see 'Geological record of calcified cyanobacteria' section). This could reflect real absence, or the paucity of published studies of cap carbonate petrography. Elucidation of the presence or absence of calcified cyanobacteria in cap carbonates is a topic for further study.

Following 'Snowball Earth' conditions, combination of rises in temperature and in pO_2 (Fig. 4A) would have stimulated renewed CCM development to counter photorespiration. Around the same time, increases in Ca^{2+} concentrations (Hardie, 2003), temperature and p_{CO2} (Fig. 4B) in the latest Neoproterozoic are likely to have driven up seawater carbonate's saturation state. These changes are suggested here to have triggered relatively rapid and widespread calcification among diverse cyanobacteria in the Early Cambrian.

This dramatic development of calcified cyanobacteria led to profound changes in microbial reefs (Rowland & Shapiro, 2002). Stromatolites continued to be important in marine environments throughout the Cambrian and for the remainder of the Palaeozoic, but at the Neoproterozoic–Cambrian transition stromatolites were augmented by abundant thrombolites and dendrolites whose conspicuously nonlaminated fabrics were products of microbial calcification (Riding, 2000). This transformation of microbial carbonate fabrics created the first quasi-skeletal frameworks that dominate many Cambrian reefs (Riding, 2000; Rowland & Shapiro, 2002) with dendrolite fabrics resulting from the erect calcified cyanobacterial filaments (Riding, 2000). In addition to changes in atmospheric composition, diffusion limitation of cyanobacterial photosynthesis in microbial mats is likely to be a factor promoting CCM development (Raven, 1997b; Badger *et al.*, 2002; p. 169; Giordano *et al.*, 2005; p. 118). It is therefore possible that adoption of erect growth, reflected by dendrolite fabrics in Cambrian microbial carbonates, may have improved diffusive acquisition of DIC and removal of O_2 by cyanobacteria, and could therefore represent an additional ecological response to altered atmospheric composition.

Role of carbon dioxide

It can be expected that by increasing HCO_3^- uptake into cells, CCMs raise sheath pH and thereby stimulate cyanobacterial

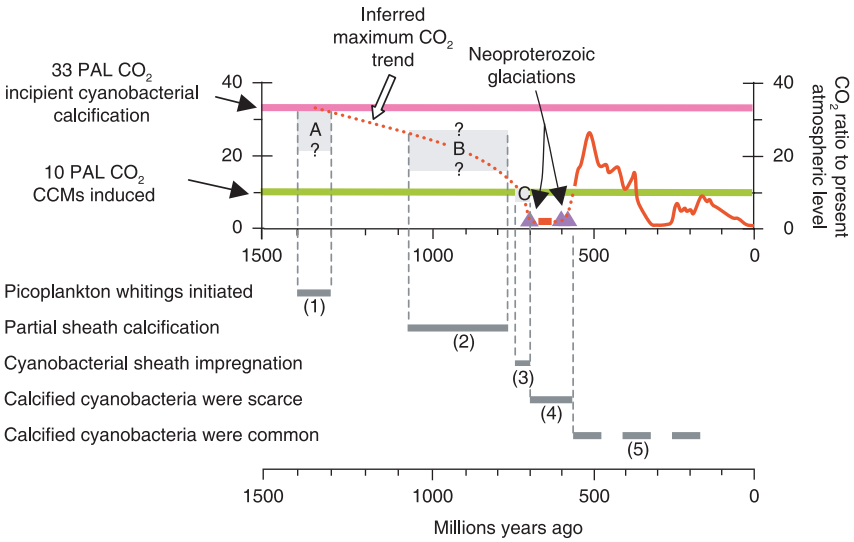

Fig. 5. Trend of maximum atmospheric p_{CO2}–1400–700 Ma (dotted line), inferred from carbonate mud production and cyanobacterial calcification. A: transition to carbonate mud-dominated platforms ~1400–1300 Ma (Sherman *et al*., 2000). B: possible *in vivo* calcified filaments, ~1083–779 Myr Little Dal reef (Turner *et al*., 1993, 2000a,b). C: *in vivo* sheath impregnation (*Girvanella*), 750–700 Myr Draken Group (Knoll *et al*., 1993). Interpretation: (1) Picoplanktic whiting production and incipient, partial, sheath calcification commenced ~1400–1300 Ma in response to lower pH buffering of seawater when p_{CO2} = 33 PAL, generating abundant carbonate mud (A). (2) As p_{CO2} declined further, sheath calcification increased to the point that partially calcified filaments could be preserved (B), although these may represent post-mortem rather than *in vivo* calcification (see Discussion: 'Calcification in *Girvanella*'). Note that both p_{CO2} level (33–10 PAL) and age (~1083–779 Myr) are poorly constrained. (3) Sheath impregnation, indicated by *Girvanella*, reflects p_{CO2} = 10 PAL that triggered cyanobacterial CCMs 750–700 Ma. CCMs were also induced in cyanobacterial picoplankton, increasing biogenic whiting production. (4) During 'Snowball' glacial conditions ~700–570 Ma, sheath calcified cyanobacteria were scarce. This reflects both reduction in CCM development in response to low temperatures that favoured diffusive entry of CO_2 into cells, and also lower seawater saturation state resulting from reduction in temperature and p_{CO2}. (5) At the Neoproterozoic–Cambrian transition, increases in temperature, p_{CO2} and calcium levels raised seawater saturation state, and increasing oxygen and temperature levels revived CCM development. Sheath calcification and whiting production developed extensively. Subsequent Phanerozoic patterns of cyanobacterial sheath calcification and whiting production were largely mediated by fluctuations in seawater saturation state and CCM induction; the latter related to interplay of ecological carbon limitation (in mats and blooms) and periods when atmospheric p_{CO2} levels were reduced. Sources for the 700–0 Myr p_{CO2} trend: see Fig. 4.

calcification (Merz, 1992) (Fig. 3). In addition to this biological influence, environmental factors also significantly determine whether cyanobacterial sheath calcification will occur. These include the degree of pH buffering (Arp *et al*., 2001) and the saturation state for carbonate minerals (Kempe & Kazmierczak, 1994) in the ambient water. All of these influences on cyanobacterial calcification – pH buffering, CCMs and carbonate saturation state – are related to p_{CO2}. Change in their relative importance through time as atmospheric CO_2 levels altered are therefore likely, and will have significantly affected the history of cyanobacterial calcification.

pH buffering

When solution pH is highly buffered, sheath pH may not be shifted sufficiently by photosynthesis to facilitate calcification (Arp *et al*., 2001). This should apply both in high p_{CO2} conditions with slightly acidic to near neutral seawater pH, as may have obtained in the mid-Proterozoic (Grotzinger & Kasting, 1993), and in low p_{CO2} conditions in alkaline waters, as in present-day soda lakes (Arp *et al*., 2001; p. 1703). Empirical and modelled estimates suggest falling CO_2 levels during much of the Proterozoic (Figs 4 and 5). Arp *et al*. (2001) inferred that when p_{CO2} levels fell to less than 10^{-2} atm (~1%, 33 PAL), the resulting lowered DIC concentrations would have permitted cyanobacterial sheath calcification. The influence of pH buffering on cyanobacterial sheath calcification is demonstrated by studies of soda lakes in which springs input calcium-rich water but where cyanobacteria do not exhibit sheath calcification (Arp *et al*., 1999a,b), even though they probably employ CCMs (G. Arp, pers. comm., 2006).

However, it is argued here that although pH buffering can exert an overriding influence on cyanobacterial sheath calcification, as in soda lakes, it had no observable influence on sheath calcification in Proterozoic seas because CCMs did not develop until p_{CO2} fell even further, to below ~10 PAL. This is based on the assumption (Merz, 1992) that CCMs are essential for well-developed sheath calcification. In this view, although elevated pH buffering (at p_{CO2} = 33 PAL) may have inhibited sheath calcification, fall in p_{CO2} to = 33 PAL would not in itself have resulted in calcification because CCMs would not have been induced while p_{CO2} remained above 10 PAL. Experimental studies (Badger *et al*., 2002) show that only when p_{CO2} was = 10 PAL would CCM induction have occurred, resulting in sheath calcification (see 'The Precambrian

Enigma' section). CCMs and high pH buffering can coexist in present-day soda lakes due to the chemistry of these highly alkaline lakes. However, pH buffering and cyanobacterial CCMs would not have coexisted in the Proterozoic marine environments since high pH buffering limits sheath calcification at p_{CO2} = 33 PAL, and CCMs are induced at = 10 PAL. From the mid-Proterozoic and throughout the Phanerozoic, therefore, even though p_{CO2} may at times have reached 15–25 PAL (Berner & Kothavala, 2001), there is no evidence that pH buffering in normal marine environments ever exceeded the level of 10^{-2} atm (~1% and 33 PAL) inferred by Arp *et al.* (2001) to inhibit sheath calcification.

CO_2 concentrating mechanisms

Cyanobacteria are not known to actively transport CO_2 through the plasmalemma, but they transport HCO_3^-, concentrating it within the cells at levels up to a thousand times higher than in the external medium (Giordano *et al.*, 2005; p. 106). Since it is expected that geochemical cycling of terrestrial weathering products limits long-term fluctuation in seawater pH even under high p_{CO2} conditions (Grotzinger & Kasting, 1993), HCO_3^- should have been the dominant DIC species in seawater during the Proterozoic. The ability of cyanobacteria to actively transport HCO_3^- may therefore reflect seawater conditions as they evolved CCMs. This development of CCMs would have occurred when p_{CO2} was reduced to ~0.4% (~10 PAL), this being the approximate level at which CCMs are experimentally induced in present-day cyanobacteria (Badger *et al.*, 2002; p. 169). The appearance of *in vivo* sheath calcified cyanobacteria is therefore suggested here to indicate that p_{CO2} levels had fallen to ~0.4%, with the earliest currently known confirmed occurrence being in the ~750- to 700-Myr-old Draken Group (Figs 4 and 5). Previously, Badger *et al.* (2002) suggested that CCMs appeared in algae and cyanobacteria sometime during the Late Devonian–Late Permian (~380–265 Ma) in response to changes then in atmospheric p_{CO2} and p_{O2} levels. As pointed out here, similar changes in atmospheric composition are likely to have occurred in the Proterozoic, suggesting that CCM development began then, rather than in the Late Palaeozoic. If this is correct, then cyanobacteria possessed CCMs throughout the Palaeozoic but would only have induced them when atmospheric p_{CO2} was below ~10 PAL or under carbon-limited conditions such as planktic blooms or benthic microbial mat. When p_{CO2} declined in the Late Devonian-Early Carboniferous (Berner & Kothavala, 2001) it is reasonable to expect that CCMs were generally re-induced, possibly with significant consequences for carbonate sedimentation (Riding, 2006), but – in contrast to Badger *et al.*'s (2002) inference – this was not their first development in cyanobacteria.

Seawater carbonate saturation state

Cyanobacterial calcification is not obligate and is dependent on external factors (Pentecost & Riding, 1986) that include elevated saturation state for $CaCO_3$ minerals (Kempe & Kazmierczak, 1994; Merz-Preiß & Riding, 1999). It is inferred here that, provided pH buffering was not too high and CCMs were induced, fluctuations in carbonate saturation state will have significantly affected secular patterns of cyanobacterial calcification.

Fluctuations in p_{CO2} are an important influence on carbonate saturation state, and this is seen in calculated values of aragonite and calcite saturation state for the Phanerozoic (Riding & Liang, 2005b; fig. 5). The response of seawater chemistry to changes in atmospheric p_{CO2} depends on the length of time interval considered. In the short term, if alkalinity remains unchanged, doubling p_{CO2} should lower oceanic pH by 0.28 units (Stumm & Morgan, 1996) and result in decreases in carbonate ion concentration and saturation state for $CaCO_3$ minerals. This effect has been emphasized with regard to anthropogenic CO_2 release (e.g. Andersson *et al.*, 2003) and its possible implications for biocalcification (e.g. Langdon *et al.*, 2000; Marubini *et al.*, 2003). However, in the long term – over million year timescales – the effect of p_{CO2} increase is expected to be quite different as geochemical feedback mechanisms come into operation, and CO_2 raises global temperatures and stimulates terrestrial weathering. Silicate weathering removes CO_2 and releases Ca^{2+} and HCO_3^- via riverine input to the oceans, raising seawater alkalinity and carbonate saturation state and promoting precipitation of minerals such as aragonite, calcite and dolomite. Such CO_2 uptake by calcium and magnesium silicate weathering, followed by precipitation of calcium and magnesium carbonates, has been termed the Ebelmen-Urey reaction (Berner & Kothavala, 2001; p. 202) (see Ebelmen, 1845; Urey, 1952). An important outcome is the sequestration of atmospheric CO_2 in sedimentary carbonate rocks (Stumm & Morgan, 1996). Thus, over the geological timescales considered here, higher levels of atmospheric p_{CO2} are expected to increase oceanic DIC and, with adequate Ca^{2+} input (e.g. from rivers and weathering of basic igneous rocks at Mid-Ocean spreading centres), raise seawater saturation state for $CaCO_3$ minerals (Riding & Liang, 2005a). In the Phanerozoic this is reflected by increased abundance of marine limestones (Bosscher & Schlager, 1993) broadly at times when p_{CO2} (Berner & Kothavala, 2001) was elevated (Riding & Liang, 2005a). At a more detailed level, marine cyanobacterial calcification during the Phanerozoic also broadly appears to correspond positively with seawater saturation state (Riding & Liang, 2005b).

Information regarding Proterozoic patterns of variation in marine carbonate saturation state is scarce. The presence of thick Mesoproterozoic to early Neoproterozoic carbonate sequences precipitated without the intervention of skeletal calcifiers attests to elevated seawater saturation state (Grotzinger, 1989) during the intervals when sheath calcification first appears, e.g. in the Draken Group and possibly in the Little Dal Group (Fig. 5). Carbonate saturation levels may have fluctuated considerably during 'Snowball' glaciation intervals

(Hoffman & Schrag, 2002), and are likely to have risen sharply at the Proterozoic-Palaeozoic transition (see 'Cyanobacterial calcification and the Proterozoic–Cambrian transition' section).

It is suggested here that two main influences determining the episodic Phanerozoic history of marine cyanobacterial calcification (Riding, 1982, 1992, 1994) are likely to have been seawater chemical conditions favouring $CaCO_3$ precipitation (Riding & Liang, 2005a,b) and CCM expression. Nonetheless, additional intrinsic and extrinsic factors cannot be ruled out and require further study. These include, for example, effects of cyanobacterial sheath structure and composition on calcification (Pentecost & Riding, 1986), and concentrations of inhibitors such as fulvic acids, phosphate, etc., that influence the kinetics of carbonate precipitation.

The occurrence of cyanobacterial sheath calcification from Cambrian–Devonian (Arp *et al.*, 2001; fig. 3d) indicates that CCMs continued to be induced even when p_{CO2} is likely to have exceeded ~10 PAL (Berner & Kothavala, 2001), possibly this reflects carbon limitation in microbial mats. Broad correspondence between peaks of calculated calcite saturation state and peaks of calcified cyanobacterial abundance from Cambrian–Jurassic (Riding & Liang, 2005b; fig. 5) suggests the continued influence of saturation state on calcification, but the additional effect of p_{CO2} (on CCMs) may be seen in the Early Carboniferous where p_{CO2} decline could have stimulated CCM induction that increased calcification in both cyanobacteria and dasycladalean chlorophytes (Riding, 2006).

During the Late Cretaceous, despite high calculated carbonate saturation state, planktic calcifiers could have been responsible for reducing saturation state sufficiently to inhibit cyanobacterial calcification (Riding & Liang, 2005b; p. 113) and this effect may have continued into the Palaeogene. Since the Eocene, under the influence of low levels of Ca ions and p_{CO2}, seawater carbonate saturation appears to have been reduced to an all time Phanerozoic low (Riding & Liang, 2005b; fig. 5a). It has long been noted that cyanobacterial sheath calcification is scarce to the point of absence in present-day marine environments (Riding, 1982; Pentecost & Riding, 1986; Merz, 1992). If, as suggested here, cyanobacterial calcification is dependent on low pH buffering, induction of CCMs, and elevated carbonate saturation state, then absence of any one of these could prevent sheath calcification. Since pH buffering in seawater is expected to inhibit sheath calcification only when p_{CO2} is elevated (above ~33 PAL) (Arp *et al.*, 2001) this is not expected to have been a factor limiting marine calcification during the Phanerozoic. Many present-day marine cyanobacteria and algae possess CCMs (e.g. Huertas *et al.*, 2002). Although confirmation is still required, it is reasonable to expect that CCMs are also present in present-day marine filamentous cyanobacteria similar to those capable of sheath calcification in freshwater (see 'Cyanobacterial Calcification' section). If this is correct then the most likely obstacle to marine cyanobacterial calcification at the present day is the relatively low saturation state for $CaCO_3$ minerals (Riding, 2000; p. 205).

CCM expression, secondary endosymbioses, and algal calcification

In addition to a primary endosymbiotic origin of algal chloroplasts from cyanobacteria that gave rise to chlorophytes, rhodophytes and glaucophytes, there is evidence for secondary (and tertiary) endosymbiotic events where red or green algae were engulfed by protists, giving rise to further algal groups such as cryptophytes, haptophytes, stramenopiles, apicomplexa and dinoflagellates (McFadden, 2001; Bhattacharya *et al.*, 2004). The timing of such subsequent endosymbiotic events is debated (Raven, 1997a). Lee & Krugens (2000) postulated that since secondary endosymbiont algae were able to use inorganic carbon more efficiently, because their chloroplasts occupy an acidic vacuole, they were favoured as a result of CO_2 decline in the Late Palaeozoic. Proterozoic CO_2 decline would have had a similar effect. Cavalier-Smith (2000) suggested that major endosymbiosis occurred ~600 Ma 'shortly after (perhaps even stimulated by)' recovery from glaciation. Using DNA sequences and molecular time estimates, Yoon *et al.* (2002) inferred that cryptophyte, haptophyte, and stramenopile algae share a common plastid that arose from a secondary endosymbiotic event involving a red alga, ~1260 Ma. Given that molecular approaches can overestimate evolutionary divergences (Rodriguez-Trelles *et al.*, 2002), this event could have been connected with eukaryote diversification near the Mesoproterozoic–Neoproterozoic boundary (1000 Ma) (Knoll, 1994). It may therefore be possible to link secondary endosymbioses, algal CCM development, and eukaryote radiations to changes in atmospheric composition that occurred in the latter part of the Proterozoic.

The evolutionary origin of CCMs in cyanobacteria during the Neoproterozoic proposed here is at least 300 Myr earlier than suggested by Badger *et al.* (2002). But since it is likely that cyanobacteria were extant considerably earlier (Schopf & Klein, 1992), it appears that CCM development was nonetheless a feature of the latter part of cyanobacterial history. Consequently, a polyphyletic origin for cyanobacterial and algal CCMs (Raven, 1997a; Badger *et al.*, 2002) remains likely, since these major groups diverged well before the Neoproterozoic, and algae would have lacked CCM genes in common with cyanobacteria (Badger & Price, 2003). It is speculated here that CCM development in green and red algae may have been linked to calcification and diversification of groups in the Phanerozoic – for example Corallinaceae, Dasycladaceae, and Halimedaceae – when suitable body plans evolved. Following Neoproterozoic CCM acquisition, cyanobacterial calcification was widespread during the Palaeozoic at times when CO_2 is estimated to have been well above 15 PAL (p_{CO2} = 0.54%) (Berner & Kothavala, 2001). Once acquired, therefore, it appears that cyanobacterial CCMs continued to be expressed even when CO_2 levels increased substantially. This could especially reflect benthic microbial mat and planktic bloom conditions where carbon can become a limiting factor in

photosynthesis (see Raven, 1997b; Badger *et al.*, 2002; p. 169). High atmospheric p_{O2}, inferred to have been = 15% throughout the Phanerozoic (Berner, 2001), may also have contributed to continued CCM expression.

CO_2 concentrating mechanisms and whitings

'Whitings' are ephemeral milk-white patches in freshwater calcareous lakes and shallow tropical seas formed by dense masses of suspended small $CaCO_3$ crystals (Cloud, 1962). Varieties of the cyanobacterium *Synechococcus* are implicated in whiting formation in freshwater calcareous oligotrophic lakes (Thompson & Ferris, 1990; Dittrich *et al.*, 2004; Lee *et al.*, 2004). *Synechococcus* is a minute unicellular planktic cyanobacterium. It can be classed as picoplankton or femtoplankton: plankton with cell size ranges of 0.2–2 and 0.02–0.2 μm, respectively (Sieburth *et al.*, 1978). In contrast to relatively large and distinct calcified fossils that result from sheath calcification, such as the *Girvanella* tubes of filamentous cyanobacteria, $CaCO_3$ precipitates associated with *Synechococcus* are isolated crystals on or adjacent to the cells (Thompson & Ferris, 1990; Thompson, 2000). These crystals are sedimented through the water column to accumulate either individually, or as poorly structured aggregates along with organic cells, on lake beds.

Synechococcus and similar unicellular picoplanktic cyanobacteria are also widespread in the open ocean (Bryant, 2003) and in nearshore marine environments, forming blooms in Florida Bay for example (Phlips *et al.*, 1999). There are marine strains of *Synechococcus* that calcify under experimental conditions (Lee *et al.*, 2004) and the genus includes strains that are β-cyanobacteria with CCMs (Badger & Price, 2003). Bloom-forming picoplankton benefit from efficient CCMs because DIC availability can limit photosynthesis under bloom conditions (Rost *et al.*, 2003). If present-day marine whitings are water column precipitates then they must be a major source of carbonate mud in environments such as Great Bahama Bank. Robbins *et al.* (1997) found that at any one time during a 28-year period (1965–93), whitings occupied 35–200 km^2 of an area of Great Bahama Bank west of Andros Island. They calculated that, if precipitated in the water column, this material would account for >40% of Holocene bank top and periplatform carbonate mud 'accumulated on the west side of Great Bahama Bank'. By extrapolation, therefore, whiting precipitation could account for the large volumes of carbonate mud observed in similar ancient platform settings throughout the Phanerozoic.

However, the question whether present-day marine whitings are due to phytoplankton-induced precipitation in the water column, as in lakes, or represent re-suspension of mud, has stimulated vigorous debate (Cloud, 1962; Broecker & Takahashi, 1966; Shinn *et al.*, 1989; Morse & Mackenzie, 1990; Robbins & Blackwelder, 1992; Milliman *et al.*, 1993; Robbins *et al.*, 1997; Broecker *et al.*, 2000, 2001; Morse *et al.*, 2003). In freshwater lakes, low pH buffering capacity permits $CaCO_3$ precipitation in response to photosynthetic removal of CO_2 and HCO_3^- from water already saturated with respect to $CaCO_3$ minerals. In present-day seawater, on the other hand, buffering limits pH fluctuation, and lack of chemical differences between whiting water and nearby clear water suggests that Great Bahama Bank whitings are not due to water column precipitation (Broecker & Takahashi, 1966; Morse *et al.*, 1984; Broecker *et al.*, 2000). Significantly, whiting $CaCO_3$ has a $^{14}C/C$ ratio that differs from that of inorganic carbon in the whiting water but is similar to that of the seafloor sediment, and in locations such as the Bahama Bank, where whitings occur frequently, the saturation state is too low for pseudo-homogeneous precipitation of $CaCO_3$ (Broecker *et al.*, 2001; p. 591; Morse *et al.*, 2003). Although water column precipitation has not been ruled out in areas where seawater saturation state is higher than on the Bahama Banks, such as parts of the Persian Gulf (Morse & He, 1993), it may prove to be the case that present-day seawater saturation state is generally too low to permit $CaCO_3$ nucleation even in the vicinity of picoplankton with well-developed CCMs. Marine whitings have most commonly been reported in waters that are sufficiently shallow for them to represent carbonate mud re-suspended from the seafloor and Broecker *et al.* (2000) concluded that re-suspension of sediment is the dominant process involved in marine whitings on the Bahama Banks.

Nonetheless, these observations in present-day seas do not preclude phytoplankton-stimulated precipitation of whitings in marine environments in the geological past environment if carbonate saturation state were sufficiently high. Seawater saturation state has fluctuated through time, in response to changes in seawater chemistry (Riding & Liang, 2005a,b). At times when saturation state was sufficiently high, biogenic whitings may have been widespread and common in marine environments. This could apply especially during some parts of the Mesozoic, Palaeozoic and Proterozoic, and it has been widely supposed that a significant proportion of Proterozoic carbonate mud may have derived from whitings stimulated by photosynthetic CO_2 uptake by photosynthetic phytoplankton (Grotzinger, 1989, 1990; Knoll & Swett, 1990; p. 123; Fairchild *et al.*, 1991; Sherman *et al.*, 2000; Shields, 2005).

Planktic cyanobacteria involved in Proterozoic whiting production would, like benthic forms, have been prone to influence by p_{CO2} levels and CCM development. It can be speculated that lowering of atmospheric CO_2 levels at first reduced pH buffering sufficiently for picoplanktic whitings to be initiated, and then induced CCMs in the same picoplankton, further intensifying whiting precipitation. The protective mucilaginous sheath that envelopes benthic calcified cyanobacteria provides a diffusion limited site that enhances the pH rise resulting from carbon uptake (Fig. 3). In picoplankton such as *Synechococcus* a sheath is lacking, and calcification is instead localized on a paracrystalline surface layer that provides a binding site and this surface layer can be shed, producing whiting

crystals that are deposited from suspension. (Thompson, 2000; p. 253). It is possible therefore that the 33 PAL p_{CO2} level inferred to have induced partial sheath impregnation in benthic forms also initiated incipient whiting production by picoplankton. Within plankton blooms, photosynthetic uptake can significantly deplete p_{CO2} (Riebesell *et al.*, 1993; Rost *et al.*, 2003) and it is likely that selective pressure for picoplankton to induce CCMs first developed under bloom conditions.

Through much of the Proterozoic, carbonate mud abundance appears to exhibit a first-order trend of increase with decreasing age. Absence of carbonate mud in the Late Archaean (Sumner & Grotzinger, 2004) and scarcity in the Palaeoproterozoic (e.g. Kah & Grotzinger, 1992; Winefield, 2000) was followed by increase that led to transition from cement-rimmed margins to muddy carbonate ramps ~1400–1300 Ma (Sherman *et al.*, 2000; p. 290). In early Neoproterozoic platforms, carbonate mud is a major original component of deeper subtidal facies (e.g. Herrington & Fairchild, 1989; Knoll & Swett, 1990; Clough & Goldhammer, 2000; p. 225). It is tentatively proposed here that this secular pattern reflects increase in photosynthetically induced whiting production, as follows (Fig. 5): (i) Prior to ~1400 Ma, whiting precipitation was limited, possibly by kinetic inhibitors to carbonate precipitation (Sumner & Grotzinger, 2004) and/or by elevated p_{CO2} that buffered pH changes near picoplankton cells. (ii) Transition to carbonate mud-dominated platforms suggested ~1400–1300 Myr (Sherman *et al.*, 2000) reflects inception of incipient whiting precipitation at p_{CO2} = 33 PAL. This 'water column factory' transformed carbonate platform sedimentation by creating extensive micrite-rich subtidal deposits in which molar tooth facies developed (Sherman *et al.*, 2000; p. 290). (iii) When p_{CO2} fell to = 10 PAL, possibly early in the early Neoproterozoic, CCM development was triggered in picoplankton, further stimulating whiting production, in addition to facilitating sheath impregnation in cyanobacteria.

In this view, cyanobacterially calcification induced as DIC declined resulted initially in nucleation of isolated crystals close to the cells of both benthic and planktic forms. In ensheathed benthic filaments, this incipient weak calcification produced mutually unattached crystallites that disaggregated upon sheath decay and thereby contributed carbonate mud sediment. Crystallites also formed adjacent to planktic cells, creating whiting micrite that was deposited from suspension. Both these benthic and planktic sources produced carbonate mud that was morphologically indistinguishable and that in combination significantly increased micrite sedimentation. It is suggested here that the volumetric contribution of whiting micrite is likely to have substantially outweighed that of weakly calcified benthic filaments, because plankton occupied volumes of near-surface water that were much larger than the habitats of benthic cyanobacteria. This extensive picoplankton-induced micrite production on carbonate shelves that may have commenced ~1400–1300 Ma is likely to have continued to have exerted a major influence on carbonate sedimentation for much of subsequent geological history, so long as carbonate saturation state was sufficiently elevated. The intensity of these biogenic whitings would have been further enhanced whenever p_{CO2} levels fell below ~10 PAL and induced CCMs. If this is correct, biogenic whitings could account for a substantial part of the carbonate mud that accumulated on shallow shelves between the late Mesoproterozoic and Mesozoic. Only in the Cenozoic, as seawater carbonate saturation levels declined, did this process slow and, perhaps, cease.

SUMMARY AND CONCLUSIONS

Arp *et al.* (2001) reasoned that falling DIC levels in the Proterozoic permitted cyanobacterial sheath calcification by reducing the pH buffering capacity of seawater. It is proposed here that the development of CCMs – which actively promote sheath calcification (Merz, 1992) – was also important in determining the onset of *in vivo* cyanobacterial calcification in the Proterozoic. Given reducing pH buffering capacity and elevated saturation state, which is an additional prerequisite for cyanobacterial calcification (Kempe & Kazmierczak, 1994), it is inferred here that the first appearance of *in vivo* sheath calcified cyanobacteria in the Proterozoic reflects changes in atmospheric composition – decrease in p_{CO2} and increase in p_{O2} – that were responsible for inducing CCMs. Cyanobacterial CCMs enhance photosynthetic carbon fixation by promoting cellular uptake of HCO_3^- and its conversion to CO_2 (Fig. 3). These processes increase extracellular pH, favouring sheath calcification and whiting nucleation adjacent to cells. Based on experiments with present-day cyanobacteria (Badger *et al.*, 2002; p. 169), the aqueous CO_2 level in equilibrium with <0.4% CO_2 in the atmosphere is taken as the threshold for CCM development in cyanobacteria. The oldest confirmed report of *in vivo* sheath calcified cyanobacteria, currently *Girvanella* 750–700 Ma (Knoll *et al.*, 1993), is therefore inferred to indicate a p_{CO2} level = 0.4% (~10 PAL) by this time. This is consistent with published palaeo-atmosphere estimates (Fig. 4). It is proposed that, prior to this, biogenic whitings were stimulated by fall in p_{CO2} below ~1% (33 PAL) that resulted in lower DIC concentrations, reducing pH buffering sufficiently for isolated $CaCO_3$ crystals to nucleate adjacent to cells in cyanobacterial plankton blooms. The biogenic mud produced by these whitings began to dominate carbonate platforms ~1400–1300 Ma.

Assuming that benthic cyanobacteria were abundant during the Palaeoproterozoic and Mesoproterozoic, and that seawater saturation state was high with respect to $CaCO_3$ minerals (Knoll *et al.*, 1993; Riding, 1994), the following reading of the Proterozoic record of atmospheric change, cyanobacterial sheath calcification and carbonate sediment production is proposed (Fig. 5): (i) The scant record of sheath calcification during the early Proterozoic (Riding, 1994) reflects pH buffering due to p_{CO2} levels >33 PAL, as suggested by Arp *et al.*

(2001), and possibly also the presence of kinetic inhibitors to carbonate precipitation (Sumner & Grotzinger, 2004). These effects also hindered photosynthetically induced whiting production. (ii) Expansion of carbonate mud-dominated platforms, reported ~1400–1300 Ma (Sherman *et al.*, 2000), reflects incipient biogenic whiting precipitation that transformed carbonate sedimentation and provided a substrate in which molar tooth structure extensively formed. This development is tentatively taken to indicate reduction in p_{CO2} to = 33 PAL (see Arp *et al.* (2001). At this point, *in vivo* sheath calcification was insufficient to produce generally preservable calcified filaments, but contributed to carbonate mud production. (iii) As p_{CO2} decline continued, ~1300–750 Ma, biogenic whiting production and filament calcification increased. Partially calcified filaments were locally preserved, as in the <1083 to >779 Myr Little Dal reef (Turner *et al.*, 1993, 2000a,b), although these mainly appear to reflect post-mortem rather than *in vivo* calcification. (iv) Occurrence of *Girvanella*, 750–700 Ma (Knoll *et al.*, 1993), reflects sheath impregnation in benthic cyanobacteria resulting from CCM inception due to further lowering of p_{CO2} to = 10 PAL. CCMs also developed at this time in picoplankton, further increasing whiting production. (v) Cyanobacterial CCM development was temporarily slowed by 'Snowball' glaciations that commenced ~700 Ma. Lower temperatures favoured passive diffusion of CO_2 into cyanobacterial cells, reducing the need for CCMs. At the same time, cooling and p_{CO2} decrease lowered saturation states for $CaCO_3$ minerals, also reducing sheath calcification and whiting production. Decrease in saturation state has also been inferred to account for reduction in incidence of molar tooth structure ~750 Ma (Shields, 2002). (vi) Post ~570 Ma, in the aftermath of glaciations, increases in temperature and p_{O2} reimposed conditions for CCM development. At the same time, carbonate saturation state rose with temperature, Ca^{2+} and p_{CO2} levels. These changes resulted in CCM-induced *in vivo* sheath calcification among diverse cyanobacteria early in the Cambrian. Continued p_{CO2} increase would have reduced the need for CCMs, except in benthic microbial mats and phytoplankton blooms where carbon availability was a factor limiting growth. Adoption of erect growth by calcified cyanobacteria, which resulted in dendrolite formation in Early Palaeozoic reefs, may have been an ecological response that improved diffusive acquisition of DIC and removal of O_2 under mat conditions.

This interpretation augments explanations for several features of the late Archaean to Early Cambrian carbonate rock record: (i) Late Archaean to early Neoproterozoic increase in carbonate mud production, (ii) significance of the relatively late Proterozoic appearance of *in vivo* sheath calcified cyanobacteria such as *Girvanella*, (iii) scarcity of calcified cyanobacteria during 'Snowball' glaciations, (iv) Early Cambrian increase in abundance and diversity of calcified cyanobacteria, and (v) rise in dendrolite and thrombolite fabrics that further transformed Early Palaeozoic reefs.

The timing of cyanobacterial CCM development, proposed here on the basis of *in vivo* sheath calcified cyanobacteria 750–700 Ma, is at least 300 Myr earlier than previously suggested (Badger *et al.*, 2002; p. 169). The suggested trend of maximum p_{CO2} for the interval 1400–700 Ma, based on its relationship with cyanobacterial calcification, shows reduction to p_{CO2} 33 PAL ~1400–1300 Ma, and to p_{CO2} 10 PAL ~750–700 Ma (Fig. 5). These values lie within the broad range of published Mesoproterozoic–Neoproterozoic p_{CO2} estimates (Fig. 4), but at the same time suggest that p_{CO2} declined to ~0.4% (10 PAL) relatively late (750–700 Ma), only shortly prior to Sturtian glaciation.

Cyanobacterial biocalcification reflects changes in seawater chemistry and atmospheric composition, as well as in the structure and physiology of these aquatic microbes. Further investigations of the record of calcified cyanobacteria and their sediments in the Proterozoic and Phanerozoic, together with studies of CCMs in present-day calcified cyanobacteria, are needed to develop the concepts outlined here and more accurately specify the environmental thresholds and timings involved.

ACKNOWLEDGEMENTS

Murray Badger, Julie Bartley, Ian Fairchild, James Kasting, Allan Pentecost, John Raven, Dawn Sumner and several anonymous reviewers read drafts of this article. I am very grateful for all these constructive and stimulating comments. Special thanks go to Liyuan Liang and John Raven for their patient and helpful responses to barrages of queries.

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