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C

CALCAREOUS ALGAE

The term "calcareous algae" refers to various kinds of benthic and planktonic algae whose thalli contain biochemically precipitated calcium carbonate ($CaCO_3$) as skeletal material (Wray, 1977; Braga and Riding, 2005). Precipitation of $CaCO_3$ (as calcite and/or aragonite) may occur within or on the algal bodies. The term may also include mechanically accreted deposits of calcium carbonate caused by algae, usually as an interaction of biological and physical processes. Calcareous algae are a highly artificial group that constitutes calcifying members of the Chlorophyta (green algae), Rhodophyta (red algae), and Phaeophyta (brown algae) and is sometimes also used for Cyanobacteria. At present, calcareous algae are one of the most important reef builders (see "*Carbonate Environments*"). For a detailed reading, please refer to "*Algae (Eukaryotic)*."

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CALCIFICATION

See entries "*Animal Biocalcification, Evolution*," "*Biofilms and Fossilization*," "*Calcified Cyanobacteria*," "*Calcite Precipitation, Microbially Induced*," "*Calcium Biogeochemistry*," "*Carbonate Environments*," "*Dolomite, Microbial*," "*Microbialites, Modern*," "*Microbialites, Stromatolites, and Thrombolites*," and "*Pedogenic Carbonates*."

CALCIFIED CYANOBACTERIA

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Definition

Cyanobacteria are alga-like bacteria that can perform oxygenic photosynthesis and nitrogen fixation (Whitton and Potts, 2000; Herrero and Flores, 2008). They have a long history and are diverse and widespread in marine, freshwater, and terrestrial environments at the present-day, where they are key primary producers in both microbial mat and planktic ecosystems. As the initiators of plastids, they have played a fundamental role in algal and plant evolution (Raven, 2002). Cyanobacteria occupy benthic substrates and can also drift in the water column. Their photosynthetic uptake of inorganic carbon can stimulate $CaCO_3$ precipitation. This calcification can produce filamentous microfossils in benthic mats that are preserved as stromatolites and thrombolites, and can also cause water column precipitation of carbonate mud that settles to lake and sea floors.

Introduction

However, cyanobacterial calcification is not obligatory and is directly dependent on environmental conditions. This accounts for apparent discrepancies between the geological ranges of organic-walled and calcified cyanobacterial fossils. Calcified cyanobacteria have not been recognized in marine sediments older than ~1200 Ma ago (Kah and Riding, 2007), whereas there is evidence that cyanobacteria appeared in the late Archaean or Palaeoproterozoic, in the range ~2900–2150 Ma ago (Cavalier-Smith et al., 2006; Hofmann, 1976). This mid-Proterozoic appearance of sheath-calcified cyanobacteria is thought to reflect the development of CO_2-concentrating

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mechanisms (CCMs) as atmospheric CO_2 levels declined (Riding, 2006). Calcified cyanobacterial fossils remained conspicuous components of marine stromatolites and thrombolites through much of the Neoproterozoic, Palaeozoic, and Mesozoic, but became vanishingly scarce in the Cenozoic, including present-day seas (Riding, 1982), probably due to decline in seawater saturation for $CaCO_3$ minerals (Riding, 1993, p. 514; 2000, p. 200; Kempe and Kazmierczak, 1994). Cyanobacterial calcification is thus a good example of "induced," as opposed to "controlled" biocalcification. Its close environmental dependence can be used to interpret changes in past conditions such as carbonate saturation state and the availability of inorganic carbon for photosynthesis. In addition to their sedimentological importance, calcified cyanobacteria can therefore assist in the reconstruction of seawater chemistry and atmospheric composition over long geological time scales.

Controls on calcification

The ability of cyanobacteria to grow and reproduce whether they are calcified or uncalcified illustrates the non-obligate nature of their calcification (Pentecost and Riding, 1986). Two factors that directly influence cyanobacterial calcification are the saturation state of ambient waters and the mechanism of photosynthetic uptake of inorganic carbon (Riding, 2006).

Carbonate saturation state: Cyanobacterial calcification requires waters in which $CaCO_3$ precipitation is thermodynamically favored (Pentecost, 1981; Kempe and Kazmierczak, 1994; Merz-Preiβ and Riding, 1999). It has been very common in marine environments at times since the Neoproterozoic, but these episodes are markedly episodic and can be interspersed by long periods when cyanobacterial calcification is scarce (Riding, 1992). Cyanobacterial sheath calcification has not been confidently recognized in present-day marine environments, and is rare to absent throughout the Cenozoic (Riding, 1982; Arp et al., 2001). In contrast, cyanobacterial calcification is locally well-developed in present-day calcareous streams and lakes, and is often significantly involved in the formation of tufa and oncoids (Golubic, 1973; Pedley, 1990; Pentecost, 2005). In streams, calcification reflects increased saturation state that results from warming and degassing of spring waters, especially in turbulent zones, together with the stimulus of photosynthetic carbon removal (Merz-Preiβ and Riding, 1999; Bissett et al., 2008). In lakes, precipitation is stimulated by seasonal warming as well as the activity of phytoplankton blooms that include cyanobacteria (Kelts et al., 1978; Thompson and Ferris, 1990). These present-day environments are vulnerable to pollutants such as agricultural fertilizers. Cyanobacterial calcification has declined over the past century in temperate climate hardwater streams and lakes of Europe and North America, largely in response to these anthropogenic changes (Pentecost, 2005, pp. 283–287), among which phosphate inhibition of $CaCO_3$ precipitation (Raistrick, 1949) may be important (Hägele et al., 2006).

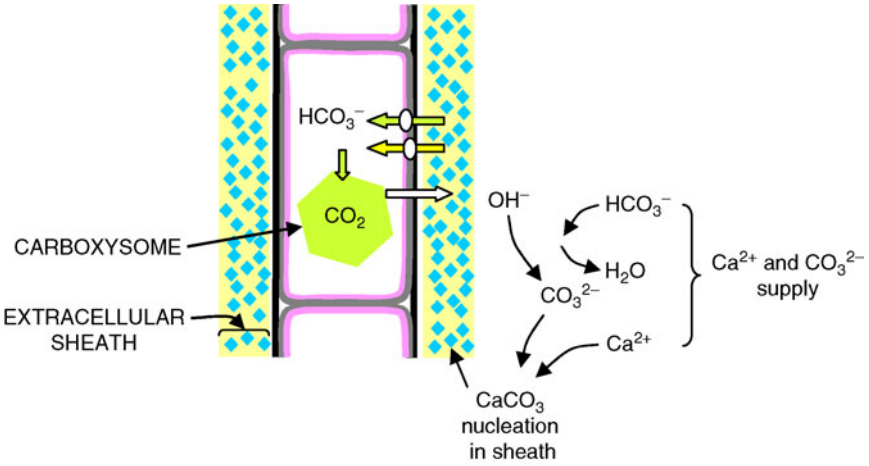
CO_2-concentrating mechanisms: Photosynthetic carbon uptake can directly influence cyanobacterial calcification. Diffusive entry of CO_2 into the cell may not significantly affect ambient pH, but active bicarbonate uptake increases pH near the cell (Miller and Colman, 1980) that promotes calcification (Thompson and Ferris, 1990). Bicarbonate (HCO_3^-) is actively transported into the cell and intracellularly converted to CO_2 for photosynthesis. These processes lead to increased pH in the immediate vicinity of the cell. Where ambient waters are sufficiently saturated for $CaCO_3$ minerals then this localized pH increase can trigger the nucleation of $CaCO_3$ crystallites on or near the cell surface or in the enveloping mucilaginous sheath (Figures 1 and 2):

$$2HCO_3^- + Ca^{2+} \rightarrow CH_2O + CaCO_3 + O_2$$

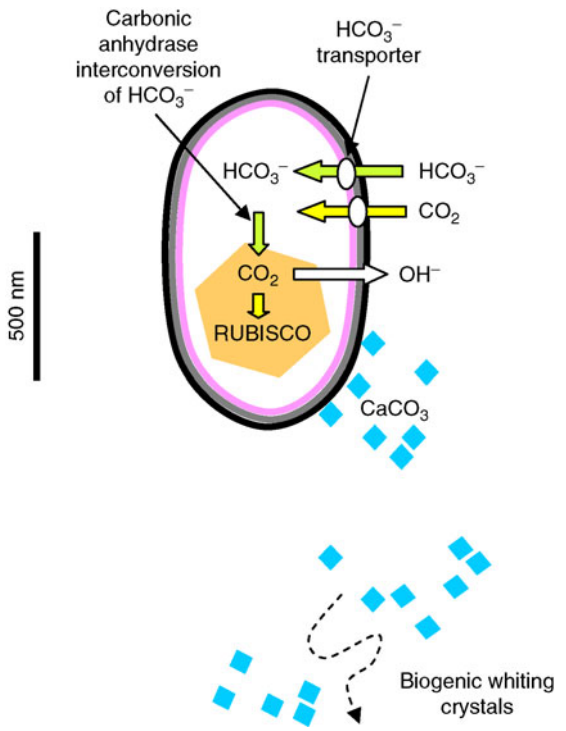
Active bicarbonate uptake and its conversion within the cell to CO_2 by carbonic anhydrase are adaptations to reduced availability of CO_2. They constitute CCMs (Kaplan and Reinhold, 1999). CCM induction can be triggered by localized carbon limitation, e.g., within microbial mats or phytoplankton blooms, and also by fall in global atmospheric CO_2 levels. Modeled estimates suggest that atmospheric CO_2 has fluctuated widely during the Phanerozoic, up to levels that are 25 or more times higher than present atmospheric level (PAL) (Berner and Kothavala, 2001). CCMs are well-developed in cyanobacteria (Kaplan et al., 1980; Giordano et al., 2005) and experiments suggest that they are induced when ambient CO_2 falls below a critical threshold that is roughly equivalent to 10 PAL (Badger et al., 2002). It therefore seems likely that CCM induction plays a significant role in cyanobacterial calcification (Thompson and Ferris, 1990; Merz, 1992), especially at times in the geological past when CO_2 levels have been below 10 PAL (Riding, 2006, p. 302).

Sites of calcification

Calcification in cyanobacteria is close, but external, to the cell. $CaCO_3$ crystals nucleate either within the protective mucilaginous sheath, or on or close to the cell surface (Thompson and Ferris, 1990; Merz, 1992). Sheath impregnation by crystallites (Figure 1) can produce coherent tubular and shrub-like calcified structures that preserve the sheath morphology and can be preserved as microfossils for hundreds of millions of years (Riding, 1991). In contrast, if isolated crystals form near the cell surface, they do not form a preservable shape but can be released as allochthonous particles ("whitings") (Figure 2). These can accumulate as masses of micron-size carbonate mud sediment on lake and sea floors and can also survive as ancient geological deposits. However, they are not known to possess features that distinguish them as



Calcified Cyanobacteria, Figure 1 Model of in vivo sheath calcification in a filamentous cyanobacterium related to CO_2-concentrating mechanism (CCM)-enhanced photosynthesis (based on information in Riding, 2006, Fig. 3). The CCMs involve active carbon transport into the cell and conversions that liberate OH^- ions. Calcification is stimulated by photosynthetic carbon uptake and OH^- release which elevates sheath pH. If ambient carbonate saturation is already elevated, with raised pH, extracellular HCO_3^- converts into CO_3^-, further increasing saturation state that promotes $CaCO_3$ nucleation in the sheath.

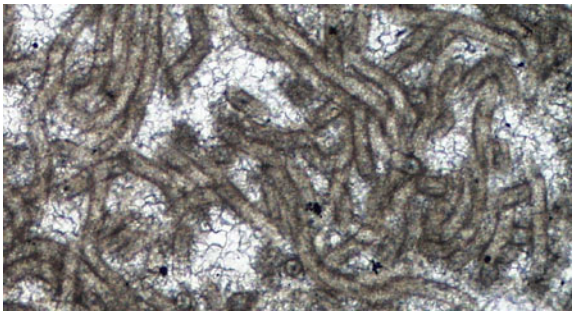


Calcified Cyanobacteria, Figure 2 Model of in vivo sheath calcification in a picoplanktic coccoid cyanobacterium related to CCM-enhanced photosynthesis (based on information in Riding, 2006, Fig. 3). The $CaCO_3$ nucleation (blue diamonds) occurs on and near the cell surface. The crystals can ultimately be sedimented to the lake or sea floor as carbonate mud.

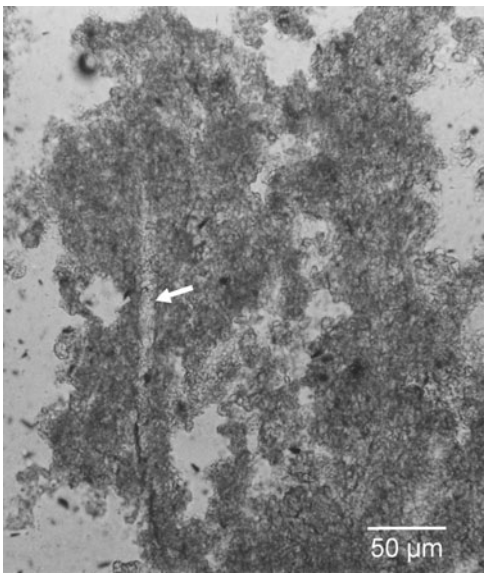
cyanobacterially induced precipitates, and cannot at present be differentiated from carbonate mud of other origins.

Sheath calcification: The protective mucilaginous sheath that envelops benthic calcified cyanobacteria provides a diffusion limited site that enhances the pH rise resulting from carbon uptake (Figures 3 and 4). The sheath is a structured form of EPS (Drews and Weckesser, 1982) providing support, stability, and protection against physical damage, dehydration, and grazers (Dudman, 1977). It can contain the pigment scytonemin that acts as a barrier to ultraviolet radiation (Garcia-Pichel and Castenholz, 1991; Proteau et al., 1993; Dillon and Castenholz, 1999), binds nutrients and metals (Yee et al., 2004), and facilitates gliding motility (Stal, 1995, p. 4; Hoiczyk, 1998). Sheath calcification can be partial or complete, and can be limited to the sheath interior (sheath impregnation) or form an external crust (sheath encrustation) (Riding, 1977). For example, it can occur as isolated crystals (Pentecost, 1987, Fig. 1d), form a crystalline network (e.g., Friedmann, 1979, Fig. 9), or create a relatively solid tube of closely juxtaposed crystals (e.g., Couté and Bury, 1988, pl. 2).

Although saturation state with respect to carbonate minerals and CCM induction appear to be key controls on cyanobacterial sheath calcification over geological timescales (Riding, 2006), differences in degree of calcification between different species/strains of cyanobacteria in the same environment also indicate taxonomic specificity for calcification (Golubic, 1973; Merz, 1992; Défarge et al., 1994). Further research is required to elucidate the extent to which such specificity may reflect differences in sheath structure and sheath development, CCM induction, or other factors.



Calcified Cyanobacteria, Figure 3 *Girvanella*, calcified cyanobacterial sheath, early mid-Ordovician, Lunnan, Tarim, China. Width of view 1 mm. Thin-section courtesy Jia-Song Fan.



Calcified Cyanobacteria, Figure 4 Thin-section of present-day oncoid microfabric showing calcified shrub-like sheath surrounding space left by the strand of cells (trichome, arrowed). The cyanobacterium is thought to be the oscillatoriacean *Schizothrix calcicola*, and the calcified sheath closely resembles the microfossil *Angulocellularia* (also *Angusticellularia*), which is locally common in Cambro-Ordovician reefs (Riding and Voronova, 1982). Squaw Island, Canandaigua Lake, New York State, USA.

In addition to in vivo sheath calcification, postmortem sheath degradation by heterotrophic bacteria can result in partial external calcification (Chafetz and Buczynski, 1992), although in culture experiments this may in part be related to the growth medium used (Arp et al., 2002). This incomplete and irregular calcification of decomposing sheaths contrasts with sheath impregnation that produces well-defined tubiform fossils such as *Girvanella* in which wall-thickness remains constant in individual specimens (Riding, 1977, 2006).

Biogenic whiting precipitation: In contrast with relatively large and distinct calcified fossils, such as *Girvanella*, that result from sheath calcification, $CaCO_3$ precipitates associated with coccoid cyanobacterial blooms are most noticeable as "whitings". These 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). Whiting is a descriptive term, and all whitings are not necessarily biogenic. In addition to the triggering effect of phytoplankton photosynthesis, they could reflect essentially abiogenic $CaCO_3$ crystal nucleation in the water column, and also – in very shallow water – bottom mud re-suspended by currents or fish (Shinn et al., 1989).

Biogenic cyanobacterial whitings are documented by studies of seasonal blooms of unicellular picoplanktic (cell size in range 0.2–2 µm) cyanobacteria, such as *Synechococcus*. These benefit from efficient CCMs (Badger and Price, 2003) where dissolved inorganic carbon (DIC) availability is limited, as under bloom conditions (Rost et al., 2003).Together with diatoms and other planktic algae, *Synechococcus* is implicated in stimulating biogenic whiting precipitation in present-day freshwater calcareous oligotrophic lakes (Thompson and Ferris, 1990; Dittrich et al., 2004; Lee et al., 2004). Since a sheath is lacking in picoplankton such as *Synechococcus*, calcification is instead localized on a paracrystalline surface layer that provides a binding site (Thompson, 2000, p. 253). This surface layer can be shed, producing biogenic whiting crystals that are deposited from suspension, either individually or as poorly structured aggregates along with organic cells, on lake beds.

In addition to lakes, picoplanktic cyanobacteria are widespread in the open ocean and in nearshore marine environments. They form blooms in Florida Bay, and marine strains of *Synechococcus* calcify under experimental conditions (Lee et al., 2004). There has been much debate concerning whether marine whitings in shallow tropical seas, such as the Bahama Banks, have a similar origin to those in temperate calcareous lakes, and could therefore potentially account for abundant lime mud production on ancient carbonate platforms. If marine whitings on the Bahama Banks are water column precipitates, then they would be important sources of carbonate mud and could be triggered by planktic cyanobacteria (Robbins and Blackwelder, 1992; Robbins et al., 1997). However, $CaCO_3$ precipitation in freshwater lakes is favored by low pH buffering, whereas in present-day seawater buffering limits pH fluctuation, thereby reducing the response to photosynthetic removal of CO_2 and HCO_3^-. Several studies have suggested that Great Bahama Bank whitings are not due to water column precipitation (Broecker and Takahashi, 1966; Morse et al., 1984; Broecker et al., 2000). For example, 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. In addition, the saturation state of Bahama Bank waters appears to be too low for pseudohomogeneous precipitation of $CaCO_3$

(Broecker et al., 2001, p. 591; Morse et al., 2003). Broecker et al. (2000) concluded that resuspension of sediment is the dominant process involved in marine whitings on the Bahama Banks. Further work is required to resolve this question, but present-day seawater saturation state in general may be too low to permit $CaCO_3$ nucleation even within blooms of picoplankton that are operating CCMs.

Nonetheless, biogenic whitings may have occurred under different conditions of seawater chemistry in the geological past, and could therefore have been important sources of fine-grained carbonate. Within plankton blooms, photosynthetic uptake can significantly deplete pCO_2 (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.

Fossil calcified cyanobacteria

Calcified cyanobacterial fossils have long been noticed in limestones, although they have often been confused with other organisms. Sheath calcified cyanobacteria are morphologically simple fossils, mainly with the appearance of shrub-like dendritic masses (Figure 4) and tangled or erect, sometimes radially arranged, tubes (Figure 3). Densely micritic branched filaments such as *Epiphyton*, and chambered clusters such as *Renalcis* have also often been regarded as possible calcified cyanobacteria. At the same time, because of their general lack of distinguishing features, many of these fossils have often also been compared with calcified green and red algae, and also with foraminifers and sponges. For example, when Nicholson and Etheridge (1878) named *Girvanella* they compared it with foraminifers, and it has subsequently variously been regarded as a calcareous sponge (Seely, 1885), green alga (Rothpletz, 1891), and red alga (Korde, 1973). Bornemann (1886) recognized its cyanobacterial nature, and Pollock (1918) identified it as a calcified sheath. Individual calcified cyanobacteria are normally microscopic, but they commonly form much larger aggregates that are significant components of stromatolites, oncoids, thrombolites, dendrolites, reef crusts, and freshwater tufa deposits that range up to decametric in size.

Three main morphological groups can be distinguished (Riding, 1991): tubes, dendritic shrubs and filaments, and hollow chambers.

Tubes: *Girvanella*, originally described from the Middle Ordovician of Scotland, is very simple: unbranched, often irregularly tangled, tubular filaments of uniform diameter, usually <50 microns, and a thin wall of even thickness (Figure 3). Similar tubes, but often organized into cable-like strands, include *Batinivia*, *Botominella*, *Cladogirvanella*, *Razumovskia*, and *Subtifloria*. *Obruchevella* is coiled. *Ortonella* was decribed from the Mississippian of England (Garwood, 1914) where it forms oncoids (spherical stromatolite nodules) and stromatolitic crusts. It consists of tubes similar in size to those of *Girvanella*, but distinguished by being erect and branched. Somewhat similar forms include *Bajanophyton*, *Bija*, *Botomaella*, *Cayeuxia*, and *Hedstroemia*. Pia (1927, pp. 36–40) recognized that very small tubiform fossils such as *Girvanella* and *Ortonella* were cyanobacteria when he placed them in a new group, the Porostromata.

Dendritic shrubs and filaments: *Angusticellularia* (also named *Angulocellularia*) described from the Cambrian of Siberia by Vologdin (1962) is a submillimetric vertically orientated and irregularly dendritic shrub-like mass of dense micrite (Figure 4). In contrast, narrow branched micritic filaments, usually not tubiform but in some cases with light-colored transverse bands, comprise a group that includes *Epiphyton*, originally described from the Cambrian of Sardinia by Bornemann (1886), and among others, *Epiphytonoides*, *Gordonophyton*, and *Tubomorphophyton*.

Hollow chambers: *Renalcis*, described from the Cambrian of southern Siberia by Vologdin (1932), is a hollow thick-walled chambered microfossil that typically forms irregular submillimetric clusters. Broadly similar fossils, such as *Izhella* and *Shuguria*, are distinguished by wall thickness and number of chambers. Some form millimetric dendritic growths. *Chabakovia* filaments consist of thin-walled chambers. In contrast, *Gemma* and *Tarthina* have few chambers with very thick walls.

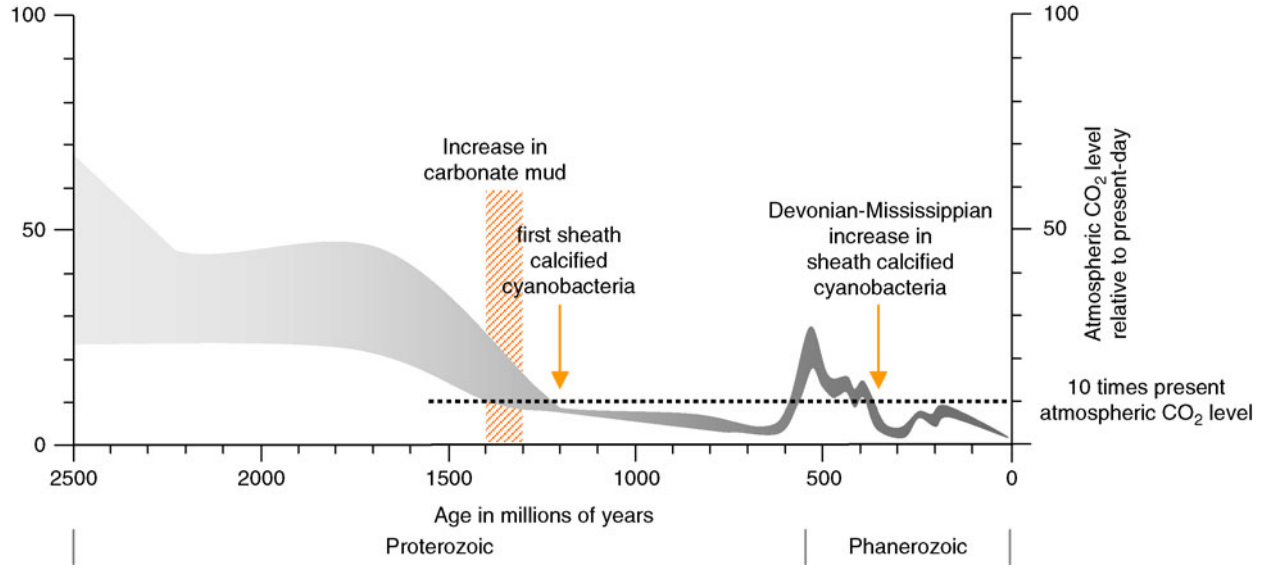
There is considerable mingling of characters among some of these generally simply organized fossils that can make them difficult to distinguish within these broad groups (Pratt, 1984; Riding and Voronova, 1985; Woo et al., 2008). Dense filaments and chambered forms are much more problematic, whereas tubiform and shrub-like forms can often be compared with present-day sheath calcified cyanobacteria. These include sedimentologically important Cambrian and late Devonian fossils such as *Epiphyton* and *Renalcis* that have some resemblances to cyanobacteria but are not identical to modern examples, and are generally referred to as calcimicrobes. Some *Epiphyton* closely resemble red algae (Luchinina and Terleev, 2008).

Proterozoic record and secular controls

The possibilities that marine carbonate saturation state and changes in atmospheric CO_2 level could be reflected in the geological record of cyanobacterial calcified microfossils and carbonate mud (Riding, 2006, p. 309) focuses attention on the mid-Proterozoic interval when calcified sheaths first appeared (Kah and Riding, 2007) and carbonate mud became abundant (Sherman et al., 2000, p. 290) (Figure 5).

CCM induction

Badger et al. (2002) suggested that cyanobacterial CCMs developed in the late Palaeozoic as CO_2 declined and O_2 increased. However, both modeling and palaeosol proxies (Kasting, 1987; Sheldon, 2006) suggest that similar decline in CO_2 occurred in the mid-Proterozoic. It can therefore be suggested that the Mesoporoterozic appearance of calcified sheath microfossils reflects development of CCMs as CO_2 fell below a critical threshold that may



Calcified Cyanobacteria, Figure 5 Increase in marine carbonate mud accumulation ~1400–1300 Ma ago (Sherman et al., 2000) and first appearance of sheath-calcified cyanobacteria ~1200 Ma ago (Kah and Riding, 2007) compared with decline in estimated atmospheric CO_2 values. It is suggested that decline in CO_2 to ~10× present atmospheric level favored development of CCMs that promoted cyanobacterial sheath calcification and whiting production (Riding, 2006). Incorporation of calcified filaments in microbial carbonates gave rise to calcified microbe thrombolites and dendrolites. Inferred Proterozoic CO_2 trend based on Sheldon (2006), Kah and Riding (2007), Hyde et al. (2000), and Ridgwell et al. (2003). Phanerozoic CO_2 trend from Berner and Kothavala (2001, Fig. 13). Threshold for CCMs based on Badger et al. (2002). Decline in CO_2 level below 10× present-level was repeated ~350 Ma ago and coincides with marked Devonian-Mississippian increase in calcified cyanobacteria (see Arp et al., 2001, Figs. 3d and 8b).

have been ~10× PAL (Badger et al., 2002; Riding, 2006; Kah and Riding, 2007). Under high early Proterozoic CO_2 levels, cyanobacterial photosynthesis may have relied on CO_2 diffusion that may not have significantly altered pH near the cell surface. Falling CO_2 levels would have encouraged active carbon uptake to maintain photosynthesis and this, in turn, promoted calcification (Figures 1 and 5).

Carbonate mud: Carbonate mud appears to have been scarce in the late Archaean (Sumner and Grotzinger, 2004), but it increased in abundance during the Proterozoic (Kah and Grotzinger, 1992) and was widespread in the Neoproterozoic (Herrington and Fairchild, 1989). Much of it is thought to have been produced by whitings stimulated by phytoplankton photosynthesis (Grotzinger, 1989, 1990). A significant increase in carbonate mud occurred ~1400–1300 Ma ago (Sherman et al., 2000, p. 290), prior to the appearance of sheath calcification (Kah and Riding, 2007). This "water column factory" transformed carbonate platform sedimentation by creating extensive micrite-rich subtidal deposits (Sherman et al., 2000, p. 290). The timing of this increase in carbonate mud therefore broadly coincided with the first appearance of *Girvanella*-like and other sheath-calcified fossils (see below), and may be linked to CCM development in cyanobacteria, but in this case to planktic forms, possibly similar to present-day *Synechococcus* (Riding, 2006). Muddy carbonate platforms were the deposits in which distinctive molar tooth facies developed (James et al., 1998; Sherman et al., 2000, p. 290). It can therefore be speculated that mid-late Proterozoic increase in micrites and molar tooth facies, together with *Girvanella* and thrombolites, all reflect decline in atmospheric CO_2 that stimulated CCM induction and calcification in cyanobacteria (Riding, 2006) (Figure 5).

Cyanobacterial sheath calcification: The first appearance of calcified cyanobacteria in the mid-Proterozoic – interpreted to reflect the first development of CCMs in photosynthetic organisms (Riding, 2006) – marked a radical change from stromatolitic to thrombolitic fabrics. Mesoproterozoic examples reported from the ~1200 Ma Society Cliffs Fm are currently the oldest known *Girvanella*-like calcified filaments, and are associated with micritic bush-like structures also interpreted as calcified cyanobacteria (Kah and Riding, 2007). The presence of filamentous fabrics had long been recognized in late Proterozoic and early Palaeozoic stromatolites. Microstructure with filament moulds was termed Canaliphorida and Filiformita by Komar (1976, 1989, see Bertrand-Sarfati et al., 1994, p. 182, Fig. 18). Aitken (1989, pp. 15–16) described "dendriform" and "lamelliform elements" as important components of Little Dal reefs in the Mackenzie Mountains. He regarded both as stromatolites with "unusual" or "unique" characteristics: thin-walled tubes and *Renalcis*-like objects in dendriform element, and a reticulate "ladder-rung" arrangement that "may be formed by a meshwork of tubes" in lamelliform element. He remarked that these fabrics "are not typically

stromatolitic" and that "sediment trapping may not have been the dominant process in their formation" (p. 15). Dendriform and lamelliform elements look quite similar in two of his illustrations (Figs. 10 and 13). Subsequently, Turner et al. (1993, 2000a, Fig. 10b, 2000b) compared the tubules with *Girvanella* and noted that the lamelliform fabric consists of alternating dark layers of "calcimicrobial filaments" and lighter "more cement-rich" areas. Little Dal "hollow tubules with micritic walls" are figured by Batten et al. (2004, Fig. 9b). Knoll and Semikhatov (1998, p. 410, Figs. 3 and 4) described well-preserved "filmy or platy" microstructure in early Neoproterozoic *Baicalia lacera* stromatolites from the Chernaya Rechka Fm, Igarka, Siberia. They found it to be associated with "a distinctly filamentous microstructure" in which "laminae comprising densely interwoven to scattered, vertically, or subhorizontally oriented filaments are interspersed with layers of spongy or dense microspar." They interpreted the 8–10 μm tubes as "sheaths of LPP-type (*Lyngbya*, *Phormidium*, *Plectonema*) cyanobacteria and preserved as drusy microspar encrustations" (Knoll and Semikhatov, 1998, p. 411). Similar *Baicalia lacera* fabrics in the ~ 1Ga Burovaya Formation of west-central Siberia locally contain calcified tubes resembling *Siphonophycus* (Petrov and Semikhatov, 2001, p. 270). The lamelliform element shown by Turner et al. (2000a, Fig. 10b) resembles the distinctive "filmy" microstructure of similar age *Baicalia lacera* (Petrov and Semikhatov, 2001, Figs. 5b and 6a) which also has steeply dipping laminae and, as noted above, quite possibly filamentous microstructure too. In these examples, layers of filamentous fabric are generally interleaved with lighter, sparry, layers. If the sparry layers were lacking, the deposit would be indistinguishable from "skeletal stromatolite" (Riding, 1977) and "porostromate stromatolite" (Monty, 1981). In addition to the Little Dal and Chernaya Rechka examples, calcified filaments reminiscent of *Girvanella* are relatively widespread elsewhere in the Neoproteroccur, e.g., in the ~750–700 Ma Draken Fm, ~725–675 Ma Svanbergfgellet Fm, and ~700 Ma Upper Eleonore Bay Supergroup, Greenland (refs in Knoll and Semikhatov, 1998, p. 413). Throughout the Neoproterozoic, these thrombolites with calcified microbial fabrics (Kennard and James, 1986) are intimately associated with stromatolites but typically occur in deeper subtidal environments (Aitken, 1967).

Marine carbonate saturation

Inception of cyanobacterial calcification would have required overall seawater carbonate saturation to be relatively high. Grotzinger (1990) has argued that seawater saturation state progressively reduced during the Proterozoic and that this could account for concomitant decline in stromatolite abundance. Nonetheless, the widespread continued development of microbial carbonates into the Neoproterozoic, together with calcified sheaths themselves, indicates that saturation state was not low. This may have changed during widespread glaciations that occurred in the late Proterozoic ~700–570 Ma ago (Walter et al., 2000). Sheath-calcified cyanobacteria appear to have been scarce during "Snowball" glaciations. Lower temperature and pCO_2 levels would have decreased seawater saturation state, hindering microbial calcification generally. Shields (2002) attributed decline in Molar Tooth facies ~750 Ma ago to reduction in carbonate saturation. Since cooling would also have favored diffusive entry of CO_2 into cells (Raven et al., 2002) it could have slowed CCM development, further reducing cyanobacterial calcification. As Earth emerged from these snowball glaciations, global warming and O_2 rise could have reactivated CCM development, and rising temperature, calcium, and pCO_2 levels would have increased seawater saturation state, stimulating calcification (Riding, 2006). Calcified cyanobacteria became relatively diverse

Calcified Cyanobacteria, Figure 6 Early Cambrian (Botomian) dendrolite-thrombolite reef, ~70 m thick, near Tafraoute, Anti-Atlas Mountains, Morocco. Figures in foreground for scale.

in the earliest Cambrian (Nemakit-Daldynian) (Riding and Voronova, 1984) and were important components of Cambrian reefs (Riding, 2000; Rowland and Shapiro, 2002).

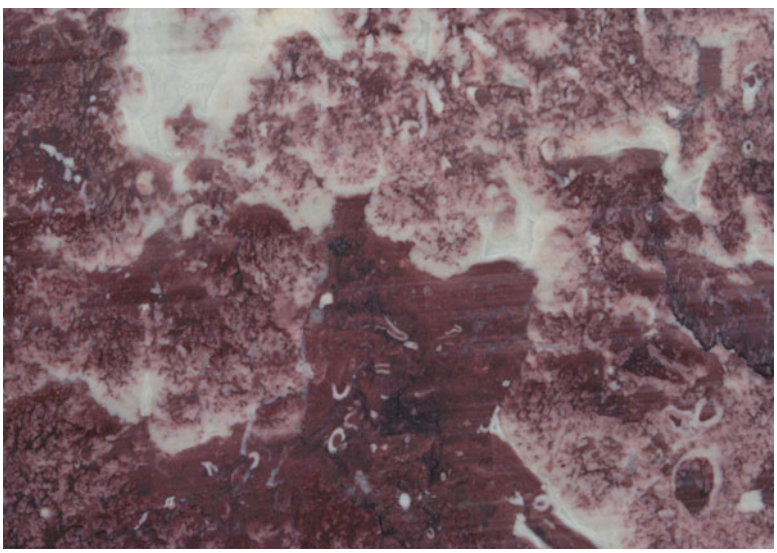
Calcimicrobial reefs and the Cambrian radiation

Calcified microfossils such as *Epiphyton*, *Renalcis*, and *Angusticellularia* are major components of Cambrian reefs (Figures 6 and 7) and similar forms reappeared in the late Devonian. The widespread development of microbial reefs in the early Cambrian may have directly contributed to marine invertebrate diversification. Reefs constructed by calcified microbes appeared in the latest Neoproterozoic, ~550 Ma ago (Grotzinger et al., 2000) and were common in Siberia, Altai Sayan, and Mongolia during the Nemakit-Daldynian (543–526 Ma ago) (Riding, 2002). In the Tommotian, 526–522 Ma ago, this reef-building association was augmented by archaeocyath sponges, with calcified microbes generally being volumetrically dominant (Rowland and Shapiro, 2002), and the reefs became large and cavernous. The exceptional biodiversity that characterizes reefs in general is largely due to the process of reef bioconstruction itself (Cocito, 2004). Rapid accretion of framework with synoptic relief and internal growth cavities creates substrates and spaces that differ in incident light, water movement, and sedimentation, as well as accessibility. This increased habitat size and partitioning generates heterogeneity that promotes biodiversity. For example, Cambrian trilobites show peak diversity in reefal environments (Westrop and Adrain, 2001), and comparison of level-bottom and reef communities in general shows that early Cambrian reefs were centers of diversity (Burzin et al., 2001, Fig. 10.2) with number of reef-building species comparable to that of late Neogene fossil reefs (Kiessling, 2002, Fig. 20). The expansion of these globally distributed reef communities corresponded with rapid diversification of the shallow marine biota, especially during the Tommotian-early Botomian (~526–517 Ma ago) (Zhuravlev 2001, Fig. 8.1), suggesting a direct link between microbial carbonate development and metazoan evolution.

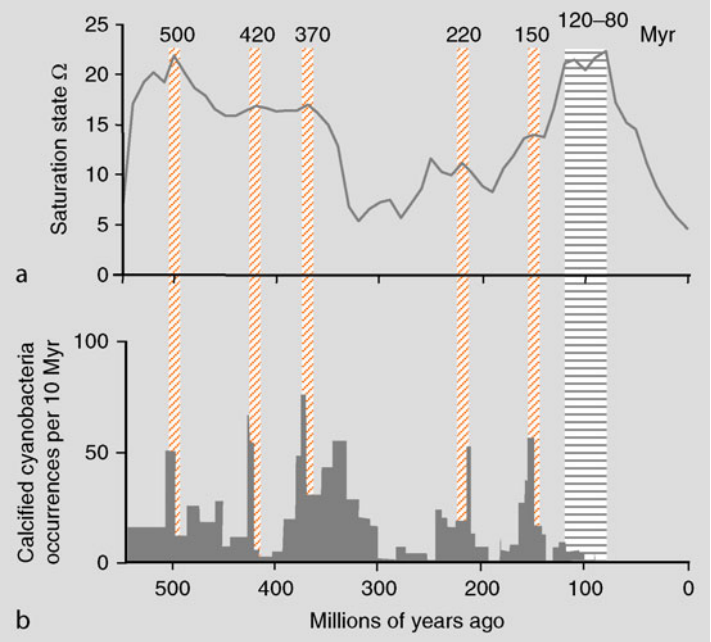
Phanerozoic record and secular controls

Cyanobacterial sheath calcification: Following their Mesoproterozoic inception, sheath-calcified cyanobacteria remained generally common in shallow-water marine carbonates during much of the Palaeozoic and until the late Jurassic (Arp et al., 2001) (Figure 8b). The abundance of sheath-calcified cyanobacteria during the early Palaeozoic (when CO_2 levels are thought to have been high, see Berner and Kothavala, 2001), suggests that CCMs continued to be induced even when pCO_2 substantially exceeded 10 PAL. This may reflect calcification in habitats subject to carbon limitation that induced CCMs, such as microbial mats and reefs (Riding, 2006). Nonetheless, enhancement of CCMs by overall decline in atmospheric CO_2 could be reflected by increased calcified-sheath abundance in the Mississippian, ~335 Ma ago (Riding, 2006) (Figure 5). However, it seems that this increase in calcified-sheath abundance promoted by falling CO_2 was itself terminated by subsequent steep decline in seawater saturation state ~325 Ma ago, before the end of the Mississippian (Figure 8a).

Broad similarities between calcified-sheath abundance and carbonate saturation are suggested by peaks in the late Cambrian (~500 Ma), late Silurian (~420 Ma), late Devonian (~370 Ma), late Triassic (~220 Ma), and late



Calcified Cyanobacteria, Figure 7 Early Cambrian calcimicrobial reef framework, showing clusters of mainly pendant filaments, early cement and geopetal cavity fill. Near Taroudannt, Anti-Atlas Mountains, Morocco. Width of view ~35 cm.



Calcified Cyanobacteria, Figure 8 Comparison of (**a**) Marine saturation ratio (Ω) for calcite, calculated from estimates of seawater and atmospheric composition, and (**b**) abundance of marine sheath-calcified cyanobacteria (Arp et al. 2001, Fig. 3d) (from Riding and Liang, 2005, Fig. 5). Obliquely ruled areas indicate five intervals approximately 500, 420, 370, 220, and 150 millions of years (Myr) ago where peaks of calculated saturation ratio broadly coincide with increased abundances of calcified cyanobacteria. This correspondence supports the view that cyanobacterial calcification has been increased at times of generally elevated seawater saturation for $CaCO_3$ minerals. The horizontally ruled area indicates the interval ~120–80 Myr ago in which high calculated saturation contrasts with low abundance of calcified cyanobacteria. This anomaly could reflect lowered Cretaceous carbonate saturation due to widespread deposition of pelagic carbonate by coccolithophore algae and globigerine foraminifers, since biological removal of $CaCO_3$ is not incorporated into the calculation of saturation values.

Jurassic (~150 Ma) (Figure 8), supporting the view that saturation state has significantly influenced the degree of cyanobacterial sheath calcification over geological time (Riding and Liang, 2005).

Reduced abundance of sheath-calcified cyanobacteria ~120–80 Ma ago contrasts with calculated saturation state which is elevated during this interval. This anomaly is thought to reflect reduction in actual (as opposed to calculated) saturation state due to burial of $CaCO_3$ precipitated as calcified skeletons by plankton such as coccolithophore algae and globigerine foraminifers (Riding and Liang, 2005). Such biological removal of calcium is not included in the input used to calculate the saturation values shown. This effect of planktic calcifiers on the seawater system may have continued into the Palaeogene. During the past 50 Ma, from the early Eocene onward calculated saturation has declined steeply in response to low values of Ca^{2+} ions and pCO2, and this is consistent with scarcity of marine calcified cyanobacteria. Consequently, although low pCO2 values during the Cenozoic (see Berner and Kothavala, 2001) are expected to induce cyanobacterial CCMs, the absence of sheath calcification in marine cyanobacteria presumably reflects the overriding effect of low carbonate saturation.

Biogenic whitings: It can be inferred that, following the development of CCMs in the mid-Proterozoic, picoplanktic cyanobacterial activity could have been an important source of marine carbonate mud whenever inorganic carbon could be a limiting resource, as in plankton blooms (Rost et al., 2003), even when overall atmospheric CO_2 levels were high. If this is correct, then the principal factor determining biogenic whiting occurrence would have been carbonate saturation state. Calculations suggest that saturation was relatively elevated during much of the early-mid Palaeozoic and parts of the Mesozoic (Riding and Liang, 2005; and Figure 8a).

The origins of micrite are notoriously difficult to interpret even in present-day seas, and it is known that calcified green algae can also be significant producers (Stockman and Ginsburg, 1967). How can the possible contribution of biogenic whitings therefore be assessed in the geological past? One line of reasoning is to assume that sheath-calcified cyanobacteria reflect generally similar conditions to those that favor picoplanctic whiting precipitation. The geological record of sheath-calcified fossils such as *Girvanella* is relatively well-documented, and they show marked fluctuations in abundance (Arp et al., 2001, Fig. 3d) (Figure 8b). It could therefore be predicted that picoplanctic mud should show a similar pattern of

abundance, with peaks for example in the late Cambrian, Devonian-Mississippian, and late Jurassic. It should be possible to test whether carbonate mud was relatively abundant at these times. It is also possible that biogenic whitings – and sheath calcification – should have been further intensified whenever pCO_2 levels fell to levels near or below ~10 PAL, as for example ~350 Ma ago (Figure 5).

Cenozoic decline in seawater carbonate saturation, suggested by calculations based on modeled values (Riding and Liang, 2005, Figs. 5a and 8a), would be expected to have reduced biogenic whiting precipitation. Certainly, sheath calcification is scarce to absent during most of the past 100 Ma (Arp et al., 2001, Fig. 3d) (Figure 8b). In this context, it is not surprising that there is uncertainty whether present-day marine whitings on the Bahaman Banks are biogenic or mainly reflect sediment resuspension (Broecker et al., 2000). From a geobiological perspective, however, even if present-day marine conditions do not greatly favor phytoplankton-stimulated precipitation of whitings, these may have been very important at times in the geologic past environment when carbonate saturation state was sufficiently high. 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.

Summary

Calcified cyanobacteria are easily overlooked fossils, yet their long history coupled with their sensitivity to environmental controls on their calcification, make them potentially significant indices of changes in seawater chemistry and atmospheric CO_2 level throughout the Proterozoic and Phanerozoic. Locally they are also sedimentologically important reef components, and they have played a major role in the formation of calcimicrobial thrombolites that are especially widespread in the Neoproterozoic and early Palaeozoic. At the present day their vanishing scarcity in marine environments is thought to reflect relatively low seawater carbonate saturation that has persisted throughout the Cenozoic. However, their local abundance in oncoids and tufas of freshwater calcareous streams and lakes, and their involvement in lacustrine whitings, are reminders of the ability of cyanobacteria to promote intense $CaCO_3$ deposition when conditions that include ambient saturation state, are favorable.

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Cross-references

Alkalinity
Biosignatures in Rocks
Calcite Precipitation, Microbially Induced
Carbonate Environments
Cyanobacteria
Divalent Earth Alkaline Cations in Seawater
Extracellular Polymeric Substances (EPS)
Microbial Biomineralization
Microbialites, Modern
Microbialites, Stromatolites, and Thrombolites
Organomineralization
Soda Ocean Hypothesis
Stromatolites
Tufa, Freshwater

CALCITE PRECIPITATION, MICROBIALLY INDUCED

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Definition

Microbially induced calcite precipitation describes the formation of calcium carbonate minerals from a solution due to the presence of microbial cells, biosynthetic products, or metabolic activity.

Calcium carbonate precipitation

The most basic requirement for the precipitation of calcium carbonate ($CaCO_3$) minerals, calcite, and aragonite is that the product of the concentrations of calcium [Ca^{2+}] and carbonate ions [CO_3^{2-}] exceeds the solubility product of calcite (Equation 1) and aragonite, respectively.

$$[Ca^{2+}][CO_3^{2-}] > 10^{-8.35} \quad (1)$$

The solubility of carbonate minerals depends on the temperature and pressure, decreasing with increasing temperatures and increasing with the increasing pressure. When a solution is in equilibrium with carbon dioxide, [CO_3^{2-}] is determined by pH. In solutions that are undersaturated or not highly saturated, such as modern seawater, the biological activity can strongly control the precipitation of $CaCO_3$. Biological processes exert considerably less control on the precipitation of $CaCO_3$ in environments characterized by high temperature, high pH, and high evaporation and degassing rates such as soda lakes, hot springs, caves, and freshwater tufas.

Microbial processes that promote the precipitation of $CaCO_3$

Culture-dependent and culture-independent studies have shown that microbes (Bacteria and Archaea) can induce extracellular precipitation of calcium carbonate minerals by:

(a) Increasing the local pH and the concentration of carbonate ion
(b) Promoting the nucleation of calcium carbonate minerals and removing the kinetic inhibitors of $CaCO_3$ precipitation.

Increase in local pH and the concentration of carbonate ion

Because the concentration of carbonate ion increases with the increasing pH, the precipitation of calcium carbonate minerals will also increase with the increasing pH. Many microbial metabolic processes can increase the pH and/or the concentration of carbonate ions: sulfate reduction in marine sediments (Dupraz and Visscher, 2005; Van Lith et al., 2003; Visscher et al., 2000), oxygenic