Formation and diagenesis of modern marine calcified cyanobacteria

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ABSTRACT

Calcified cyanobacterial microfossils are common in carbonate environments through most of the Phanerzoic, but are absent from the marine rock record over the past 65 Myr. There has been long-standing debate on the factors controlling the formation and temporal distribution of these fossils, fostered by the lack of a suitable modern analog. We describe calcified cyanobacteria filaments in a modern marine reef setting at Highborne Cay, Bahamas. Our observations and stable isotope data suggest that initial calcification occurs in living cyanobacteria and is photosynthetically induced. A single variety of cyanobacteria, Dichothrix sp., produces calcified filaments. Adjacent cyanobacterial mats form well-laminated stromatolites, rather than calcified filaments, indicating there can be a strong taxonomic control over the mechanism of microbial calcification. Petrographic analyses indicate that the calcified filaments are degraded during early diagenesis and are not present in well-lithified microbialites. The early diagenetic destruction of calcified filaments at Highborne Cay indicates that the absence of calcified cyanobacteria from periods of the Phanerzoic is likely to be caused by low preservation potential as well as inhibited formation.

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INTRODUCTION

Calcified cyanobacteria microfossils are a common component of marine carbonate reefs and sediments deposited from 550 to 100 Ma (Riding, 2000; Arp et al., 2001). Calcified microfossils morphologies are diverse, and many have been assigned formal taxonomic names (Riding, 2000). Filamentous taxa, such as Girvanella are likely the most common calcified cyanobacteria, and have a morphology that can be directly related to modern cyanobacteria. These once common fossils are absent from the marine rock record since the Late Cretaceous (Sumner & Grotzinger, 1996; Arp et al., 2001; Riding & Liang, 2005).

Modern calcified cyanobacteria that are morphologically comparable to ancient marine counterparts are commonly found in freshwater settings and have been extensively studied (e.g. Merz, 1992). However, since freshwater systems have carbonate and other major ion compositions that are dramatically different from those of marine settings, these modern calcified cyanobacteria are not direct analogs for ancient marine cyanobacterial microfossils (Knoll et al., 1993; Dupraz et al., in press). Calcified cyanobacteria are found in several marine environments (Winland & Matthews, 1974; Hardie, 1977; Riding, 1977; MacIntyre et al., 1996), but there has not been an extensive study of the calcification mechanisms in any of these occurrences. The lack of a suitable, well-studied modern analog for ancient marine calcified cyanobacteria has fostered long-standing debate on the factors controlling the formation, temporal distribution, and abundance of these microfossils (Knoll et al., 1993).

The formation of calcified cyanobacterial microfossils is ultimately caused by a local increase in calcium carbonate saturation state driven by microbial metabolic activity. It has been heavily debated if this shift in carbonate saturation state is induced by cyanobacterial photosynthesis or heterotrophic microbial metabolisms (Visscher et al., 1998; Riding, 2000; Arp et al., 2001; Dupraz & Visscher, 2005; Dupraz et al., in press). Uptake of carbon dioxide during cyanobacterial photosynthesis increases the pH surrounding the cyanobacterial cell, which favors carbonate precipitation. Bicarbonate is
the product of microbial sulfate and nitrate reduction, and its production also promotes calcium carbonate precipitation (see Morse & MacKenzie, 1990; Dupraz & Visscher, 2005; Visscher & Stolz, 2005; Dupraz et al., in press for extensive reviews of the effects of different microbial metabolisms on calcium carbonate saturation state). These modes of calcified cyanobacteria formation – photosynthetic and organic matter remineralization induced carbonate precipitation – have typically been viewed as part of a binary system (Turner et al., 2000; Arp et al., 2001; Kah & Riding, 2007). It has become increasingly clear that extrapolymeric substances (EPS) produced by cyanobacteria and heterotrophic bacteria also play a key role in calcification (e.g. Decho, 2000; Braissant et al., 2007, 2009). Freshly produced EPS can have an inhibitory effect on calcification through binding of cations (e.g., Ca$^{2+}$, Mg$^{2+}$; Dupraz & Visscher, 2005). When the cation-binding capacity is saturated (Arp et al., 2003), or when EPS is degraded through microbial and/or physiochemical processes, large amounts of Ca$^{2+}$ ions are released, promoting calcification (Dupraz & Visscher, 2005).

The factors controlling the temporal distribution of calcified cyanobacteria are also debated. Calcified cyanobacteria first appear in rock record in the middle Precambrian (Kah & Riding, 2007), but show a major increase in abundance in the early Cambrian (Arp et al., 2001). This Cambrian event may have been caused by cyanobacterial evolution or major changes in the marine carbonic acid system (Walter & Heys, 1985; Knoll et al., 1993; Turner et al., 2000; Arp et al., 2001; Riding & Liang, 2005). Calcified cyanobacteria are abundant through the most of the Paleozoic, but are rare or absent for periods in the Mesozoic. Notably, calcified cyanobacteria are rare in the Permian and Early Jurassic, despite the presence of microbial carbonates during this time period. Arp et al. (2001) proposed that the rarity of mid-Mesozoic calcified cyanobacteria is linked with low marine calcium concentrations. Calcified cyanobacteria are rare in the Cretaceous and disappear from the marine rock record in the Late Cretaceous. Their absence over the past 65 Ma is thought to be due to low marine calcium or carbonate ion concentrations, which would have lowered the calcium carbonate saturation state and inhibited microfossil formation (Sumner & Grozinger, 1996; Riding, 2000; Arp et al., 2001).

Here we describe calcified cyanobacterial filaments from a modern marine setting at Highborne Cay in the Bahamas. We document the growth and early diagenetic history of the calcified cyanobacteria at Highborne – presenting information from field observations, petrographic examinations, and stable isotope work. Our documentation of a modern marine calcifying cyanobacterium allows us to test models that explain the formation, temporal distribution, and abundance of ancient calcified cyanobacteria. Our study strengthens the view that understanding the geochemical dynamics of modern microbial ecosystems is essential to link microbial processes with sediments in the geological record and to understand the evolution of microbial carbonate production.

**STUDY AND LOCATION AND ENVIRONMENT**

The calcified-cyanobacteria filaments are located in an open marine environment at Highborne Cay (76°49′W, 24°43′N) Exuma, Bahamas. Tufts of the filaments are found on thrombolitic microbialites. These microbialites are up to a meter tall and are located the intertidal region of the back reef of an algal-ridge fringing reef complex that extends for 2.5 km along the eastern shore of the Pleistocene island Highborne Cay (Fig. 1). Sampled thrombolitic microbialites are located at Highborne Cay Sites 6 and 8 of Andres & Reid (2006). Several of the thrombolitic microbialites were found growing on top of 1084-year-old vermetid-gastropod rock fragments, indicating recent growth (Planavsky and Reid, unpublished data). This age is based on radiometric (14C) dating performed on cleaned shell fragments using Accelerator Mass Spectrometry at Beta Analytical, Miami, Florida.

The Highborne Cay fringing reef complex contains well-laminated stromatolites, in addition to the thrombolitic microbialites (Reid et al., 1999, 2000). The stromatolites are also best developed in the back-reef setting. The reef is a highly dynamic system, and all of the microbialites are periodically covered by carbonate sand (Andres & Reid, 2006). Continuous monitoring of the Highborne reef complex for over 2 years (2005–2006) indicates that there are periods when eukaryotes – rather than cayanobacteria – are the dominant photosynthetic organisms on the surfaces of thrombolitic microbialites. The eukaryotes include green algae, red algae, and a pink layer rich in EPS and spherical spores, which have not received proper taxonomic treatment (see Littler et al., 2005, for discussion of Highborne Cay algae). Micritic argonite precipitates in the pink layer forming crude laminations at the top of nearshore buildups (Reid et al., 1999). Except for these micritic laminations, the thrombolitic microbialites have clotted and mottled fabrics (Fig. 2) (Reid et al., 1999).

**MATERIALS AND METHODS**

Cyanobacterial mats were examined within an hour of collection using light and fluorescence microscopy. The fluorescence microscope (using a 490-nm excitation filter) was used to visualize carbonate precipitates and examine the degree of cyanobacterial autofluorescence. Cyanobacterial fluorescence, as viewed with the 490-nm excitation filter, is caused by accessory photosynthetic pigments – predominantly phyco-biliproteins – and can thus be used to estimate photosynthetic ability.

Clusters of cyanobacterial cells were fixed in 4.5% gultaraldehyde in sodium cacodylate buffered solution within an hour of collection for electron microscopy work. We did a
post-fixation with osmium tetroxide, within a week of the initial fixation. Material used for electron microscopy was coated in palladium and viewed using a FEI/Philips XL30 environmental scanning electron microscope (E-SEM) with an Oxford L300Qi-Link ISIS EDS at University of Miami, Department of Geology.

Our observations on the early diagenetic history of calcified cyanobacteria are from 42 standard petrographic thin sections. All material was embedded under vacuum with epoxy prior to sectioning. Nineteen of these thin sections come from two complete thrombolitic microbialites excavated from Highborne Cay (Site 6 of Andres & Reid, 2006). The remaining thin sections are from the upper, surficial sections of Highborne Cay thrombolitic microbialites.

We extracted calcified, autofluorescent cyanobacteria cells for carbonate carbon and oxygen isotopic analysis. The calcified filaments were isolated from surrounding sediment at \(50\times\) magnification using a dissecting microscope. The purity of a subset of the calcified filament samples was checked using scanning electron microscopy (SEM). All samples examined using SEM contained minor amounts of sediment impurities. The isotopic values, therefore, are a qualitative, rather than truly quantitative, estimate of the calcified filament isotopic values.

Carbonates were isotopically analyzed with a Kiel III automated carbonate device interfaced to a Thermo Finnigan Delta-plus stable isotope ratio mass spectrometer at the Stable Isotope Laboratory at the Rosenstiel School of Marine and Atmospheric Science, Miami Fl. Results were corrected for standard drift and isobaric interferences and are expressed relative to Vienna Pee Dee belemnite. Instrument precision was better than 0.15‰ for \(\delta^{18}O\) and \(\delta^{13}C\) (2σ).

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The carbonate mineralogy of filaments was determined using X-ray diffraction with a PAN analytical X’Pert X-ray diffractometer operated at the Stable Isotope Laboratory of the Rosenstiel School of Marine and Atmospheric Sciences. Similar to the isotopic work, calcified, autofluorescent cyanobacteria cells were isolated from surrounding sediment using a dissecting microscope. Additionally, using electron dispersive spectroscopy (EDS) we were able to determine carbonate mineralogy at the micron scale (see Planavsky & Ginsburg, 2009, for information about determining mineralogy with EDS).

RESULTS

Description of calcified filaments

Calcified cyanobacteria filaments, along with trapped and bound sand grains, form unlaminated tuffs or buttons that cover the tops and sides of the thrombolitic microbialites. The tuffs are typically between 1 and 5 cm across and many are exposed at low tide (Fig. 3A). A single variety of cyanobacteria, Dichothrix, form the calcified filaments that define the unlaminated tuffs on the Highborne Cay thrombolitic structures. We identified the filaments as Dichothrix based on the presence of common lateral false branching, with the branch first running parallel to the original trichome, as well as the presence of basal heterocytes, obligatory sheaths, narrowing apical ends, and a lack of akinetes. All observed Dichothrix filaments have some degree of calcification, but the initial calcification was rarely observed to complete coat the filaments. Other cyanobacteria can be present within the tuffs, including cyanobacteria in genus Oscillatoria. The Oscillatoria, in contrast to the Dichothrix filaments, do not show well-defined mucilaginous sheaths. Although, the tuffs are dominated by vertically oriented cyanobacteria (Fig. 3A), occasional red algae may be interspersed, especially on the tops upper surfaces of the more seaward microbialites. No carbonate precipitates were observed on the red algae or the adjacent sediment.

Initial calcification occurs around Dichothrix filaments that lack obvious signs of filament or sheath degradation (Figs 4A and 5A). Surficial calcifying filaments are strongly autofluorescence (viewed with 490-nm excitation filter). The degree of autofluorescence in the Dichothrix cell decreases markedly over a centimeter scale with depth in the filament tuffs (Fig. 4B). The initial carbonate precipitation occurs in the

Fig. 2 Photos of cut thrombolitic microbialites. (A) Microbialite from the distal section of the backreef in Highborne Cay Site 6. Slab is ~1 m across. (B) Microbialite from the near-shore section of the backreef in Highborne Cay Site 6. Slab is ~1.5 m across. Both microbialites lack prominent laminations, contain abundant voids, and have a weakly clotted fabric.

Fig. 3 Photos of the calcified cyanobacterial filaments. (A) Photo of a tuft of vertically oriented calcified Dichothrix filaments from the surface of a thrombolitic microbialite. Scale bar is 1 cm. (B) Photo showing the carbonate coating on Dichothrix filaments. Scale 1 mm.
exopolymeric sheath surrounding the cyanobacterial cell (Fig. 5A). The initial carbonate precipitates are randomly oriented fine-grained (submicron to ~50 μm crystals) acicular aragonite (Figs 6A and 7A).

The distinct calcified filaments present on the uppermost section of the microbialite grade gradually downward from the surface into poorly defined, degraded calcified cells and associated fine-grained, micrite precipitates (Fig. 5). The mucilaginous sheaths in degraded cyanobacterial cells are typically absent or non-continuous (Figs 5B and 6B). Carbonate precipitates on filaments with signs of degradation are sporadic, and the aragonite crystals exhibit fused and indistinct crystal faces (Fig. 7B). These crystal features are similar to those observed in other organic-rich modern carbonates that have experienced penecontemporaneous aragonite recrystallization (Macintyre & Reid, 1995; Reid & MacIntyre, 1998). The poorly defined cells and associated precipitates grade into a fabric that lacks distinguishable remnants of cyanobacterial cells (Fig. 5C). The amount of intergranular carbonate precipitate increases during the transition from distinct calcified cells surrounded by sand grains into well-cemented sand lacking distinct calcified cyanobacteria (Fig. 5C). We observe this diagenetic progression – from well-defined calcified cyanobacterial cells to abundant micritic cements – over a depth range of a several centimeters. Calcified cyanobacteria were not observed lower than ~6.5 cm below the microbial mat-water interface.

The lower, older sections of the thrombolic microbialites at depths of 10 cm to 1 m contain abundant submarine precipitates. These precipitates are typically micritic, although fibrous aragonite cement is locally abundant. The lower sections of the microbialites are also heavily bored and locally contain abundant encrusting foraminifera. Extensive micritization is common. In some cases, the tuffs of calcified filaments are growing on a distinct micritization front.

Fig. 4 Light micrographs of calcified Dichothrix filaments under florescent light with a 490-nm excitation filter. The carbonate and photosynthetic pigment are fluorescing blue and orange, respectively. (A) Micrograph of a Dichothrix filament from the surifical section of a tuft of filaments. The cell shows strong autofluorescence, indicating photosynthetic ability. (B) Micrograph of a Dichothrix filament from the basal section of a tuft of filaments. The cell does not display autofluorescence and contains unevenly distributed carbonate precipitates in the cell’s sheath. Scale bars 20 μm.

Fig. 5 (A–C) Light micrographs illustrating the early diagenetic transition from distinct calcified cyanobacterial filaments to patchy fine-grained carbonate cements. The light micrographs in A–C are taken from a single microbialite over a 7-cm vertical distance. Calcified filaments are also absent from more basal sections of the microbialite indicating that the calcified cyanobacterial microfossils would not be preserved in the geological record. Scale bars 100 μm.
Stable isotope results

Carbonate from the calcified filaments has δ¹³C isotope values ranging from +4.50‰ to +5.82‰ (Fig. 8). Detrital carbonate grains and fine-grained precipitates from the adjacent stromatolites at Highborne Cay have a range of δ¹³C values from +4.61‰ to +4.83‰ and +3.1‰ to +4.58‰, respectively (Andrés et al., 2006). Bulk samples of the un laminated microbialites have carbonate δ¹³C values that range from +4.3‰ to +4.79‰ (Fig. 8). The δ¹³C values of the calcified filaments are significantly higher than the Highborne Cay sediments, the bulk thrombolitic microbialites, and the precipitates from the adjacent stromatolites.

Carbonate oxygen isotopes values from the calcified filaments, with limited exceptions, are 0 ± 0.5‰, similar to the Highborne Cay sediments, the bulk thrombolitic microbialites, and the precipitates from the adjacent stromatolites (Andrés et al., 2006). Three samples of calcified filaments display δ¹⁸O values ≤+1‰ (Fig. 8).

DISCUSSION

Formation of calcified cyanobacteria

Several lines of evidence from the present study indicate in vivo cyanobacterial calcification in a normal salinity, modern marine environment. Calcification is occurring in the uppermost section of the Dichothrix tusfts, where there are high rates of photosynthesis indicating an active cyanobacterial community (Myshrall et al., 2008). The presence of some degree of sheath calcification in all of the observed Dichothrix filaments provides strong support for calcification occurring during the cyanobacterial life cycle. Strong autofluorescence in surficial calcified cells likely indicates photosynthetic ability. The lack of obvious signs of heterotrophic degradation in the initial calcified cells also provides support for in vivo calcification (Fig. 9).
The presence _in vivo_ calcification within the _Dichothrix_ sheath is consistent with photosynthesis-induced carbonate precipitation: cyanobacterial sheaths experience a significant increase in pH during photosynthesis due to carbon dioxide uptake (Visscher & van Gemerden, 1991; Arp et al., 2001).

Carbon dioxide degassing is not inducing carbonate precipitation within the _Dichothrix_ tufts. The lack of carbonate precipitation on the red algae interspersed with the calcifying filaments or the adjacent sediment is inconsistent with carbon dioxide degassing driving carbonate precipitation. _Dichothrix_ filaments are calcifying on the sides of microbialites that are unaffected by exposure. Further, oxygen isotopes from the carbonate precipitates from _Dichothrix_ sheaths, with limited exception, do not show an evaporative signal (carbonate with high δ18O values). An evaporative signal would likely be present if carbon dioxide degassing linked with elevated temperatures had driven calcification. However, carbon dioxide degassing can also be caused by increased agitation, which would not result in an evaporative signature in carbonate oxygen isotope values.

The carbonate δ13C isotope values from Highborne Cay microbialites provide additional insights into the mechanisms driving calcium carbonate precipitation. Significantly more positive δ13C isotope values in the calcified filaments than in the adjacent stromatolite precipitates indicate that the mode of calcification is distinctly different in each microbialite type. The micritic laminations in the Highborne Cay stromatolites precipitate in a zone of localized, intense sulfate reduction (Visscher et al., 2000). This correlation was shown through silver-foil experiments in the microbial ecosystems forming the stromatolites, which track microbial sulfide production from sulfate (Visscher et al., 2000). The stromatolite precipitates contain carbon isotope values that are lower than would be predicted if precipitation occurred from the ambient dissolved inorganic carbon (DIC) reservoir (Andres et al., 2006). The light δ13C isotope values are likely due to precipitation in an environment with bicarbonate derived from isotopically light organic matter remineralization (Andres et al., 2006).

Significantly more positive δ13C values in the calcified filaments of the thrombolitic microbialites – compared to those in the adjacent stromatolite precipitates or the surrounding sediment – suggests carbonate precipitation in the sheath of these filaments was in part photosynthetically induced. During cyanobacterial photosynthesis, preferential uptake of 13C-enriched carbon dioxide or bicarbonate creates a 13C-enriched microenvironment with an elevated pH in the mucilaginous sheath (for review see Riding, 2000, 2006). Since the calcified filaments analyzed isotopically contained minor amounts of contaminating carbonate sediment, the
carbonate $\delta^{13}C$ values cannot be used to quantitatively resolve DIC reservoir shifts. Highborne Cay sediments have significantly lower $\delta^{13}C$ values than the calcified filament precipitates, indicating the true values of these precipitates are slightly higher than reported.

*Dictothrix* filaments have a different calcification history than the *Schizothrix* filaments in adjacent stromatolites. Initial calcification in *Dictothrix* is occurring *in vivo* and photosynthetic activity appears to be one of the processes inducing calcification. There is no evidence for *in vivo* calcification of *Schizothrix* filaments (Reid et al., 2000; Visscher et al., 2000; Andres et al., 2006). However, this does not support that initial *Dictothrix* calcification is a strictly photosynthetically induced process. In previous work, higher rates of heterotrophic activity were found in sections of Bahamian microbial mats with living, highly productive cyanobacteria than in sections with decaying cyanobacteria (including heterotrophic metabolisms likely to induce carbonate precipitation like sulfate reduction) (Visscher et al., 2000; Braissant et al., 2009). Therefore, it is likely that the initial carbonate precipitates in the *Dictothrix* sheath are linked with both heterotrophic and photosynthetic activity. This interpretation is consistent with the presence of distinct but small differences in carbon isotope values between the likely heterotrophically induced stromatolite precipitates and the *Dictothrix* sheath precipitates. Further, more microbiologically oriented research will be required to elucidate the relative importance of heterotrophic and photosynthetic activity in causing the initial *Dictothrix* filament calcification.

The absence of filament calcification in cyanobacteria other than *Dictothrix* at Highborne Cay may be linked with differences in EPS composition, since EPS has been shown to have a strong influence on the style and extent of microbial calcification (e.g. Braissant et al., 2007; Dupraz et al., in press). The EPS of the sheathed cyanobacteria *Schizothrix*, the dominant cyanobacterium in the stromatolites at Highborne Cay, initially has a strong inhibitory effect on carbonate precipitation (Kawaguchi & Decho, 2002). It is possible that the EPS produced by *Dictothrix* has less pronounced inhibitory effect on calcification (e.g. through a reduced Ca-binding capacity compared to other cyanobacterial EPS), allowing for sheath calcification. Alternatively, the local production of EPS by *Dictothrix* could be in balance with degradation by heterotrophic bacteria, effectively reducing the cation-binding potential. Furthermore, if the dense clusters of cyanobacteria in the thrombolites locally have very high rates of photosynthesis, this will result in a pH increase, as is typically observed in microbial mats (Revsebch & Jorgensen, 1986; Visscher et al., 1991). The elevated pH not only favors chemical conditions for precipitation, it also causes the EPS to form gels (Sutherland, 2001) potentially eliminating inhibition of carbonate precipitation. The different calcification mechanisms at Highborne Cay clearly indicate that benthic microbial communities can have a strong control on the type of microbial carbonate precipitation.

The Highborne Cay thrombolitic microbialites demonstrate that penecontemporaneous diageneis can have a strong influence on microbial carbonate fabrics. Abundant carbonate precipitation occurs after the initial, *in vivo* calcification that forms the calcified filaments. The loss of the distinct shape of the calcified cells suggests that there is localized carbonate dissolution as well as precipitation of secondary carbonate cements during early diageneis (Fig. 9). The fine-scale microstructures in the calcified filaments provide additional evidence for carbonate dissolution. The fused and indistinct aragonite crystals present in the *Dictothrix* sheaths that have undergone structural degradation are indicative of multiple stages of aragonite dissolution and reprecipitation (MacIntyre & Reid, 1995; Reid & MacIntyre, 1998). This altered aragonite fabric is a contrast to that present in calcified filaments that have undergone little structural degradation, where aragonite crystals are acicular and distinct. Localized dissolution–reprecipitation is common in a wide range of modern shallow marine carbonates (Reid & MacIntyre, 1998) including subtidal Bahamian microbialites (Planavsky & Ginsburg, 2009). Carbonate under-saturation is likely induced by a combination of sulfide production during initial stages of sulfate reduction, sulfide oxidation, and aerobic respiration (Morse & MacKenzie, 1990; Walter et al., 1993; Visscher et al., 1998; Dupraz & Visscher, 2005; Visscher & Stolz, 2005; Hu & Burdige, 2007).

**Temporal distribution and abundance of calcified cyanobacteria**

Our study offers insights into the factors controlling the temporal distribution of calcified cyanobacteria microfossils (Fig. 10). The rarity of these microfossils since the early Cretaceous (around 145 Ma) (Fig. 10A) has been linked with inhibited fossil formation due to low Ca concentrations (and hence a lower calcium carbonate saturation state) (Arp et al., 2001). Calcium concentration drawdown was linked with the radiation of planktonic calcareous algae such as coccoliths (Arp et al., 2001). This model of ocean chemistry is at odds with modeling work on Phanerozoic cation concentrations, which suggest that the Cretaceous contained the highest Ca$^{2+}$ concentrations in the Phanerozoic (Fig. 10B) (Hardie, 1996; Lowenstein et al., 2001). The model of Hardie (1996) does not take into account the effects planktonic calcareous algae radiation (Arp et al., 2001), but (based on carbonate petrology) the early Cretaceous appears to be a ‘calcite sea’ time period (e.g. Sandberg, 1983), which is consistent with high Ca$^{2+}$ concentrations (Lowenstein et al., 2001). Coccolith radiation is also inferred to have lowered the global marine carbonate saturation state by decreasing the carbonate ion concentrations, which – again – may have decreased the ability of cyanobacteria to form calcified microfossils (Riding, 2000). However, the widespread occurrence of calcifying cyanobacterial filaments in several modern marine localities reveals that
Filament calcification is not a ubiquitous process. Modern oceans, however, demonstrates that cyanobacteria limited number of occurrences of calcified filaments in the Phanerozoic (Ridgwell & Zeebe, 2005) in the Phanerozoic (Fig. 10B). The lowest levels of carbonate supersaturation (Ridgwell, 2005; Hardie, 1996; Lowenstein squares; Horita et al., 2002) estimates of Ca concentration throughout the Phanerozoic. (C) Model of surface calcite saturation state through the Phanerozoic in an ocean with deep-sea carbonate burial caused by a rain of calcified planktonic organisms (lower black line) and in an ocean with carbonate production occurring exclusively on shelf environments (upper black line) (from Ridgwell, 2005). The formation and early diagenetic destruction of calcified filaments in the modern oceans suggests that the low abundance of calcified cyanobacterial microfossils over last 150 Ma and from 250 to 300 Ma may be the results of low preservation potential as well as inhibited microfossil formation due to low calcium or carbonate ion concentrations.

Precursors to these microfossils can form in modern oceans. Besides Highborne Cay, calcified filaments are common in the reef tract off Stocking Island (eastern Bahamas) (MacIntyre et al., 1996) in peritidal environments off Andros Island (western Bahamas) (Hardie, 1977), and in pools on Aldabra Atoll (Seychelles) (Riding, 1977). Their presence is significant since modern oceans are inferred to contain some of the lowest marine Ca$^{2+}$ concentrations (Hardie, 1996; Lowenstein et al., 2001) and have close to the lowest levels of carbonate supersaturation (Ridgwell, 2005; Ridgwell & Zeebe, 2005) in the Phanerozoic (Fig. 10B). The limited number of occurrences of calcified filaments in the modern oceans, however, demonstrates that cyanobacteria filament calcification is not a ubiquitous process.

The destruction of the Highborne Cay cyanobacterial microfossils during early diagenesis suggests that preservation potential could exert a strong control on the abundance of the calcified cyanobacteria in the fossil record. The shift to widespread carbonate production by pelagic organisms dramatically altered the carbon cycle by shifting the dominant carbonate sink from shallow to deep-sea environments (Ridgwell, 2005; Ridgwell & Zeebe, 2005). Geochemical box models of atmosphere-ocean-sediment carbon cycling suggest that this transformation caused a sharp drop in the calcium carbonate saturation states and decreased the size of the DIC reservoir (Ridgwell, 2005) (Fig. 10C). These decreases would have resulted in a marked decline in the acid buffering capacity of seawater, increasing the importance of carbonate dissolution during early diagenesis. We propose that the rarity of cyanobacterial calcimicrofossils since the early Cretaceous is linked in part with this restructuring of the carbon cycle and the corresponding increase in potential for destruction of cyanobacterial microfossils during early diagenesis.

The limited abundance of calcified cyanobacteria microfossils in the Permian (Arp et al., 2001) may also be partially caused by low preservation potential. The Permian was a time of non-skeletal aragonite or high Mg-calcite (e.g. Sandberg, 1983; Lowenstein et al., 2001) and metastable aragonite and high Mg-calcite will be more severely altered during early diagenesis than low Mg-calcite. However, the Triassic is also time of an ‘aragonite sea’ and contains notably more reported occurrences of calcified cyanobacteria than in the Permian. It is likely, therefore, that inhibited formation of calcified cyanobacteria and possibly rock abundance biases are also significant factors controlling the number of occurrences/abundance of calcified cyanobacterial microfossils in the Phanerozoic.

The abundance of calcified filaments in the late Jurassic (Fig. 10A) indicates an interval of high preservation and calcifying potential. This is at odds with models that suggest that the restructuring of the carbon cycle to a system with predominately deep-sea carbonate deposition occurred by this time. As discussed above, the shift to a deep-sea-dominated carbonate cycle would have likely greatly decreased the preservation and calcifying potential of calcified cyanobacteria. Therefore, although there was a large increase in diversity and abundance of calcifying pelagic organisms in the Jurassic (Martin, 1995), it appears they did not become abundant enough to revolutionize the carbon cycle until the Cretaceous. This is in accordance with sedimentological evidence that suggests deep-sea carbonate burial increased throughout the Mesozoic and reached it zenith during the Cretaceous (Siesser, 1993). Thus, the record of calcified cyanobacteria provides insights into the timing of one of the major transitions in Earth’s history and biosphere that is difficult to gauge through traditional proxies, such as the diversity of calcifying pelagic organisms (Martin, 1995) or the percent of ophite complexes containing carbonate (Boss & Wilkinson, 1991).
These traditional proxies for pelagic carbonate production are only weakly linked to amount of carbonate deposition.

CONCLUSIONS

We documented the formation and early diagenetic history of calcified cyanobacteria from a modern open marine setting at Highborne Cay, Bahamas. A single variety of cyanobacteria at Highborne Cay, identified as *Dichothrix* sp., produce the calcified filaments. Calcification initially occurs *in vivo* within the cyanobacterial sheath. The calcified filaments have significantly more positive carbonate δ¹³C isotope values than precipitates from adjacent stromatolites or than the surrounding sediment. These isotopic values suggest photosynthetic activity was the central process driving carbonate precipitation in the sheaths of *Dichothrix* cells. Variation in the calcification styles of Highborne Cay benthic ecosystems (e.g. formation of well-laminated stromatolites versus (non-laminated) thrombolitic microbialites) clearly indicates that there can be a strong ecosystem control on microbial calcification.

During early diagenesis, the calcified filaments are degraded and there is abundant carbonate precipitation. The lack of preservation of the Highborne Cay calcified filaments suggests that the absence of calcified cyanobacteria from periods in the Phanerozoic does not necessarily imply inhibited formation. Poor preservation potential is likely a factor responsible for the lack of calcified cyanobacterial fossils over the past 65 Myr as well as inhibited formation.

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REFERENCES


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**SUPPORTING INFORMATION**

Additional Supporting Information may be found in the online version of this article:

Table S1 Stable isotope values and sample identification for data shown in main text Fig. 8.

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