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Building biogenic beachrock: Visualizing microbially-mediated carbonate cement precipitation using XFM and a strontium tracer

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Abstract
The fate of reef islands is a topic of ongoing debate in the face of climate change-induced sea-level rise and increased cyclone intensity. Increased erosion and changes to the supply of reef-derived sediment may put sand reef cays at risk of dramatic morphological changes. These changes may have negative implications for the existence of reef cay environments, which host vital sea turtle and bird rookery habitats. Beachrock, consolidated carbonate beach sediment in the intertidal zone, forms naturally on many tropical beaches and reduces the erosion rates of these beaches when compared to unconsolidated sand. In spite of the critical role beachrock plays in stabilizing some reef cay shores, the method of beachrock formation is still incompletely understood. In this investigation, beachrock was synthesized using beach sand and beachrock samples from Heron Island (Great Barrier Reef, Australia) in aquarium experiments in which natural beachrock formation conditions were simulated. Beachrock was produced in two aquaria wherein the water chemistry was influenced by microorganisms derived from the natural beachrock ‘inoculum’, whereas no cementation occurred in an aquarium that lacked a microbial inoculum and was controlled only by physicochemical evapoconcentration. The new cements in the synthesized beachrock were analyzed using synchrotron-based X-ray fluorescence microscopy and were identified using a Sr-tracer added to the experimental seawater. The resulting precipitates cement sand grains together and contain abundant microfossils of the microorganisms on whose exopolymer they nucleated, demonstrating the fundamental role microbes play in beachrock formation. These results are of interest because beachrock could be utilized as a natural coastline stabilization strategy on sand reef cays, and in turn, protect the unique habitats reef islands support.
1. Introduction

Of all coastal environments that will be influenced by sea-level rise and increased cyclone intensity, sandy beaches on low elevation coral reef cays are among the most vulnerable due to their susceptibility to erosion. The complex geomorphological changes to coral reef sand cay size, shape, and structure resulting from sea-level rise have been the focus of several recent investigations (Cowell and Kench, 2001; Gibbons and Nicholls, 2006; Perry et al., 2011; Webb and Kench, 2010; Woodroffe, 2008; Zhang et al., 2004). Additionally, damage to coral reefs caused by an anticipated increase in cyclone intensity will likely outpace the recovery rate of corals, which in turn negatively affects other species dependent on the reef (Cheal et al., 2017). These changes, along with island inundation, have the potential to negatively influence sand cays populated by humans (Ford, 2012) and those that provide valuable wildlife habitats such as turtle and bird rookeries (Fuentes et al., 2009; Fuentes et al., 2011; Pike et al., 2015; Poloczanska et al., 2009). Understanding, and potentially counteracting, these alterations to island morphology may be a necessity for the future of life on reef islands.

An important factor in understanding how sand cays will respond to sea-level rise is the role ecosystems play in maintaining coastal stability (Perry et al., 2011; Spalding et al., 2014). Saltwater marshes and mangroves are known to reduce wave energy, wave height, water velocity and turbulence, and thus reduce erosion and/or increase sedimentation (Christiansen et al., 2000; Gedan et al., 2010; Möller et al., 1999; Spalding et al., 2014). Reefs generate the carbonate sediment that make up reef islands, while also providing protection for the islands by reducing wave energy and thus, erosion rates (Kench and Brander, 2006b; Sheppard et al., 2005).

A coastal ecosystem that has received little attention for its potential to aid in maintaining sand cay stability is beachrock. Beachrock forms on many subtropical beaches through the lithification of sediment by cement composed of one or both, aragonite and calcite.
(Gischler, 2008; Hanor, 1978; Neumeier, 1999; Scoffin and Stoddard, 1983; Vousdoukas et al., 2007; Webb et al., 1999). Beachrock formation has previously been attributed to strictly abiotic physicochemical processes (Alexandersson, 1969; Alexandersson, 1972; Davies and Kinsey, 1973; Dickinson, 1999; El-Sayed, 1988; Ginsburg, 1953; Gischler and Lomando, 1997; Meyers, 1987; Moore, 1973; Russell and McIntire, 1965). Biological processes also have been suggested (Davies and Kinsey, 1973; Krumbein, 1979; Maxwell, 1962) with recent studies highlighting the potential importance of microorganisms in beachrock cementation processes (Danjo and Kawasaki, 2013; Khan et al., 2016; Krumbein, 1979; Neumeier, 1999; Novitsky, 1981; Webb and Jell, 1997; Webb et al., 1999). Our recent work (McCutcheon et al., 2016) examining beachrock from Heron Island (Capricorn Group, Great Barrier Reef, Australia) demonstrated that microbes are actively contributing to carbonate dissolution and precipitation in beachrock. Beachrock hosts a unique shoreline ecosystem of lithophytic microorganisms that aid in generating these lithified deposits by enabling carbonate cement precipitation (Díez et al., 2007; McCutcheon et al., 2016; Webb and Jell, 1997; Webb et al., 1999). Beachrock forms only in the intertidal zone, and is known to form relatively quickly on timescales as short as a few years (Chivas et al., 1986; Easton, 1974; Frankel, 1968; Vousdoukas et al., 2007). These spatial and temporal constraints on beachrock cementation have allowed relict beachrock to be utilized as Quaternary sea-level and shore-line indicators (Mauz et al., 2015; Ramsay and Cooper, 2002; Tatumi et al., 2003; Vousdoukas et al., 2007). Although beachrock has long been known to reduce erosion of unconsolidated beach sediments by protecting them from wave action (Calvet et al., 2003; Chowdhury et al., 1997; Dickinson, 1999; Kindler and Bain, 1993), there has been little investigation into the potential use of beachrock as a means of stabilizing beaches that are susceptible to erosion. In addition, as the health of many coral reefs decline (Pandolfi et al., 2011) the extent of the protection they provide to their associated islands decreases, making it critical to seek alternative strategies for protecting reef islands (Sheppard et al., 2005).
Although there is a growing body of research suggesting that microorganisms play an important role in beachrock formation, there has been little experimental work linking microbial activity to beachrock cement precipitation. In this investigation, natural beachrock formation conditions were simulated in the laboratory to test the role of microbial activity in beachrock cementation. Synchrotron-based X-ray fluorescence microscopy (XFM) was used to characterize the newly formed carbonate cements. These results provide a better understanding of the role of microorganisms in beachrock generation, and could be used to guide future studies examining in situ beachrock formation with the aim of stabilizing reef islands as sea-level rises.

2. Materials and Methods

2.1 Field site description and sample collection. Heron Island (750 m × 240 m) is a sand cay on Heron Reef, a lagoonal platform reef (4.5 km × 10 km) in the Capricorn Group in the southern Great Barrier Reef (Fig. 1a) (Jell and Webb, 2012; Webb et al., 1999). The northern and southern shores of Heron Island host beachrock outcrops as much as 20 m in width, which dip seaward at slopes of 4-16°. The beachrock is lithified primarily by isopachous, acicular aragonite as well as micritic cements (Gischler, 2008; Webb et al., 1999). The presence of cemented microbialites in the Heron Island beachrock has been one of the primary pieces of evidence suggesting a microbial influence in the lithification of these deposits (McCutcheon et al., 2016; Webb and Jell, 1997; Webb et al., 1999). The microbial beachrock ecosystem is composed of a consortium of microbial endoliths living on, within, and between the carbonate grains that make up these deposits (McCutcheon et al., 2016). Several generations of beachrock occur on Heron Island, with blocks of older beachrock cemented in place by younger beachrock. Examination of the different beachrock generations suggests that cementation is an ongoing process; boring of carbonate grains by euendolithic cyanobacteria releases ions into solution which are precipitated as new cement (McCutcheon
et al., 2016). Over time, this process results in a transition from high porosity and low cement content, to low porosity and high cement content. The ‘self-healing’ property of beachrock to re-cement blocks into place after they have been ripped up by storm activity is examined in this study. Samples of carbonate beach sand, the apparent youngest generation of beachrock and associated microbial endoliths were collected from the southern beachrock outcrop of Heron Island. The carbonate beach sand was collected from the supratidal portion of the beach and consisted of carbonate sediment 0.5-3 mm in diameter. The apparent youngest generation of beachrock was selected as a starting material for this study because it contains less cement than its older counterpart, a characteristic of beachrock that results in the younger generations being more porous and hosting more microbial biomass relative to older beachrock (McCutcheon et al., 2016). Furthermore, younger beachrock was chosen for experimental use as it contains less cement than the older beachrock, making it easier to discern the precipitation of new cements during the experiment.

2.2 Experimental aquaria design. The samples described above were used in three experimental aquaria to reconstruct the biogeochemical conditions of the Heron Island beach. The aquaria were housed in a Conviron Adaptis A1000 growth chamber operating at 25°C, and 12 h of light (06:00 - 18:00; light intensity: 700 μmol) and 12 h of dark (18:00 - 06:00). Each aquarium was 25 × 17 × 19 cm (l × w × h) in size and contained 8 cm of sediment in the bottom (Fig. 2). Two of the aquaria acted as experimental systems while the third was used as a control. The beachrock samples were fragmented so that the ~1 cm-thick surface layer containing macroscopically visible endoliths was separated from the underlying ‘inner’ beachrock. The ‘fragmented beachrock’ (henceforth referred to as FBR) aquarium contained 7 cm of fragmented inner beachrock covered with 1 cm of the fragmented surface layer beachrock (Fig. 2). The ‘sand’ aquarium (henceforth referred to as Sand) contained 7 cm of 90% (by weight) beach sand seeded with 10% inner beachrock fragments. This layer was
topped with 1 cm of 90% beach sand seeded with 10% surface beachrock fragments (Fig. 2). The control aquarium (Control) contained 8 cm of beach sand from Heron Island with no beachrock ‘inoculum’. The base of each aquarium was wrapped with aluminium foil up to the surface of the sediment to prevent light from stimulating cyanobacteria growth through the sides of the glass.

One end of each aquarium was partitioned off with a plastic mesh screen creating a sediment-free reservoir for the addition and removal of seawater. The seawater was able to passively flow through the screen to infiltrate the sediment as a means of mimicking tidal activity. In each aquarium, the alternating addition (06:00 – 06:30 and 18:00 – 18:30), and removal of seawater (00:00 - 00:30 and 12:00 - 12:30) occurred at 6 hour intervals using Masterflex L/S® Precision Variable-Speed Console Drive (07528 series) peristaltic pumps and Norprene® tubing (internal diameter of 2.4 mm). A volume of 1 L of seawater remained in each aquarium at all times saturating the bottom 2 cm of the sediment and acted as ‘low tide’. A volume of 3 L was added to each aquarium as an incoming ‘high tide’, resulting in a water depth of 13 cm (5 cm above the surface of the sediment). It is important to note that ‘fresh’ seawater (Tropic Marin™ Sea Salt, salinity of 35.0) was prepared for each incoming tide and the ‘old’ seawater discarded after each outgoing tide. Nitrogen and phosphorous were added to the seawater in concentrations equal to 10% of those in standard BG-11 cyanobacteria growth medium (109 mg/L NO₃⁻ added as NaNO₃; 2.2 mg/L PO₄³⁻ added as K₂HPO₄) (Vonshak, 1986). These concentrations are comparable to those measured in groundwater on Heron Island (Chen, 2000). Strontium (40 mg/L Sr²⁺ added as SrCl₂·6H₂O) was used as a tracer to distinguish new carbonate cement from that already present in the natural material (Banner, 1995; Capo et al., 1998). The concentration of Sr was chosen such that new cement could be identified by a higher than normal Sr content, but would not be so high as to interfere with mineral precipitation or cause the aquaria to be supersaturated with
respect to strontium carbonate minerals. This latter point was confirmed by checking mineral saturation indices using PHREEQC Interactive Version 3.1.1 (Parkhurst and Appelo, 1999). The experimental aquaria were run for eight weeks.

2.3 Water chemistry analysis. Water samples were collected every 7 days. On each sampling day, waters were collected at 07:00, 09:00, 11:00, 19:00, 21:00, and 23:00; providing a means of documenting aqueous geochemistry conditions in the aquaria at the beginning, middle, and end of high tide under both light and dark conditions. The pH, conductivity (mS/cm, then converted to salinity) and dissolved oxygen (DO) (mg/L) of the bulk water were measured in each aquarium at each sampling time point. Dissolved inorganic carbon was determined by analyzing water samples using a Shimadzu TOC-L CSH Total Organic Carbon Analyzer by measuring total inorganic carbon (TIC). Water samples were collected, filtered (0.45 µm pore-size), and analyzed for cations (Ca\(^{2+}\), K\(^{+}\), Mg\(^{2+}\), S\(^{6+}\), Sr\(^{2+}\)) using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) using a Perkin Elmer Optima 3300 DV (measurement uncertainty: ≤12%). Phosphorous (P as PO\(_4^{3-}\)) and nitrogen (N as NO\(_x\)) concentrations were measured using a Lachat QuikChem8500 Flow Injection Analyzer (FIA).

2.4 Cement characterization. The surface of the sediment in each aquarium was visually checked weekly for signs of lithification, with samples of what appeared to be newly lithified beachrock being collected each week after the first two weeks. Polished thin sections of the original beach sand, fragmented inner beachrock, fragmented surface beachrock, and weekly samples of synthetic beachrock collected from the Sand and FBR aquaria were analyzed on the X-ray fluorescence microscopy (XFM) beamline at the Australian Synchrotron (Paterson et al., 2011). The petrographic thin sections were affixed to a Perspex sample holder using Mylar tape and mounted on the sample translation stages of the X-ray microprobe. A monochromatic X-ray beam (18.5 keV) was focused to ~2.0 µm using Kirkpatrick-Baez
mirrors (Paterson et al., 2011). The Maia detection system used on the XFM beamline enables fast, high definition elemental mapping of complex natural materials (Paterson et al., 2011; Ryan et al., 2010; Ryan et al., 2014). Regions of interest on each thin section were raster-scanned on-the-fly through the focused beam to accumulate X-ray fluorescence spectra at each scan pixel. The pixel size was 1×1 µm, 2×2 µm or 10×10 µm and the dwell time per pixel was between 0.33 and 1.0 msec. GeoPIXE software was used to produce elemental concentration maps from the raw data (CSIRO, 2011). Elemental concentrations were quantified by calibrating to thin foil standards of Pt, Fe, and Mn of known areal density. A large number of elements were simultaneously mapped and analyzed (P, S, Cl, Ar, K, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, Br, Sr) and the information from maps of Ca and Sr were the main focus of this investigation.

The polished thin sections of synthesized beachrock and whole mount samples of the associated microbial mats collected from the aquaria were characterized using scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDS) using a JEOL JSM-7100F Field Emission SEM (FE-SEM). The whole mount samples of microbial mat and associated grains were fixed using 2.5% glutaraldehyde and dehydrated through an ethanol dehydration series (25%, 50%, 75%, 100%, 100%, 100%) using a Pelco Biowave microwave (each step: 250 W, 40 s, no vacuum) prior to being critical point dried (Tousimis Samdri-PVT-3B critical point dryer). The dried samples were mounted on stainless steel slug stubs using adhesive carbon tabs. All thin sections and whole mount samples were coated with 5 nm of iridium using a Quarum Q150T S sputter coater. The thin sections were examined using back-scattered electron (BSE-SEM) mode at 15 kV and a working distance of 12 mm. Whole mount samples were examined using secondary electron (SE-SEM) mode at 1, 2, or 5 kV at a working distance of 9 mm. Polished thin-sections of beachrock were observed using a Leica DM6000M microscope equipped with a Leica DFC310 FX camera. The starting
materials used to construct the aquaria were characterized using light microscopy and XFM as described above (Fig. 3).

3. Results

3.1 Water chemistry. The average pH, and DO of the initial seawater were 8.30 and 9.1 mg/L, respectively (Fig. 4a-b). The pH of the FBR and Sand aquaria increased during the day to average values of 8.77 and 8.79 at 11:00, respectively; and decreased during the night to average values of 8.15 and 8.18 at 23:00, respectively (Fig. 4a). The pH of the Control aquarium remained steady at ~8.30 during both light and dark conditions (Fig. 4a). The DO of the FBR and Sand aquaria increased to average values of 16.8 and 15.5 mg/L at 11:00 and decreased to average values of 4.1 and 4.9 at 23:00, respectively (Fig. 4b). The 11:00 averages are underestimates of the oxygen content of the FBR and Sand aquaria, as they reached the saturation limit of the DO meter of 20 mg/L by week 5 and 4 of the experiment, respectively. The DO of the seawater decreased upon addition to the Control aquarium, followed by a slight increase during the day to a 11:00 time point average of 8.6 mg/L, and a small decrease at night to a 23:00 time point average of 7.4 mg/L (Fig. 4b). The salinity of the initial seawater was 35.0, and the average salinity in the FBR, Sand, and Control aquaria over the course of the experiment were 38.4, 38.3, and 37.9, respectively.

The concentration of DIC in the Control aquarium increased from 30.4 mg/L in the initial seawater during the day to 33.4 mg/L at 11:00, and at night to 33.6 mg/L h at 23:00 (Fig. 4c). DIC in the FBR and Sand aquaria followed the same trend, increasing by 9:00 to 32.5 mg/L and 33.2 mg/L, and then respectively declining to 26.9 mg/L and 28.0 mg/L by 11:00. At night, the DIC increased to 38.2 mg/L in both aquaria by 23:00 (Fig. 4c).

The concentrations of Ca$^{2+}$ and Mg$^{2+}$ increased during both light and dark conditions in all three aquaria (Fig. 4d,e). The concentration of Sr$^{2+}$ measured in the initial seawater was 39.1
ppm (vs. target of 40 ppm) and exhibited minor fluctuations between 38.4 and 40.9 ppm in all three aquaria during light and dark conditions (Fig. 4f). Nutrient (N and P) concentrations decreased during both light and dark conditions in the FBR and Sand aquaria (Fig. 4g,h). From an initial seawater concentration of 24.7 ppm, nitrogen (as N in NO₃⁻) decreased in the FBR and Sand aquaria to 11:00 average values of 22.9 and 21.5 ppm, and 23:00 average values of 23.9 and 22.2 ppm, respectively (Fig. 4g). Phosphorous (as P in PO₄³⁻) decreased from 0.79 ppm in the initial seawater to 0.56 and 0.49 ppm by 11:00 and to 0.72 and 0.61 ppm by 23:00 in the FBR and Sand aquaria, respectively (Fig. 4h).

3.2 Cement formation and characterization. Over the eight week experiment, microbial growth in the FBR and Sand aquaria resulted in the formation of microbial mats on the surface of the sediment, reminiscent of those found on the beachrock on Heron Island. Secondary electron SEM of whole-mount samples of the microbial mats revealed extensive growth of filamentous cyanobacteria in association with cocci and bacilli bacteria (Fig. 5).

Small, millimeter- to centimeter-sized pieces of beachrock were synthesized in the top 5 cm of sediment in the FBR and Sand aquaria. Beachrock synthesis was first observed three weeks into the experiment. The relative size of the new beachrock grains increased over time to a maximum grain diameter of 2 cm. No cemented grains were found in the Control aquarium at any point during the experiment.

X-ray florescence microscopy of thin sections of the synthesized beachrock from the FBR and Sand aquaria revealed that the new cement precipitates could be easily identified due to being enrichment in Sr (Fig. 6-9,11) compared to the original carbonate sediment and cements (Fig. 3). The original aragonite sand grains and cements contained 0.13 atomic % Sr while the new cements precipitated during the experiment contained an average of 0.85 atomic % Sr based on EDS analysis. Figure 6 shows cement precipitation in a large region of a sample collected from the surface of the FBR aquarium after eight weeks, in which the
plane of the thin section is parallel to the surface of the sediment in the aquarium, while Figures 7-9a-d highlight smaller structures within this region. The new precipitates can be seen cementing sand grains together and coating grain surfaces (Fig. 7a,d,e). Viewing the new cements using SEM revealed abundant microfossils exhibiting a diverse range of cell morphologies (Fig. 7b) that are commonly preserved as fossilized microcolonies (Fig. 7f-h). Many of the cement coatings on grain surfaces form dendritic microbialites; they contain mineralized cells as well as new microbial borings (Fig. 8). Structurally, these newly formed microbialites are very similar to those pre-existing in the fragmented beachrock added to the aquaria but can be differentiated from those due to the difference in Sr content (Fig. 9).

Some of the precipitates exhibit a ‘wheat-sheaf’ morphology, interpreted as aragonite (Fig. 10a,b), while others are present as nanoscale granules (c,d). When viewed in a whole-mount sample, these precipitates are found in association with extracellular polymeric substances (EPS) (Fig. 10a,c). EDS of the cement (Fig. 10 e-g) showed a range of Mg-content, from 0.01 to 12 atomic %, suggesting that co-precipitation of aragonite and calcite may be occurring within microenvironments in the beachrock system (Berner, 1975; Ries et al., 2008). The biofilm observed growing on the top surface of the sediment and in the interstices between sediment grains contains both trapped-and-bound material and newly precipitated carbonate (Fig. 11).

4. Discussion

4.1 Diurnal microbial activity as a trigger for beachrock cementation through carbonate dissolution and precipitation. The data presented in Figure 4 is intended to demonstrate the overall trends in the water chemistry as a function of the diurnal changes in microbial activity in the FBR and Sand aquaria. During the day, cyanobacterial and algal oxygenic photosynthesis resulted in the measured increase in dissolved oxygen, coincidentally
increasing the pH through hydroxyl anion production. At night, heterotrophy would have been the dominant form of microbial metabolism, resulting in oxygen consumption and a decline in pH after dark. Note, the changes in water chemistry only reflect the bulk water overlying the sediment and do not represent the pore water in the biofilm or underlying sand. As a result, the changes that were measured are a diluted product of what is taking place in the sediment and it is expected that changes in water chemistry between the grains are far greater in magnitude. There is also potential that the bulk water chemistry does not reflect other forms of microbial metabolism known to contribute to carbonate mineral precipitation, such as that of sulfate reducing bacteria (SRB) (Braissant et al., 2007; Gallagher et al., 2012) and ureolytic bacteria (Ferris et al., 2004; Mitchell and Ferris, 2006). Although natural beachrock forms in the intertidal zone, and is thus well oxygenated overall, these organisms could be found in protected anaerobic microenvironments below the surface of the beachrock.

The increase in the concentrations of Ca$^{2+}$ and Mg$^{2+}$ in the Control aquarium are likely a result of evaporation (Fig. 4d,e). Interpreting the changes in cation concentrations in the FBR and Sand aquaria is more difficult because they represent the combined effects of: evaporation, microbial processes, mineral dissolution, and mineral precipitation. The summation of these processes makes it difficult to discern which processes took place in the aquaria at any given time. However, the overall changes in Ca$^{2+}$ and Mg$^{2+}$ concentrations are expected to be largely representative of the net balance between mineral dissolution and precipitation. For instance, the concentration of Ca$^{2+}$ measured at 07:00 in all three aquaria was greater than that measured in the ‘fresh’ seawater added at 06:00. The increase in Ca$^{2+}$ concentration measured in the Control aquaria was likely a result of evaporation, however, the greater magnitude increases measured in the FBR and Sand aquaria were likely the product of two microbial processes taking place contemporaneously: 1) mineral dissolution
resulting from cyanobacteria boring into the grains; and 2) heterotrophic consumption of EPS. First, endolithic cyanobacteria in the FBR and Sand aquaria were dissolving carbonate in detrital grains, producing cations in solution. Some cyanobacteria are known to induce spontaneous carbonate dissolution at the cell-borehole interface by causing a reduction in the ion activity product of carbonate (Garcia-Pichel et al., 2010). Once in solution, the Ca$^{2+}$ ions are internalized by the apical cell of the cyanobacterium filament, transported down the length of the filament through intercellular Ca$^{2+}$-ATPase pumps, and finally expelled away from the borehole into the surrounding solution (Garcia-Pichel et al., 2010). Antiparallel transport of two protons along the filament towards the boring front is necessary to balance each Ca$^{2+}$ ion moving away from the excavation site via this intercellular pathway (Garcia-Pichel et al., 2010). These protons can then contribute to carbonate dissolution, after which the resultant HCO$_3^-$ can be utilized by the cyanobacterium for photosynthesis (Garcia-Pichel et al., 2010). Previous studies on the occurrence of phototrophic boring in coastal environments suggest that it can dissolve up to 0.6 kg of CaCO$_3$/m$^2$/year (Chazottes et al., 1995). In natural beachrock formation in the intertidal zone, possible explanations for cyanobacterial boring include: nutrient or space acquisition; and protection from grazing, UV radiation, wave activity, and desiccation during low tide (Cockell and Herrera, 2008; McCutcheon et al., 2016). Some of the borings were likely present in the grains prior to sample collection; however, those found in the newly precipitated cements indicate that active microbial boring was taking place during the experiment (Fig. 8b). In the aquaria, the microbes lacked stressors such as wave activity, macroscopic grazers, nutrient limitation, and solar UV radiation, suggesting that space acquisition or protection from desiccation during low tide may be the incentive for microbial boring in beachrock. Some of the pre-existing and new borings have been filled with new cement made visible by its high Sr-content (Fig. 6, 7), which is consistent with reports of carbonate re-precipitation as a result of localized
microenvironments of carbonate supersaturation where Ca$^{2+}$ ions are being excreted by boring phototrophs (Bathurst, 1966; Garcia-Pichel et al., 2010; Margolis and Rex, 1971). The presence of cement-filled borings across grain boundaries has been known to provide strength to carbonate structures, such as stromatolites (Macintyre et al., 2000).

The second possible cause for the increase in Ca$^{2+}$ concentration is heterotrophic consumption of EPS. This substance is rich in carboxyl groups that give it a net negative charge, enabling it to bind cations such as Ca$^{2+}$ that, in turn, attract low molecular weight organic compounds (Braissant et al., 2009; Flemming and Wingender, 2010; Körstgens et al., 2001). Decho et al. (2005) demonstrated that the EPS production rate in cyanobacterial mats coincides closely with photosynthesis, with the greatest EPS production occurring during midday. In the present study, as cyanobacterial photosynthesis began to produce oxygen in the morning, heterotrophic metabolism in the aquarium would have increased and destabilized the EPS structure by oxidizing the organic compounds to bicarbonate (Braissant et al., 2009; Decho et al., 2005). The bicarbonate would have then been able to react with the ‘reservoir’ of cations available in the EPS microenvironment. Decho et al. (2005) also demonstrated that heterotrophic consumption of EPS has a diurnal cycle that peaks with maximum photosynthesis during the day, as well as just after dark. Consumption of the EPS releases the adsorbed cations back into solution, causing the concentration of Ca$^{2+}$ in solution to increase and making carbonate precipitation favorable. Carbonate mineral precipitation by this process has resulted in mat lithification in many past and modern environments (Aloisi, 2008; Altermann et al., 2006; Braissant et al., 2007; Dupraz et al., 2009; Dupraz and Visscher, 2005). Note, the intricate relationships between the dissolved cations and mineral dissolution and precipitation, biofilm adsorption, and evaporation make it difficult to interpret the cation concentration data beyond the described overarching trends.
The beginning of the cementation process, which resulted in the formation of the mineralized microbialites observed in the aquaria (Fig. 7-10), is captured in the nucleation of new Sr-enriched carbonate grains within the biofilms (Fig. 11). The production of biofilm on near surface grains in the FBR and Sand aquaria was extensive enough to provide nucleation sites for carbonate precipitation such that the resultant cements were able to connect grains in the span of only eight weeks, demonstrating the rapid nature of this process. This characteristic is also highlighted by the presence of borings in the new cements (Fig. 8b) and new cements filling borings, illustrating that beachrock is exceptionally dynamic. It is likely that the initial stabilization and cementation of sand by microbes allows the longer-term, more pervasive isopachous cement, common in the older beachrock, to form in the underlying sand. As consolidation progresses, it appears that the interstitial spaces in the beachrock become increasingly filled with cement, causing a reduction in the volume of pore space available for habitation by endolithic cyanobacteria (McCutcheon et al., 2016). The reduced porosity has a two-fold effect on microbial growth: while decreasing the space available for biofilm growth it also reduces the amount of water than can be retained in the beachrock interstices during low tide, thus increasing the likelihood of biofilm desiccation. Although the older beachrock still hosts an endolithic microbial community, a decline in microbial biomass over time would likely cause a corresponding decrease in the microbial contribution to cementation. A subsequent increase in porosity of the beachrock, such as would occur through damage to the outcrop by storm activity, could instigate a resurgence of microbial activity and cementation.

4.2 Sea-level rise, beachrock, and island stability. The response of reef islands to sea-level rise is one of ongoing discussion. Several studies have suggested that these islands will be vulnerable to sea-level rise through increased erosion, inundation, and salinization of the water table (Church et al., 2006; Gibbons and Nicholls, 2006; Khan et al., 2002; McLean and
Tsyban, 2001; Mimura, 1999; Nicholls et al., 2007; Roy and Connell, 1991; Woodroffe, 2008; Yamano et al., 2007). The prevailing hypothesis, that reef islands will be subjected to extensive erosion in the event of sea-level rise, is largely due to application of the Bruun Rule to these shorelines (Bruun, 1962; Schwartz, 1967). Such predictions, however, have been criticized because island shores cannot be treated in the same manner as linear continental coastlines (Cooper and Pilkey, 2004; Cowell and Kench, 2001; Webb and Kench, 2010). Reef islands, and particularly sand cays, are dynamic structures that change in morphology as a result of changes in: wave regimes, longshore currents, ocean dynamics, sea-level, and weather, particularly storm events (Cheal et al., 2017; Church et al., 2006; Kench and Brander, 2006a; Mimura et al., 2007). High energy events such as cyclones and tsunamis can result in either net island erosion (Harmelin-Vivien, 1994; Stoddart, 1963) or accretion (Kench et al., 2006; Maragos et al., 1973). Cyclone intensity is predicted to increase in the coming years and result in degradation of coral reefs, a trend already being observed in the central-south part of the GBR (Cheal et al., 2017). The frequency at which a particular reef island experiences storms affects the size of the sediment of which the island is comprised. Sand-sized grains dominate islands that experience low storm frequencies, while islands that experience frequent storms tend to be composed of rubble (Chivas et al., 1986; Gourlay, 1988; Stoddart, 1963). Some models suggest that reef islands are less delicate than previously thought and will remain stable in the event of the projected sea-level rise of ~0.5 m by 2100 (Kench et al., 2005). That is not to say, however, that island morphology and location will not change with increasing sea-level. Predicting these changes requires a better understanding of the many factors that influence reef island morphodynamics, which necessitates better monitoring of current changes to reef island morphology (Kench and Harvey, 2003; Webb and Kench, 2010).
A major factor in reef island sedimentological processes is the type and health of the reef from which the islands' sediments are derived (Woodroffe et al., 2007). The reef acts as a sediment factory by producing carbonate grains from the skeletal remains of invertebrates living in and on the reef, as well as through erosion of the reef framework by physical and biological processes (Perry et al., 2011). Once sediment is generated by the reef, the grains are susceptible to physical abrasion, microbial boring, and chemical dissolution; the summation of these processes alter size, shape, and density of the sediment that reaches the island (Perry, 2000). The sediment is deposited on the beach, where it becomes the starting material for potential beachrock formation. The species richness and relative abundances of the organisms (corals, coralline algae, foraminifera, molluscs) from which reef sediment is generated will alter the type, quantity, hydrodynamic properties, and rate of deposition of the sediment available for island building (Perry et al., 2011; Yamano et al., 2000). Predicting how ecological problems such as overfishing, pollution, coral disease and bleaching, changes in storm intensity, sea-level-rise, and ocean acidification will alter reef health is not a small task (Hoegh-Guldberg et al., 2007; Jackson et al., 2001; Kuroyanagi et al., 2009; Pandolfi et al., 2003; Perry et al., 2011; Ries et al., 2009), however, understanding how reefs will respond to these changes is necessary for predicting their ability to supply sediment for reef island building as sea-level rises.

The dynamic nature of reef islands means that it will not be possible to avoid all changes to island shape, size, and position on the reef flat. In cases where island erosion is likely to increase in undesirable locations, such as those inhabited by humans or that provide unique habitats for organisms, implementing strategies to minimize erosion may be necessary. Beaches dominated by sand-sized grains are more susceptible to erosion than those composed of rubble (Perry et al., 2011), and the prevalence of beaches composed of rubble grade sediment may increase in the event of mass coral bleaching (Baker et al., 2008). The combination of these factors means that sand beaches may be particularly vulnerable, and erosion or inundation of
these shorelines may negatively impact sea turtles that rely on supratidal sandy beaches for nesting (Fuentes et al., 2009; Fuentes et al., 2011; Pike et al., 2015; Van Houtan and Bass, 2007). Beachrock formation may provide a natural means of reducing erosion of sand beaches on reef islands. The intrinsic process by which beachrock forms, demonstrated in this study, restricts it to the intertidal zone where it will absorb a large portion of the wave energy that reaches the shore and protect the supratidal part of the beach from storm activity and erosion. Since lithification is limited to the intertidal zone, the supratidal sand remains unconsolidated and suitable for nesting. Beachrock is found naturally on islands that host turtle rookeries, which is a critical point in the potential to employ beachrock as a means of stabilizing beaches because it maintains the shore as a ‘beach’, unlike other coastline habitats such as saltwater marshes or mangroves (Christiansen et al., 2000; Gedan et al., 2010; Spalding et al., 2014). The dynamic nature of beachrock means that it may continue to form in the intertidal zone even in the event the island migrates on the reef flat, continuing to protect the unconsolidated sand further up the shore.

The beachrock on Heron Island shows evidence of multiple generations of cementation through the presence of older beachrock blocks, presumably ripped up during storms, being cemented in place by younger beachrock. We have previously proposed an explanation for how beachrock blocks are re-cemented by microbially generated precipitates (McCUTCHEON et al., 2016). This ‘self-healing’ characteristic of beachrock is useful for stabilizing shorelines because these outcrops can regenerate on decadal or shorter time scales. The FBR aquarium was, in part, designed as a means of investigating this self-healing property of beachrock and successfully recreated a small-scale version of a beachrock outcrop damaged by a storm. This system also provides a natural analogue to the recent advances in self-healing bioconcrete (Jonkers et al., 2010; Wiktor and Jonkers, 2011).
It is currently unknown how widespread formation of beachrock could alter large-scale beach morphodynamics through changes in sediment erosion and deposition (Cooper, 1991; Larson and Kraus, 2000; Sumer et al., 2005; Vousdoukas et al., 2007). The presence of beachrock on cay shores should be considered when predicting the morphological behavior of reef cays, making it necessary to understand the processes driving beachrock formation. Further investigations are required to understand how beachrock will factor into the already complex conversation surrounding reef island responses to sea-level rise and reef health, especially if there is potential to purposefully enhance these dynamic shoreline structures as a strategy for maintaining reef cay stability.

5. Conclusions

The beachrock synthesis experiment conducted in this study demonstrated the fundamental role microorganisms play in beachrock cementation processes, and suggested that physicochemical controls such as evaporation and tidal wetting and drying are not sufficient to instigate cement precipitation. The use of strontium enriched seawater enabled identification of the new cements using XFM. Cementation appears to be driven by cation generation through cyanobacteria dissolution of carbonate grains and subsequent precipitation of new cements in association with EPS. High-resolution SEM of these precipitates, composed primarily of aragonite, revealed abundant microfossils. The diversity of observed microfossils indicates that entire microbial biofilms were becoming mineralized during the beachrock formation process. These results provide a valuable contribution to the current understanding of the biogeochemical controls on beachrock formation. These findings may be applied to designing in situ beachrock cementation experiments, which, in turn, may aid in developing strategies to utilize beachrock as a natural means of stabilizing vulnerable reef islands against sea-level rise.
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Figure Captions

Figure 1. (a) Location of Heron Island on Heron Reef in the Capricorn Group of the Great Barrier Reef off the east coast of Queensland, Australia (Google Earth, 2014). (b) Beachrock in the intertidal zone along the southern shore of Heron Island. (c) The natural beachrock was used as a starting material in the beachrock synthesis experiments. (d) Visible growth of endolithic cyanobacteria near the surface of the beachrock.

Figure 2. The aquarium design used in the beachrock formation experiments. Adding and removing seawater to and from each of the three aquaria using peristaltic pumps simulated tidal activity. The three aquaria differed in their sediment content: 1) the fragmented beachrock (FBR) aquarium contained 100% broken beachrock; 2) the Sand aquarium
contained 10 wt% fragmented beachrock and 90 wt% beach sand; and 3) the Control aquarium contained 100% beach sand.

Figure 3. Characterization of the fragmented beachrock and beach sand used in the beachrock formation experiments. These materials are characterized using: 1) photography of whole samples, 2) plane-polarized light (PPL), 3) cross-polarized light (XPL), 4) XFM of Ca content, and 5) XFM of Sr content of polished thin sections. XFM scan conditions: pixel size: 10×10 µm, dwell time: 0.56 msec.

Figure 4. Water chemistry plots showing the change over time of mean (a) pH, and concentrations of (b) dissolved oxygen, (c) DIC, (d) Ca\(^{2+}\), (e) Mg\(^{2+}\), (f) Sr\(^{2+}\), (g) NO\(_x\)-N, and (h) PO\(_4^{3-}\)-P. Each data point is a time point average for the eight week experiment to reflect overall trends in the water chemistry.

Figure 5. Secondary electron micrographs showing the biofilms that formed on the surfaces of the (a-b) FBR and (c-f) Sand aquaria after the eight week experiment. The biofilms are composed of filamentous cyanobacteria producing abundant EPS, and associated heterotrophs.

Figure 6. XFM showing the (a) Sr and (b) Sr-Ca content in a sample collected from the surface of the FBR aquarium after eight weeks of the experiment. In (a) the color scale indicates Sr concentration, with bright yellow regions having the highest Sr content. In (b) bright yellow regions indicate higher Sr content, while bright blue indicates higher Ca content. Note, Sr-rich regions (bright yellow in (a) and (b)) indicate new cement precipitation. The plane of the sample is parallel to the surface of the sediment in the
aquarium. Boxes in (b) indicate regions depicted in Fig. 7-9. XFM scan conditions: pixel size: 2×2 µm, dwell time: 0.33 msec.

Figure 7. (a) XFM showing the Sr-Ca content of a portion of the week 8 Sand aquarium sample shown in Fig. 6. Note, bright yellow regions indicate higher strontium content, while bright blue indicates higher calcium content. (b-c) These new cements (yellow in (a)) show a diverse assortment of microfossil morphologies. (d-e) The newly precipitated carbonate can be seen cementing sand grains together. (f-h) In many cases the new cements contain fossilized microcolonies. XFM scan conditions: pixel size: 2×2 µm, dwell time: 0.33 msec.

Figure 8. (a) XFM and BSE-SEM showing the Sr-Ca content and structure of a small region of the sample depicted in Fig. 6. Note, bright yellow regions indicate higher strontium content, while bright blue indicates higher calcium content. (b) In-filled microfossils of filamentous cyanobacteria seen in longitudinal section along with new borings visible among the microfossils. Most of the new carbonate contains microfossils (c-f) enclosed in EPS and infilled with micritic cement (f). XFM scan conditions: pixel size: 2×2 µm, dwell time: 0.33 msec.

Figure 9. (a) XFM highlighting the Sr-Ca content and (b) BSE-SEM micrograph of a Sr-enriched microbialite that formed in the FBR aquarium. Compared to (c) XFM and (d) BSE-SEM of a natural Heron Island beachrock microbialite, cementing detrital grains together. Note, in (a) and (c), bright yellow regions indicate higher strontium content, while bright blue indicates higher calcium content. XFM scan conditions: (a) pixel size: 2×2 µm, dwell time: 0.33 msec; (c) pixel size: 2×2 µm, dwell time: 1.0 msec.
Figure 10. BSE-SEM micrographs with EDS demonstrating the structural and chemical heterogeneity of carbonate precipitates: a wheat-sheaf morphology as (a) a whole mount and (b) a thin section, interpreted as aragonite, and as nanometer-scale granules of carbonate precipitated on EPS in (c) a whole mount and (d) thin section. EDS spectra (e-g) demonstrate varying Mg-content.

Figure 11. A cross-section of an embedded biofilm collected from the surface of the Sand aquarium after eight weeks viewed using (a) optical microscopy and (b) XFM. The bright yellow grains in (b) show the occurrence of new mineral nucleation, while the blue grains indicate trapping-and-binding. Bright yellow regions indicate higher strontium content, while bright blue indicates higher calcium content. XFM scan conditions: pixel size: 1×1 μm, dwell time: 1.0 msec.

References


alkaline pH and implication for formation of carbonate minerals. Geobiology, 5: 401-411.


Fig. 1
Fig. 2
Fig. 3
Fig. 4
Fig. 6
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Fig. 9
Fig. 10
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