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Microbially mediated carbonate precipitation within microbial mat in hyper-saline lakes of the Bahamas

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Microbially mediated carbonate precipitation within microbial mat in hyper-saline lakes of the Bahamas

by

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Abstract

Difficulties is precipitating dolomite abiotically have lead to researchers examine the relationship that microorganisms may have in the process of precipitating some carbonates. It is thought that the high activity of magnesium in seawater inhibits its uptake into the crystal lattice of calcite, partly due to the high bonding affinity to sulfate, and that sulfate reducing bacteria present in microbial mats may reduce the sulfate concentration of surrounding water and therefore remove a key thermodynamic barrier to dolomite precipitation. There are also some grain morphologies of carbonates which previous work has linked to the microbial mediation of carbonate precipitation. In this study, two sediment cores, each approximately half a meter long, were examined. The cores have abundant microbial mats, and within these mats are sediment grains. These grains, along with sediment surrounding the mats, were examined using SEM images as well as X-ray diffraction (XRD). XRD showed that all these grains contain gypsum, halite, and high-magnesium calcite, and the grains within the mats contained a high-magnesium calcite with more magnesium replacement than surrounding grains, as well as some ankerite. Future work should include geochemical measurements of the in-situ environment to determine how these microbial mats are effecting their specific environment. Future work should also aim to identify with higher accuracy the mineralogy of all precipitates within the mats.

Background

One of the largest, as yet an unsolved mysteries in geology is something termed the “dolomite problem” (McKenzie and Vasconcelos, 2009, Zhang and Zhizhang 2012). The mystery concerns the observation that there are large amounts of dolomite in the geologic record, yet few places have been observed where dolomite forms in modern environments. Since geology uses the principle of Uniformitarianism, this apparent discrepancy in the amount of dolomite which forms at Earth’s surface is something which needs to be better understood. Several theories have been put forward to attempt to explain how dolomite may form in such quantities. Several theories have looked at the possibility of

geochemical processes where calcite, which is a common precipitate found still today, is transformed into dolomite through the exchange of Ca^{2+} and Mg^{2+} ions. While these theories show methods of how large amounts of dolomite may form, they have both never been proven to occur on large scales, and there are questions as to whether or not this large exchange of cations is possible on a scale massive enough to explain the dolomite found in the geologic record. The most likely solution to the dolomite problem is one that explains how dolomite may begin forming at surface conditions as a primary precipitate, but associated calcite and aragonite may be dolomitized during burial. This solution involves active microbial mats which interact with seawater to create an environment where dolomite may form authigenically at the surface.

One of the observed problems with explaining dolomite formation is the difficulty of actually precipitating dolomite under surface conditions. Many laboratory experiments have attempted to precipitate dolomite from sea water and sea water-like solutions, but very few are successful (Land, 1998). Calcite and aragonite predominately precipitate from these solutions at these temperatures. If a model that combines some primary precipitation of dolomite is to explain the dolomite problem, then we must first understand what it takes to precipitate dolomite at Earth surface conditions.

Dolomite formations in Geologic History

Dolomites are found commonly in the geologic record, ranging from Precambrian to the Holocene. Because they are so common, they must have been formed in environments which were also common consistently throughout the geologic record. Despite their commonality, though, their environmental sources are poorly understood. The abundance of dolomite decreases from the Precambrian to recent eras, which may suggest a gradual change in environments from environments in the past which aided dolomite precipitation, to modern environments, which are nearly devoid of large amounts of dolomite (Bontognali, 2010). This trend, though, may also suggest that large amounts of

dolomite may take a very long time to form. By understanding what environments are necessary to form authigenic dolomite, we may be able to learn a lot about paleoenvironments, and the nature and process of secondary dolomitization

Dolomite Formation at Surface Condition

Dolomite does not form under normal surface pressures and temperatures (Land, 1998). The concentrations of the necessary ions to form dolomite, namely calcium, magnesium, and carbonate, are high enough in sea water that it is expected that dolomite should form spontaneously as a primary mineral precipitate from sea water (via pathway of equation 1).

Equation 1. Ca^{2+} (aq) +Mg^{2+} (aq) + CO_3^{2-} -> $CaMg(CO_3)_2$ (Solid)

Dolomite does not form in this way at surface conditions. The temperature needed for equation 1 to favor the products abiotically is far above surface conditions, and therefore dolomite does not form spontaneously. Such high temperatures are likely needed due to the activity of the Mg^{2+} ion in sea water (Lith and Warthmann, 2003; Raz, Weiner and Addadi 2000). This suggests that altering the activity of magnesium in water may also favor the formation of dolomite. The Mg^{2+} ion complexes strongly with H_2O at surface pressure and temperature, and therefore is not as available as the Ca^{2+} ion to bond with carbonate (Boggs 2011). This activity of magnesium is very strong, as the typical ratio of magnesium to calcium in seawater is approximately 5:1 (Boggs, 2011). Magnesium may also bind to, or complex with, sulfate, another common ion in seawater, therefore further reducing the availability of Magnesium. Due to the activity of Magnesium, and other possible kinetic inhibitors of equation 1, dolomite does not precipitate from sea water; rather, calcite and aragonite are the primary carbonates which are formed from seawater.

Formation of Dolomite Post Deposition

The relative difficulty of precipitating authigenic dolomite has been well established, and much research into the dolomite problem has been in the post-depositional dolomitization of other carbonates, mainly calcite and aragonite and high magnesium – calcite. It is thought that, because dolomite is difficult to form as a primary precipitate mineral, it is likely created as a secondary mineral through the replacement of the calcium ion with the magnesium ion (Baker and Kastner, 1981). Several models have been proposed as to how this is accomplished. Above approximately 100^{o} Celsius, kinetic inhibitors, including the hydration and complexation of magnesium, are overcome. The following three models are taken from Boggs 2011. All three models are specific environments which are thought to be the site and source of large amounts of replacement of calcium with magnesium.

1. The first model is the Hyper-saline Model. This model pertains to shallow areas which contain seawater, and have high evaporation rates. In this model, evaporation increases the concentration of ions in seawater, and leads to large amounts of aragonite and gypsum crystallization. These two minerals greatly reduce the concentration of the Ca^{2+} ion, leaving the Mg^{2+}/ Ca^{2+} ratio greatly elevated. This increase in the Mg^{2+}/ Ca^{2+} ratio is thought to lead to dolomite formation near the surface through overcoming the kinetic inhibitors by simply greatly increasing the prevalence of the Mg^{2+} ion.
2. The second model is the Mixing-zone Model. This model suggests that dolomite may form in an area where sea water mixes with fresh water i.e. ground water. This model suggests that dolomite may form at surface conditions at low salinities, due to the lack of competition of other ions to bind to carbonate. If this model holds true, it may provide the explanation of a large environment where significant volumes of dolomite may form.

3. The third model is the Shallow Sub Tidal Model. This model relies solely on the replenishment of Mg^{2+} ions being forced through groundwater. This constant supply of magnesium in the sediments may lead to formation of dolomite.

These three models present some possible specific environments where pure physico-chemical forces may lead to the formation of dolomite. Each of these specific environments presents possible ways to overcome the chemical barriers which inhibit dolomite formation, yet each of them also has their theoretical limits to how they could aid dolomite precipitation. None of these models take into account the chemical changes which are associated with bacterial metabolisms, and are therefore limited in their representation of the possible forces which aid dolomite creation in natural environments.

Bacterial Mediation

Because so many studies have demonstrated the difficulty of abiotically producing dolomite in natural conditions at Earth's surface, numerous researchers have examined the role that life may play in the process of crystallizing dolomite from solution. Bacteria present the most likely candidate for an organism to aid in this process, due to the varying metabolisms that different types of bacteria perform. Bacteria are also ubiquitous on the surface of the Earth, and therefore are likely to be found in whatever environment dolomite may be formed. Bacteria have been active on Earth's surface for billions of years, and therefore may help to solve the dolomite problem, as some metabolisms were assuredly active in the geologic record, and may have historically aided dolomite formation.

Bontognali et al. 2010 suggests a plausible model which explains how microbial processes are capable of aiding precipitation of dolomite. The microbes present aid in sustaining an elevated pH and alkalinity, while actively decreasing the sulfate concentration of the water. These, the authors state, are the particulars which are necessary for dolomite precipitation. These authors suggest that one of the primary factors is the concentration of SO_4^{2-} in the water. Because non-complexed magnesium ions are

necessary to form dolomite, reducing sulfate will increase available magnesium by reducing the strong bonding habit of magnesium and the sulfate ion (Warthmann et al., 2000).

Warthmann et al. (2000) proved that dolomite can precipitate in the presence of bacteria, specifically sulfate-reducing bacteria (see equation 2, from Warthmann et al. 2000). In this study, the bacterial cells themselves were encapsulated within the precipitated dolomite. This suggests that the effect that these organisms have is very local to the individual cells. The end result of this type of mineralization is dumbbell-shaped grains of dolomite, which coalesce into microscopic, spherical to columnar shaped grains. Equation 2 shows the chemical pathway by which sulfate reducing bacteria elevate alkalinity, and therefore aid in the formation of dolomite (Warthmann et al. 2000)

Equation 2: $4CHO_2^- + SO_4^{2-} + H^+ \rightarrow 4\ HCO_3^- + HS^-$

A study by Glunk and Dupraz (2011) suggests that it is a combination of sulfate reduction with the degradation of exopolymeric substances (EPS), which hold the organisms in the mat together, combined which leads to the formation of microbially mediated carbonates. Ions bind to this EPS, and when they are degraded can lead to a change in the local seawater ion concentrations. It is likely that several factors must coexist to nucleate dolomite formation, but it is not yet clear which specific processes must happen simultaneously in order for dolomite to form.

Microbial Mats

It is not likely that free-living bacteria alone are influential enough to precipitate any significant amounts of dolomite. A larger quantity of more organized bacteria is needed to form the amounts of dolomite which are found in the geologic record. These quantities and this organization are found within microbial mats. Therefore, understanding microbial mats may be paramount to solving the dolomite problem.

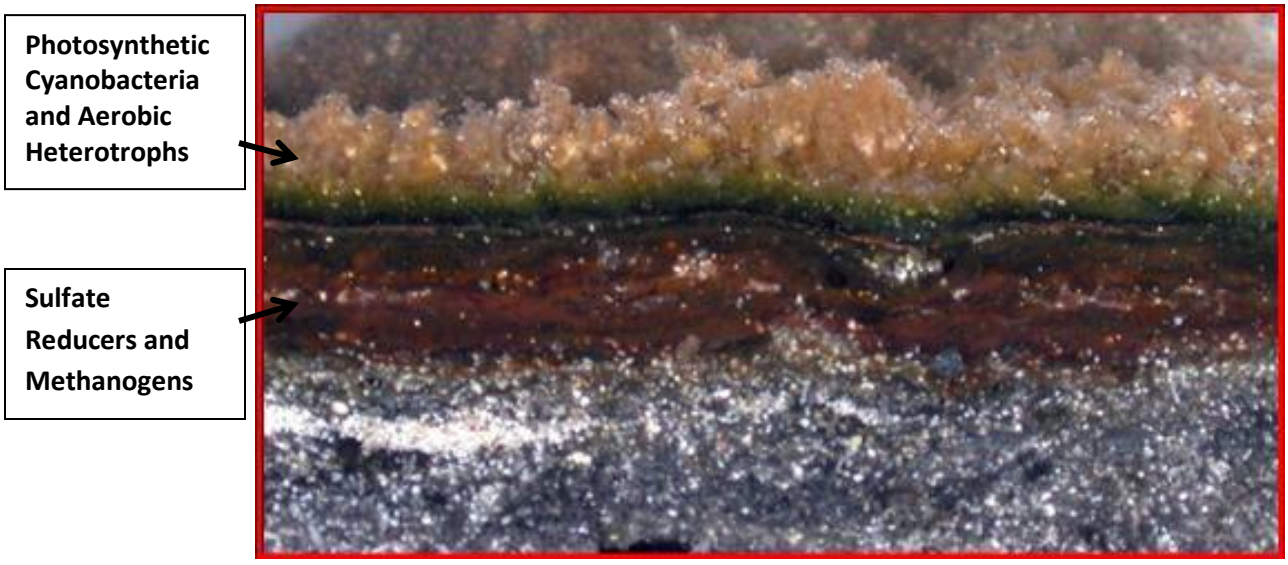

Figure 1. Typical cross section of a microbial mat. The colored section of the mat is roughly 2 cm deep. (image from http://www.sph.sc.edu/enhs/decho/microbialmats.htm)

Figure 1 shows a cross section of a microbial mat. The differentiation of the layers of microorganisms can be seen by the change in color and hue of the layers of the mat. The surface layer of the mat is the only portion which is directly exposed to the seawater (or atmosphere, if the mat is subaerial). Therefore, typically only the organisms that can tolerate light and oxidative conditions are found here. The two most important metabolisms at the surface of the mat are photosynthesis, which is carried out by cyanobacteria at the surface, and heterotrophy, which is carried out by aerobic heterotrophs near the surface of the mat. These two metabolisms comprise the upper, oxygenated part of the mat. Below this, where the oxygen has been depleted, is where the anaerobic microbes can be found. The metabolisms of the lower part of the mat are primarily methanogenesis and sulfate reduction. Between the upper and lower parts of the mat lie fermentative bacteria. These fermenters partially degrade the organic compounds left over from the upper layers of the mat, leaving behind organic acids. These organic acids are the energy source for the lower-layer organisms. Both the methanogenic bacteria and the sulfate reducing bacteria (SRB) break down these organic acids to create methane and hydrogen sulfide, respectively (see Figure 2 for schematic of metabolisms).

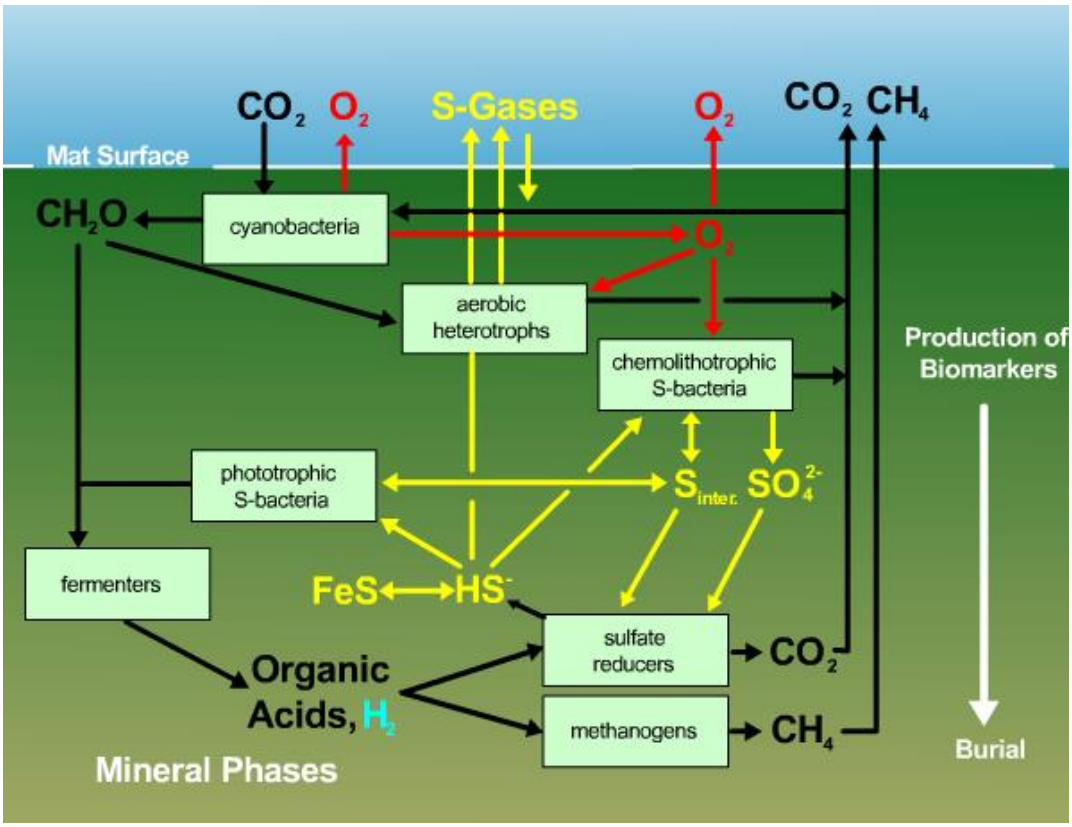

Figure 2. Metabolisms and changes in chemistry with depth within an idealized microbial mat system. Based on this image and previous discussion, it is likely that dolomite would form in the bottom part of the mat, near the sulfate reducers. (Image from http://nai.arc.nasa.gov/students/this_month/g3_funtion.swf)

All of these different types of microorganisms are held in place by a complex web of extra-cellular polymeric substances (EPS) (Decho 2000). This web of material provides structure and some rigidity to a mat which can become relatively thick (several centimeters). The constituent polysaccharides are found throughout microbial mats, and are continuously formed and degraded by the bacteria present in the mat. EPS may play an important role in forming dolomite. This process is as yet, poorly understood, and the importance of its role in forming dolomite is still unknown. The model, though, is that these polysaccharides act as a strong adsorber of cations in solution, and are likely able to alter the chemistry of the water surrounding them (Braissant et al., 2007). As these polysaccharides are degraded within the mat, they may release an abundance of cations in a short period of time, instigating the primary nucleation of dolomite, or other carbonate minerals. As seen in figure 2, the

sulfate reducing bacteria are near the bottom of the active mat, and therefore this is where dolomite should be found.

This study aims to investigate the carbonate precipitates which are found inside thick, abundant microbial mats in hyper-saline lakes of the Bahamas. Through sedimentological and mineralogical analysis, these precipitates will be identified and possibly provide a new example of modern dolomite formation. This investigation will aid future studies in this area, so that, if dolomite is found, we may be able to quantify the amount of dolomite forming in this modern environment, and we may better understand what is necessary for authigenic dolomite formation.

Sample Area

The samples were collected on Little Darby Island, Exumas of the Bahamas. The lake is less than a thousand feet wide, and is only a few feet deep (Figure 3). A number of these islands have small lakes on them. These lakes most likely were formed by deposition and cut-off of open access to the ocean, and a number of lakes are in this process, not yet cutoff form the open ocean. The result is that some lakes have partial hydrologic connection to the ocean water. The lake where our samples were collected had limited access to ocean water, and likely was only recharged with seawater during storm events. These lakes become highly evaporative, and many have very thick, abundant microbial mats at the surface. In fact, as in the image below, the lakes appear green from above, due to the abundant photosynthetic microorganisms at the surface of the mats.

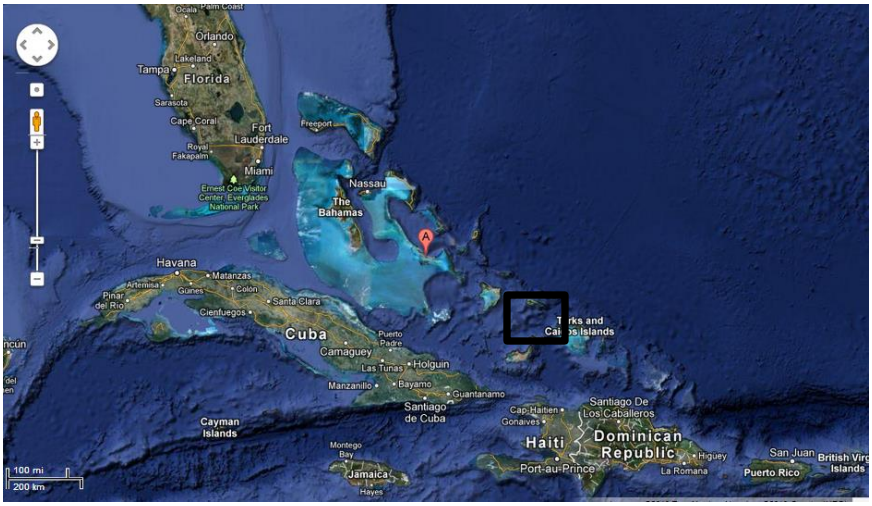

Figure 3: Location of Little Darby Island, Exumas, Bahamas. The lower image is the area within the black box (approximate). The lower image is showing the hyper saline lake at the southern tip of Little Darby Island from which samples were obtained (boxed).

Methods

The aim of this study was to analyze the mineral grains within and around microbial mats. Two push cores were collected from a shallow hyper-saline lake. The core was pushed manually approximately a half meter into the lake. The core was the capped and removed from the ground. The bottom side of the core was then sealed as well using airtight screw on core caps. The core was then

brought back from the collection location and was kept refrigerated at 4^{o} C for approximately a year and a half until the samples could be analyzed.

The core was split using a circular say calibrated to only cut through the plastic of the core. The core was split open, and one half was sealed with plastic and refrigerated at 4^{o} Celsius. The other half was allowed to dry for approximately 24 hours, and was then scanned using a Geotech © core logger equipped with a high resolution camera, a hand held x-ray fluorescence (XRF) unit, a laser profiler, and a magnetic susceptibility probe. The core was scanned in order to acquire a high resolution photograph (Figure 4*)*. The core logger also acquired XRF, although the resolution is approximately one centimeter. Magnetic susceptibility data was recovered, as well as a high resolution laser profile image of the core.

Mineral grains were extracted physically with the use of tweezers. Some samples, which were extracted at the same time as the grains for XRD, were mounted on aluminum mounts using liquid graphite glue. These samples were used for scanning electron microscope analysis. These samples were then carbon coated and analyzed using a JEOL JSM-840A Scanning Electron Microscope. These images, which are secondary electron images, seen in figures 5 and 6, were taken in order to ascertain high definition mineral grain sizes, and also in order to observe the grain morphology and crystal habit of the grains.

The material extracted for X-ray diffraction was taken from individual layers within the core. The grains were either taken from within microbial mats, or from layers of mineral precipitates which are between the mats. Grains which were later analyzed by X-ray diffraction were cleaned with a 5% sodium hypochlorite solution in order to remove the organic matter from the grains. These grains were then crushed using a mortar and pestle to a fine powder. A Panalytical Empyreon© X-ray diffractometer was used to ascertain the mineralogy of these extracted grains. The XRD was set on a rotating stage (16 second period) and the two-theta angles were between zero and ninety degrees. The X-ray diffraction

patters had significant peaks with very little background noise (Figure 8-9). The x-ray diffraction patterns were exported and analyzed using several programs. The first is PDF-2+ created by the International Centre for Diffraction Data (ICDD). The second program was Jade 6. Both of these programs were used in order to obtain standards with which to compare the experimental data to. The results of this comparison can be seen in figures 8 through 12.

Material was taken from the top 10 centimeters of the cores, in order to prepare them for lead-210 dating. The material was extracted by hand, and the mineral precipitates were crushed using a mortar and pestle. This material was then analyzed for its lead-210 content.

RESULTS

Using the Geotek© Core Logger, a high resolution picture of the core in its entirety was created (See figure 4). The top of the core is the top of the image. One can clearly see that these mats and sediments at the top are very unconsolidated. This is because these mats and sediments were at the surface when the core was taken, and consist only of newly formed mats and trapped sediment. The material directly below this section, starting at 6 cm down into the core, begins a section that is very densely populated with microbial mats. Most of these mats contain some sediment grains within them. These mats were likely much thicker when they were active near the surface, but have become dense upon burial. In this section, there are several layers of fine, white to grey sediment (see 10 cm depth). These layers are very well sorted material, and are not within a mat, but between mats. The top 28 cm of the core continues this trend, where there are thick, abundant microbial mats and only relatively thin layers sediment between them, if any at all.

The next section of the core, from 28 cm to approximately 38 cm, contains a much higher percentage of mineral grains. There are a few microbial mats within this section, but they are few, widely spaced, and much smaller than the mats in the top section. It is not clear whether this section

formed in the absence of mats, or that the mats which were once present were degraded. Either way, this section is mainly carbonate material. This section, even where no mats are present, is layered. The strata are from approximately 1 to 5 mm in thickness.

Below 38 cm, until the bottom of the core at 50 cm, contains no mats whatsoever, and is nearly devoid of any layering. This section has only one poorly defined bed at 45.5 cm, which appears to have been a microbial mat but is now mostly degraded.

X-Ray Fluorescence

The X-ray Fluorescence (XRF) results are shown below. These results are qualitative measurements of the relative abundance of different elements within the core. The XRF machine has a resolution of roughly 1 cm, so these are trends over a relatively large scale. The core was scanned in one continuous run, but due to the unconsolidated nature of parts of the core, the XRF is not available for all parts of the core for every run. In some section of the core, there is a high error value for the reading; this is likely due to the core material being loosely packed, but consolidated enough for the XRF to read a measurement. For the parts of the core where the data are available, the graphs show the relative amounts of calcium and magnesium. Due to large errors in measurement, magnesium values for the core were not available.

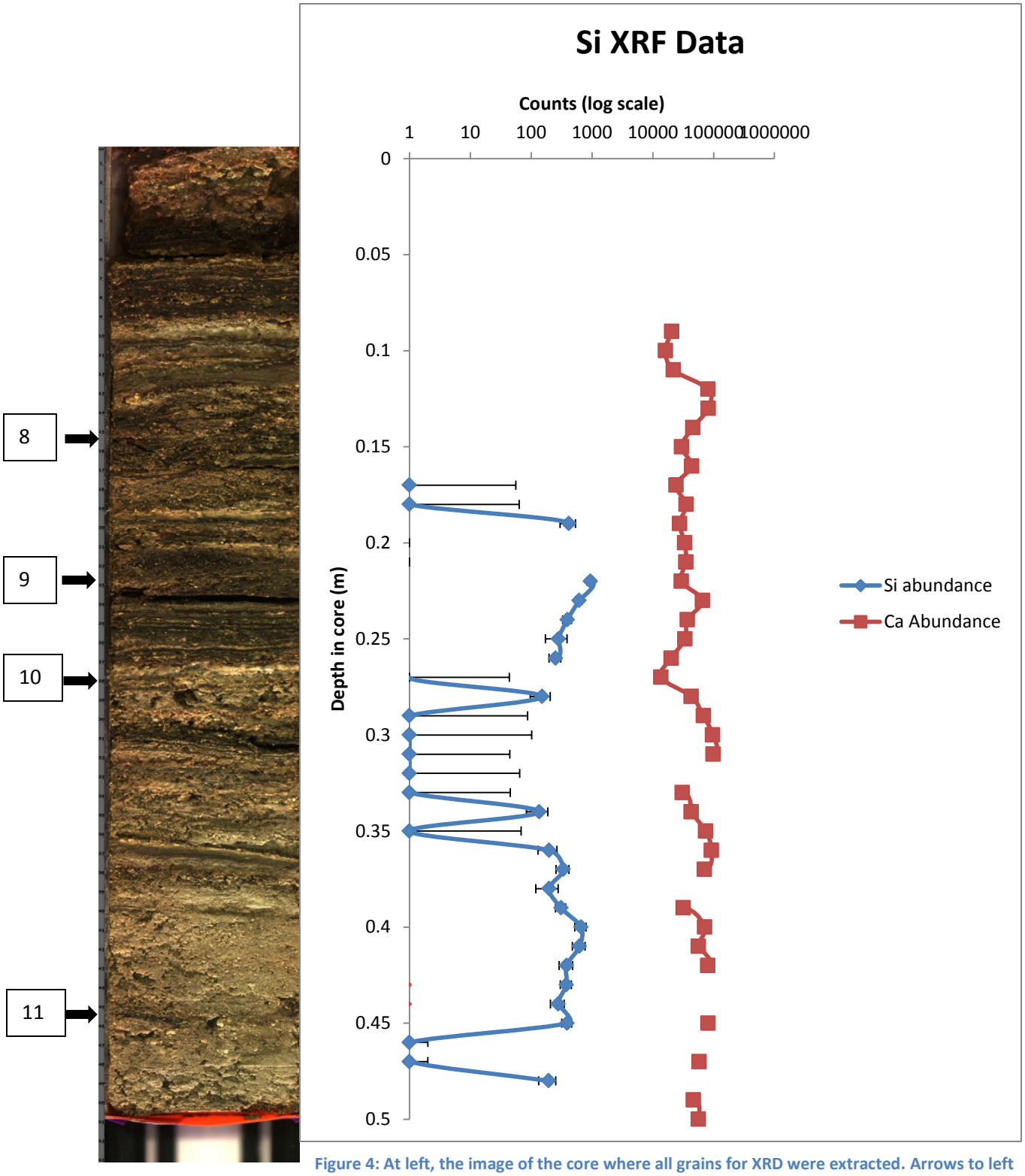

Figure 4: At left, the image of the core where all grains for XRD were extracted. Arrows to left of image show source of grains analyzed by XRD (number corresponds with figure caption number below) On right, the XRF qualitative mineral abundances for silicon and calcium are shown (log scale). Error bars for calcium are too small to see at this scale. Data for magnesium not available.

Scanning Electron Microscopy

The scanning electron microscope images were used in order to ascertain the grain morphology and grain size of individual carbonate grains extracted from the microbial mats. The grains extracted were mostly grains on the order of 250 micrometers, where larger grains were as large as 2 millimeters in diameter, and the smallest grains were micro-spheroids of less than 10 microns. Many of the grains imaged were in reality a conglomeration of smaller grains which were somehow cemented together. These smaller grains which comprised the aggregates were of only a few different grain morphologies. The smaller grains were either bladed with flat edges, where the grain was less than 20 microns thick but as long as 50-100 microns long (Figures 5 and 6). The rest of the grains were comprised of a large number of smaller, spherical carbonate grains which were less than 10 microns in diameter (figure 6). These smaller spheroids were either coating larger, globular anhedral grains, or were found on their own. These smaller, spheroidal grains were identified in another study (Dupraz et al., 2004), and were found to be most commonly associated with microbial precipitation. Dupraz et al. (2004) calls these grains micropeloidal.

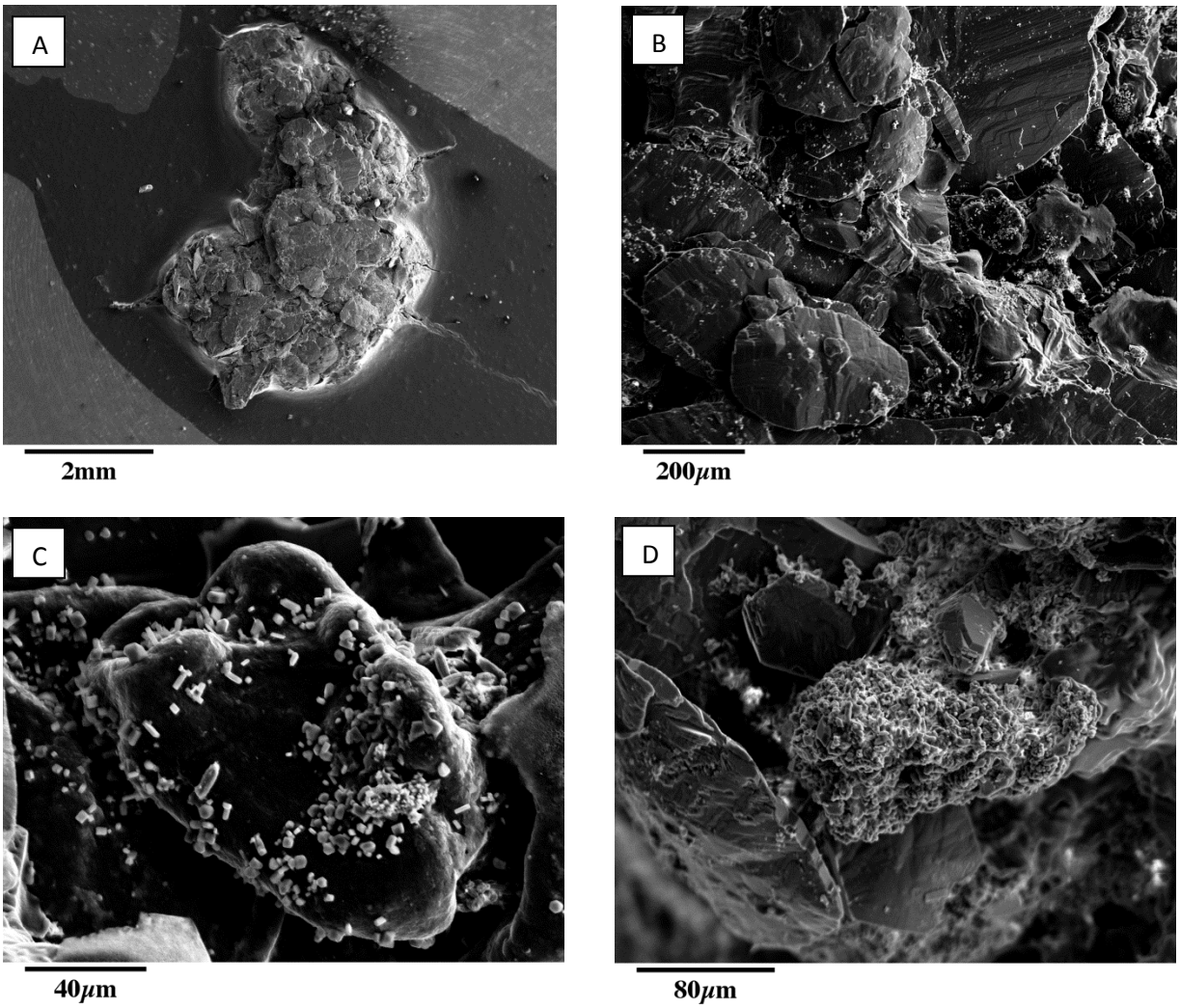

Figure 5: SEM photomicrograph of smaller grains which comprise a larger grain. The two most common grain morphologies of grains sampled are seen here; Bladed grains (A) and much smaller, spherical grains (box B). In several of the grain images, the micropeloidal structures can be seen (D). These micropeloidal grains were cited in another study to be associated with microbial precipitation (Box D, Dupraz et al., 2004).

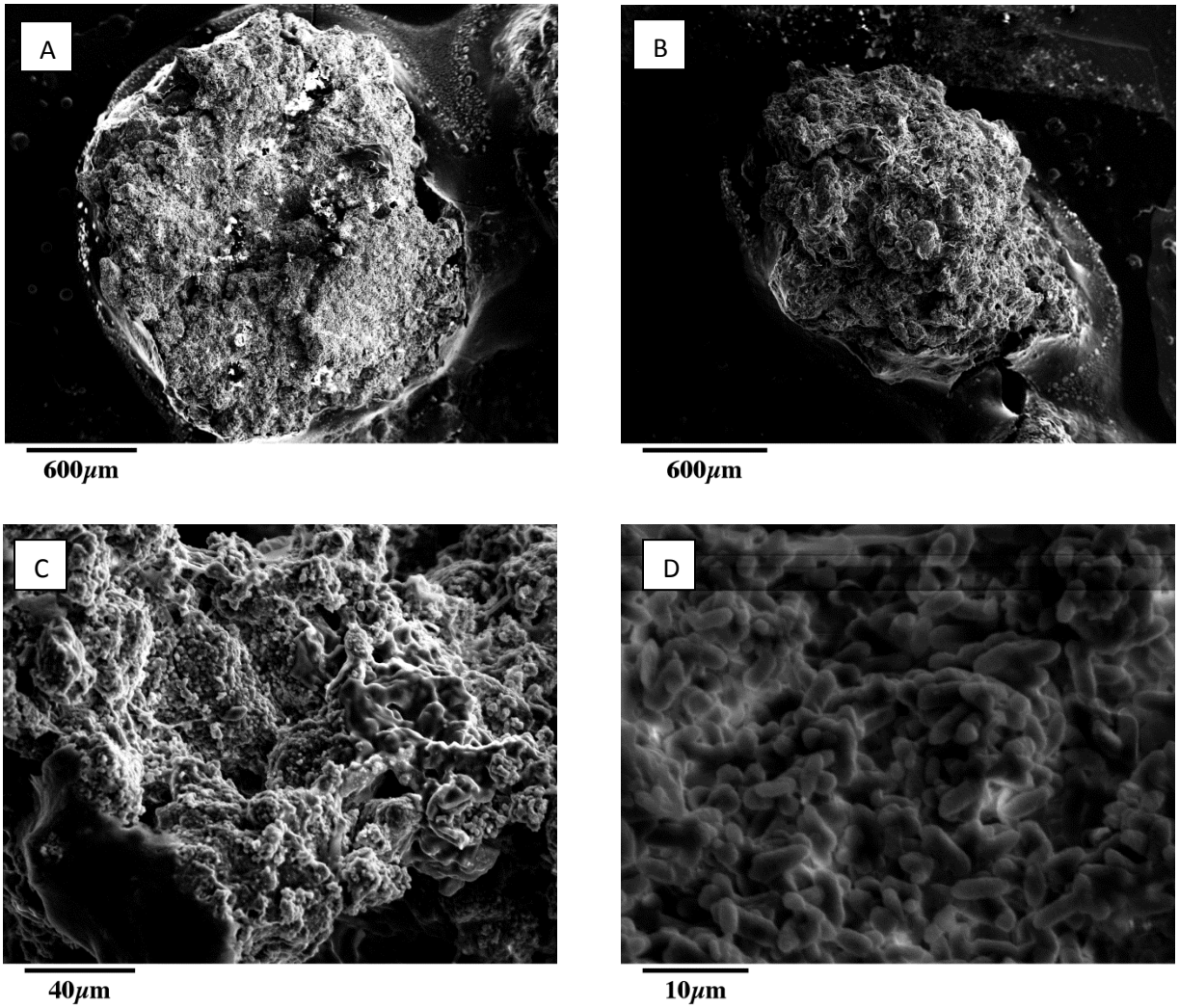

Figure 6: 4 SEM images from different grains from within the core. A and B show that some of the grains are comprised solely from much smaller, spherical grains. Image D shows that some of these small, micropeloidal grains are columnar in shape.

X-Ray Diffraction

The X-ray diffraction patterns shown in figures 8-12 are the results of the scans of grains extracted from the core. The diffraction patterns were relatively clear, with some ambiguous peaks and relatively little background noise, in most areas of the diffraction patterns. The figures show the results from the scan of our sample (red line) as compared to standards of known compositions and crystal structures (marks below the graph). Several of the grains were found to be high-magnesium calcite. This shows that the grains extracted from the core had the structure of calcite, but some of the calcium ions in the crystal structure were replaced with magnesium. Several of the samples, including sample 9, 10, 11, and 12 contained some gypsum, and all samples contained halite. The remainder of the clear peaks are attributable to calcite, high-magnesium calcite, or ankerite. As can be seen in the boxed area on figure 7, there are subsidiary peaks which could not be matched directly to a known sample. These peaks lie directly between the d-spacing of high magnesium calcite, and ankerite, with a smaller d-spacing than dolomite. As shown in figure 7, the more magnesium which replaces calcium in the calcite structure, the larger the d-spacing in the mineral. Because of this, we can infer that the secondary peaks which are present and unidentified by the program can be identified as high-magnesium calcite which has a magnesium content of at least 20% (Griffin, 1969).

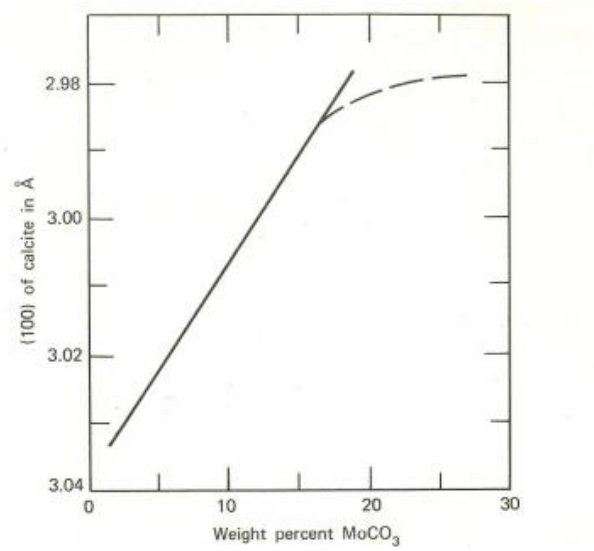

Figure 7 Weight percent $MgCO_3$ replacing $CaCO_3$ in the calcite structure, Griffin, (1969)

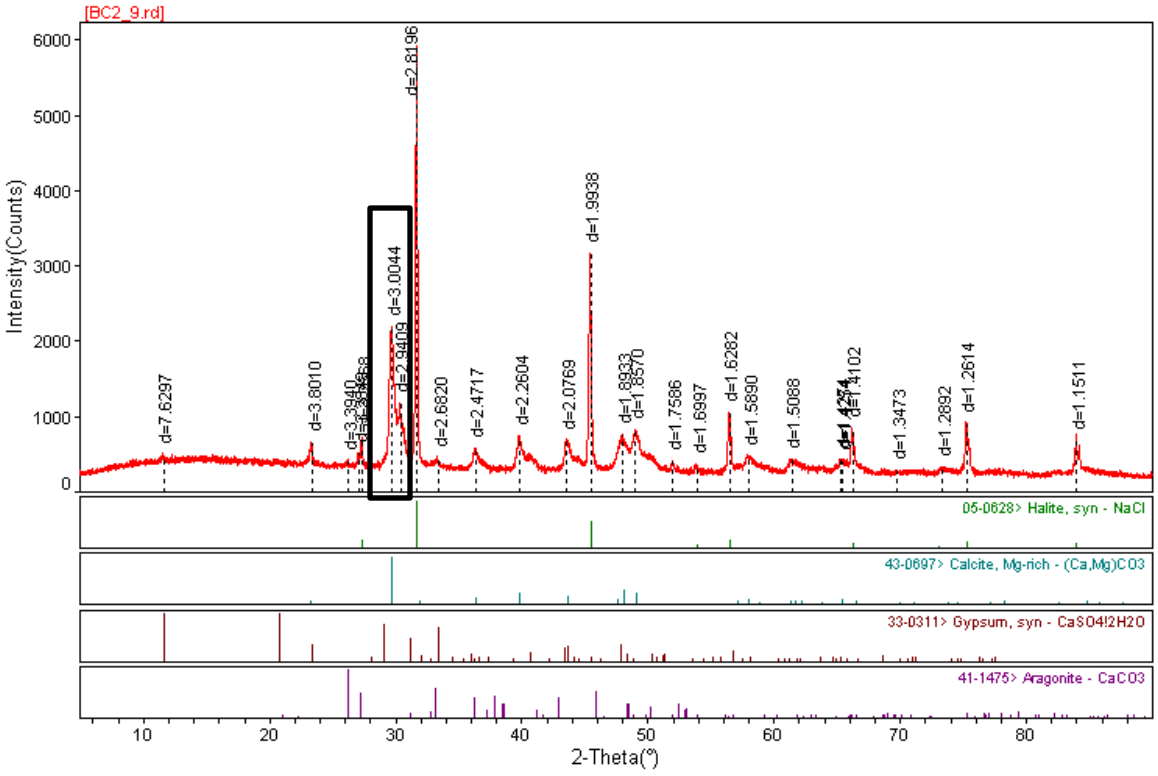

Figure 8: XRD results for sample which consisted of sand sized white – tan grains extracted from within a microbial mat. Boxed area shows un-matched peak which was not identified by the computer program.

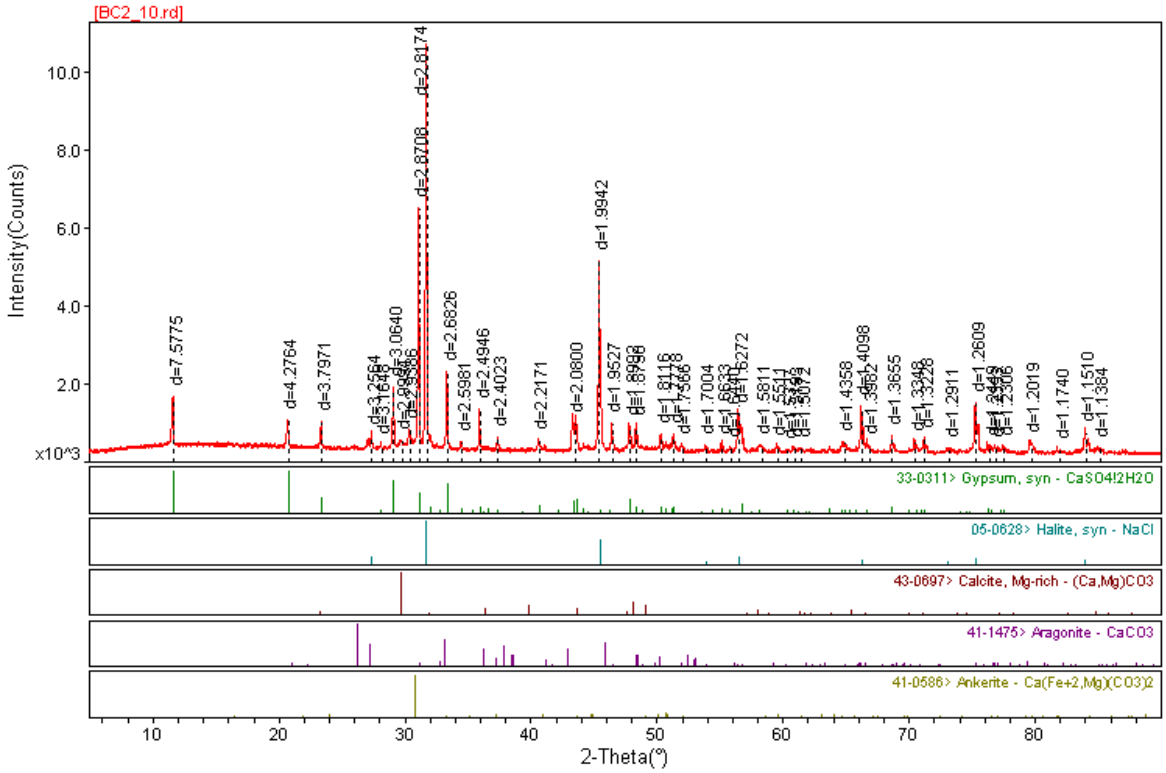

Figure 9: XRD pattern for grains extracted from a layer of white, coarse-sand sized grains found between two mats rather than within the mat.

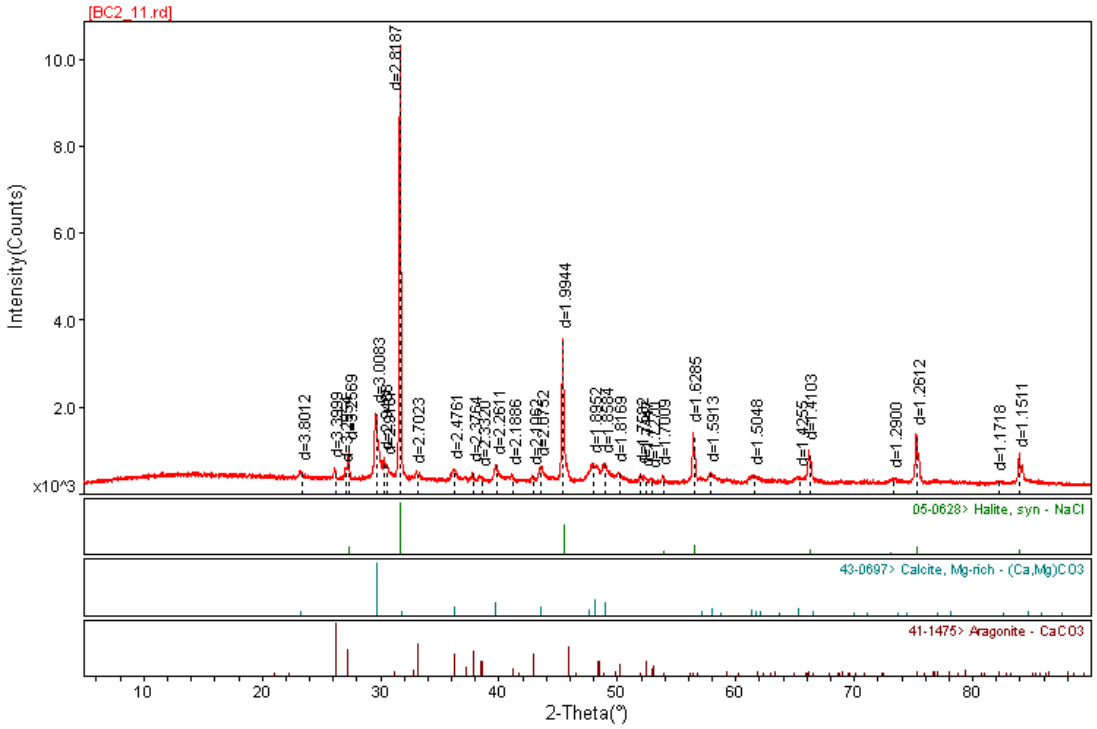

Figure 4: XRD results for grains extracted within a white, sediment grain layer. These grains were not within a mat.

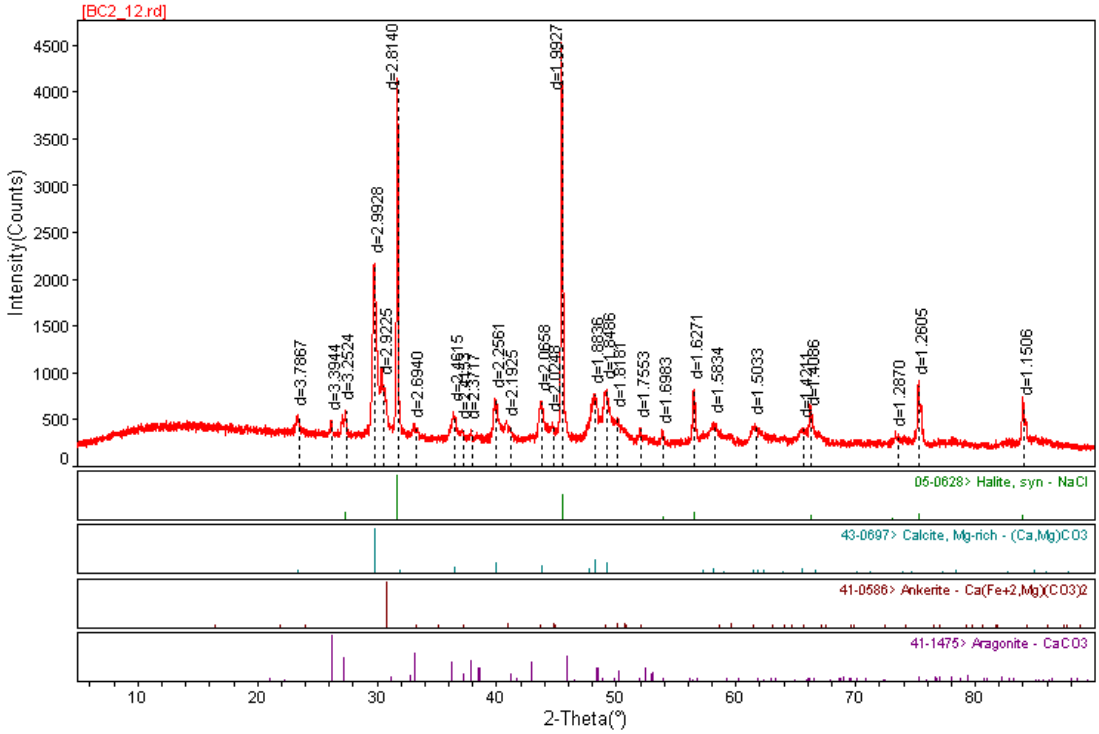

Figure 5: XRD results for grains extracted from within a poorly preserved microbial mat.

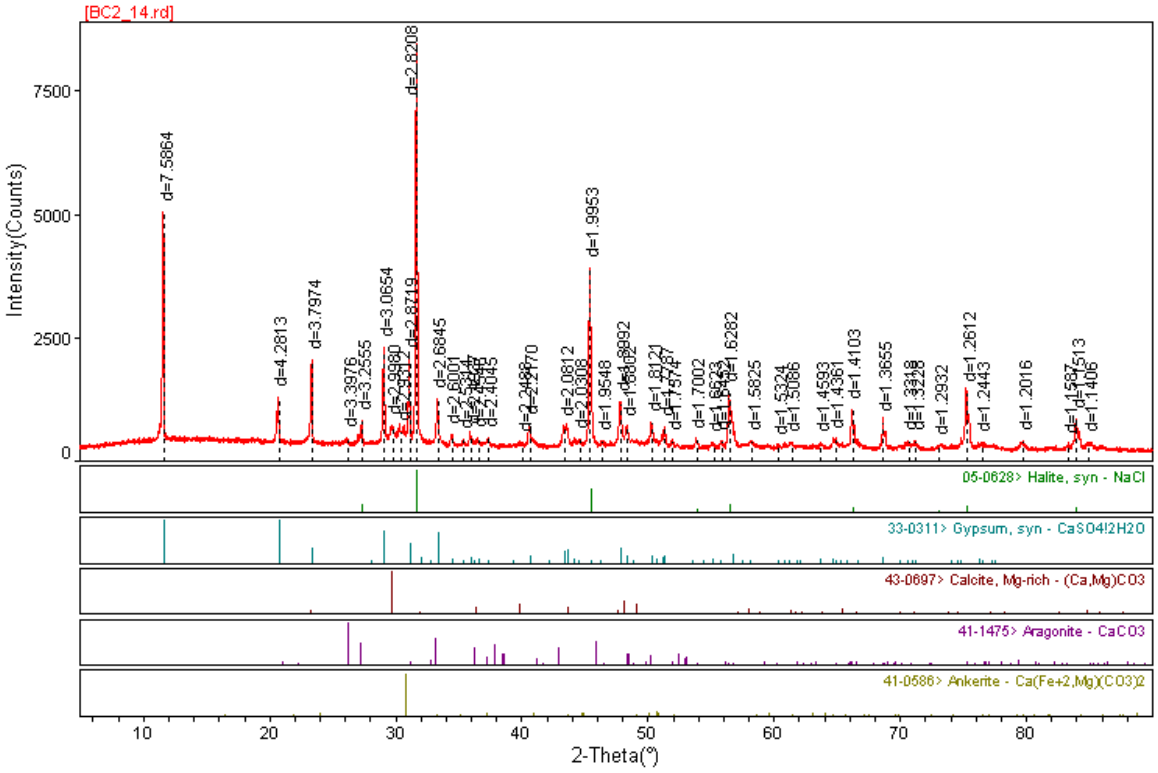

Figure 12: XRD results for crystal grains extracted from what are likely the remains of a highly degraded mat.

Lead 210 Dating

Prepared samples were analyzed for their lead-210 content, in order to ascertain an age of the rate of sedimentation. Only one sample analyzed had sufficient quantities to be dated, but only with a large error. No other samples analyzed contained sufficient quantities of lead in order to be dated using this method. Because there was not enough lead to date, no age or rate of sedimentation can be given for the material in the core.

Interpretations

Through a sedimentological survey of the core, some initial observations can be made. The amount of microbial mat material in the core decreases with depth. This suggests that the mats are being degraded as they are buried under fresh sediment, and that any deeper than the core depth, which was approximately 50 cm, there would be no more mat material remaining. The mats may also not have been present during the deposition of this lower part of the core. Due to a lack of samples from other lakes with other depositional histories, though, this conclusion cannot be confirmed. Longer cores, which allow a deeper and more long-term investigation of the depositional fate of the sediments, are needed.

The mats have unique and varying relations to the mineral grains around them. These mat have relatively large (several millimeters) grains within the mats, which are found both bound and unbound to the EPS. Also in this core, found exclusively between mats, there are thin beds of grey to off-white, very fine-grained, unconsolidated sediments which have a spongy texture to them. These beds do not appear to be part of the mats, but are found between or above/below them. These layers of material were not successfully analyzed with XRD.

None of the grains which were examined were positively identified with confidence as dolomite. Several grain layers were, however, identified as high magnesium calcite by XRD, with subsidiary ankerite. The percentage of magnesium which replaced calcium in the calcite structure ranged from near zero to at least 20%. There were peaks in the XRD results which were not able to be matched to a known sample of calcite with solid solution of magnesium, but there is an established shift of d-spacing of calcite with increasing amounts of magnesium within the crystal structure (Griffin, 1969). The main peak which was discovered in numerous samples which could present higher magnesium content than ~5% has a d-spacing of roughly 2.92-2.94. These peaks were not positively identified as any known

mineral, yet these peaks were present in several samples (Figures 8 and 11). If the graph showing d-spacing shifts according to magnesium replacement from Griffin, 1969 is extrapolated, this d-spacing would represent a magnesium content of nearly 50%. The most significant peak on an XRD intensity chart for dolomite, though, is at a d spacing of 2.89. No precise correlation of d space shift and magnesium content higher than roughly 20% was found, so these peaks are not able to be interpreted as to their mineral structure or elemental make up.

There were some general patterns that were observed once the XRD analysis of the grains was completed. All samples exterior to mats which were extracted and analyzed lacked any precipitate with higher magnesium content than the high-magnesium calcite, which had approximately 5% magnesium (the magnesium content which was identified by the computer program, peaks seen in lower part of figure 8-12). The only areas in the core which contained grains which were interpreted as having higher magnesium content than high magnesium calcite were the grains extracted from within the mats themselves. This is evidence that the mats may play an active role in the addition of magnesium into the crystal structure of the carbonate precipitates.

The environment where our core was extracted is similar to the geochemical environment of lakes examined by other researchers (Dupraz et al. 2004, Bontognali 2010, Vasconcelos and Warthman et al. 2006). If the chemical environment of this particular lake is similar to the waters which aided dolomite precipitation in the aforementioned studies, then examining the small differences between the microbes and exactly how they differ from each other may help elucidate exactly what is needed *in situ* to guarantee dolomite formation. Examining and discovering these differences may greatly aid our understanding of the complex and difficult nature of dolomite formation. Unfortunately, because *in situ* measurements of the chemical and physical properties of our sample site were not available, it is impossible, at this time, to comment on what these differences are.

These results do not present a new, independent model for how large quantities of dolomite form. If these unidentified calcium-magnesium carbonates are poorly ordered and/or non-stoichiometric dolomites, then this may be an environment which acts as an intermediary to the formation of large quantities of dolomite. If microorganisms are able to enhance the magnesium uptake of the calcite mineral, than they may act more as a precursor to the post-burial diagenetic formation of dolomite. By beginning the process of replacing calcium with magnesium in the calcite structure, these microbes may create sediment which is more thermodynamically likely to be further enriched with magnesium post-burial (Zhang and Zhizhang 2012). It is most likely that this process aids further dolomitization as the sediments are buried, and is therefore a part of another model which could explain the vast quantities of dolomite.

Future Work

There is significant future work which should be done in order to better understand this environment. One of the most significant and achievable projects to complete would be a comprehensive analysis of the field site where the samples were collected. Collecting *in situ* data of pore water chemistry, pH, and water content would greatly aid in the analysis of what is authigenic, *in situ* precipitation and what may be secondary precipitation after samples are collected. These chemical parameters should also be taken at different depths, in order to better understand how the microorganisms alter the water chemistry with depth. For instance, at depth, the microbes likely have used all available oxygen, so the water is likely anoxic when deeper that the active, surface mats. Understanding the rate of change of water chemistry with depth will elucidate, specifically, how the organisms are altering their chemical environment, and therefore altering the thermodynamics of precipitate formation.

Because the material was not able to be effectively dated, and no rate of deposition could be assigned, very little can be said about the timing of the processes in the core, or the fate of this material. Future studies should examine the long term fate of the carbonates which are formed in this environment. As the material is buried, the high-magnesium calcite may be further dolomitized through the continued replacement of calcium with magnesium at depth. Further work done must also examine the rate of accumulation of these sediments, in order to ascertain the volume of dolomite which may accumulate in this type of environment.

The project which could most advance the research already conducted is to definitively identify the precipitates within the mats. Further analysis using energy dispersive x-ray spectroscopy (EDS) would provide relative chemical abundances on individual grains. Using this method, it may be possible to identify which grains have a d-spacing of 2.92 angstroms (Figure 9, 10 and 12); EDS would then provide relative abundances of calcium and magnesium. This information would guide us in identifying whether the grain is a high magnesium calcite (with some percentage of magnesium above 20%), or if there are equal amounts of magnesium and calcite.

Another area of possible fruitful work to be done in this environment is a metagenomic or pyrosequencing study of the microorganisms which are present within the microbial mats. Only by knowing which microbes are present may we say for sure which metabolisms are present and active, and the relative activity of these biological chemical pathways. This biological analysis will greatly aid in our understanding of which precipitates are likely or possible in an area with microbial mats. Understanding the genetics of the organisms present in the mat may also aid in our identification of other places where these same processes may be occurring. Only through a comprehensive understanding of an environment, which includes biological, chemical, and physical components of the

system, may we be able to predict with any accuracy or precision which geochemical phenomena are occurring, and which are responsible for the precipitation of magnesium-bearing carbonates.

This understanding can then transcend the present, and supply us with information about what situations in the geologic past may have formed these geologically important carbonates.

Conclusions

This paper examined the precipitates found within microbial mats in a hyper saline lake of the Bahamas. Using X-ray diffraction, it was found that all these precipitates contain halite, gypsum, and high magnesium calcite, and the precipitates within the microbial mats contain high-magnesium calcite with an elevated percentage of magnesium from non-mat associated grains, as well as ankerite. There were peaks present on the XRD intensity charts which could not be accurately identified as any known mineral, and future work should aim to identify these mineral phases. Future work should also include in-situ chemical analyses of the lake environment, and identification of bacterial species should be conducted.

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