The Role of Sulphate-Reducing Bacteria and Unconsolidated Organic Matter in the Formation of Primary Dolomite

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A Thesis Presented to the Faculty

of the Department of Earth and Atmospheric Sciences

University of Houston

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

By
Jeremy S. Krimmel

May 2012

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Jeremy S. Krimmel

APPROVED:

Dr. Henry Chafetz, Advisor

Dr. Thomas Lapen

Dr. Robert Folk

Dean, College of Natural Sciences and Mathematics

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ABSTRACT

Laboratory experiments succeeded in producing primary dolomite at Earth-surface conditions using components collected from Christmas Bay near Brazosport, Texas and the Bahamas. Dolomite and calcite precipitates were observed within an anoxic sludge layer of siliciclastic sediment intermingled with decaying particulate organic vegetable matter, e.g., plant stems and roots. After experimentation lasting from 3 to 5 weeks, dolomite was identified by its elemental spectrum via energy-dispersive x-ray spectroscopy compared to known standards. Communities of sulphate-reducing bacteria in anoxic conditions gathered on the decomposing organic matter within the sludge layer. The bacteria on the decaying organic matter changed the microenvironment around them so that dolomite became supersaturated within their immediate vicinity. Although slight changes were made to the solution included in the experiment to decrease the kinetic barriers of the dolomitization reaction, it is concluded that sulphate-reducing bacteria were primarily responsible for the generation of the dolomite precipitates because (a) dolomite was only observed as being directly associated with the decaying organic matter where sulphate-reducing bacteria are thought to have preferentially accumulated, and (b) controlled changes of the chemistry of the solution appeared to have little effect on the precipitation of dolomite. Bacterial precipitates of dolomite and calcite were only found directly on or embedded within organic matter and were preferentially concentrated on organic matter devoid of siliciclastic detritus. Furthermore, dolomite was only synthesized in the presence of ooids which increased the speed and likelihood of dolomitization by contributing Ca^{2+} and CO_3^{2-} ions through aragonite dissolution. It is suggested that the reason why primary dolomite is not found

naturally within the Christmas Bay sediments is because the process of primary dolomite precipitation requires the presence of carbonate minerals.

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CHAPTER 1 - INTRODUCTION

For over two hundred years geologists have studied the mineral dolomite and dealt with what has come to be referred to as the “Dolomite Problem”; that is, dolomite has only been recorded as forming in a small number of modern localities, and for most of this time it has proven to be extremely difficult to synthesize in low-temperature conditions in laboratory settings. When these observations are contrasted with the abundance of dolomite in the rock record, it becomes clear that, after centuries of dolomite research, there has been a fundamental gap in our understanding of the formation of the mineral dolomite. Much of the motivation behind recent dolomite research is to be able to provide an answer to this century-old dilemma.

However, the question of the origin of dolomite is still as important ever. Over the last twenty years, the idea that bacteria may play an important role in the primary precipitation of dolomite has gathered much momentum. Geomicrobiologists, exobiologists, and other scientists interested in the study of life on extraterrestrial bodies might find modern dolomite research extremely interesting in that it might help to delineate the role of bacteria in the precipitation of crystals. Discoveries along these lines may allow scientists in the future to confidently identify the presence of past extraterrestrial life on other planets based solely on the precipitated crystals they left behind.

Also, those in the business of oil and gas exploration and production have an important economic stake in dolomite research. As a reservoir rock, dolomite has the ability to preserve immense porosity and permeability. However, in many basins around the globe, secondary dolomitization has occluded much of the original porosity of a reservoir formation. Therefore, the accurate prediction of the presence of dolomite and its associated relationship to the stratigraphy surrounding it is of much importance to those in the petroleum industry.

Because of these reasons, the origin of dolomite is currently an active research topic and shows all signs of remaining so well into the 21st century. A brief review of the key events in dolomite research helps to put these current research trends into their proper context.

The History of Dolomite Research

The mineral dolomite is named after the French geologist and mineralogist Deodat de Dolomieu. The first documented recognition of the mineral dolomite was in 1779 by the Italian geologist Giovanni Arduino (von Morlot, 1847 as discussed in McKenzie and Vasconcelos, 2009). Dolomieu, however, is commonly credited with the first description of the mineral in which he recognized that although dolomite resembles calcite in several ways, it only tends to effervesce weakly when brought into contact with hydrochloric acid (de Dolomieu, 1791 as discussed in McKenzie and Vasconcelos, 2009). The Italian part of the Tyrol Alps served as the setting in which both Dolomieu and Arduino worked, and subsequently, that part of the Italian Alps in which dolomite was first discovered and described are the Dolomite Mountains (McKenzie and Vasconcelos, 2009).

Almost from the initial identification of dolomite as a unique mineral until the present, dolomite has been the subject of important chemical studies. Nicolas-Theodore de Saussure (1792 as discussed in McKenzie and Vasconcelos, 2009), a colleague of Dolomieu's, performed the first laboratory study of dolomite with a thorough chemical analysis of the mineral just a year after Dolomieu's original publication. Wilhelm Haidinger attempted to explain the replacement of calcite by dolomite chemically by developing chemical reaction equations to describe this process (von Morlot, 1847). The reaction equations that he developed were based on his observations that although the rock record suggests quite strongly that dolomitization of limestone has occurred, it had yet to be observed either naturally or in laboratory settings. Thus, he concluded that these reactions must take place at great depth beneath the surface of the Earth and, subsequently, under immense pressures. This is generally considered to be one of the first times a sedimentary geochemical process was studied by geologists as a naturally occurring chemical reaction (Vasconcelos and McKenzie, 2009) and helped to usher in a suite of further studies into the geochemical nature of dolomitization.

The first documented experiment in which dolomite was synthesized under laboratory conditions occurred in the mid-nineteenth century. Experiments performed by von Morlot (1847) successfully produced dolomite under high temperature and high pressure conditions. The chemical equation reactions first developed by Haidinger (McKenzie and Vasconcelos, 2009) served as a basis for the experiments of von Morlot (1847) which suggests that although research into dolomite is still very active and our knowledge incomplete, workers understood a great deal about the nature of the dolomitization process very early in the history of dolomite research.

Although the experiments of von Morlot mark the first documented case in which dolomite was generated synthetically, it would take researchers at least another 50 years before dolomite was synthesized under *low* pressure and *low* temperature conditions (Nadson, 1928; Burns et al., 2000). Georgi A. Nadson (1928), a Russian biologist, claimed to have generated fine-grained dolomite from sulphate-reducing bacterial culture experiments around the beginning of the 20th century. Cleverly, Nadson (1928) understood the impact of this research when in his publication he suggested that perhaps the understanding of this process may help to provide an answer to the

Dolomite Problem. Although in hindsight researchers have been able to appreciate more appropriately the impact and innovativeness of Nadson's (1928) research, this research was not immediately appreciated by geologists worldwide. On the contrary, Nadson's (1928) studies were mostly ignored by geologists in Western countries for a large part of the 20th century. It was not until the study of the interaction of bacteria and sedimentation became a hot topic in the literature towards the end of the 20th century that workers properly acknowledged Nadson's (1928) groundbreaking studies (Slaughter and Hill, 1991; Chafetz and Buczynski, 1992, Bontognali et al., 2010).

The year 1965 turned out to be an extremely significant one in the field of dolomite research. Two papers were published, each describing a new location where modern dolomite was found to be naturally forming. Illing et al. (1965) discovered that modern dolomite was forming within the hypersaline sabkhas of the Arabian Gulf while Von der Borch (1965) described modern dolomite forming amongst the sediments of the hypersaline Coorong lakes of southern Australia. These discoveries were monumentally exciting to the geologic community in that they re-invigorated the research into dolomite formation by allowing researchers to study in depth two different modern settings in which dolomite was currently being produced (Wright, 1999; Burns et al., 2000; Lokier and Steuber, 2009). One of the most interesting aspects of these discoveries to geologists was that the dolomite found to be forming was fine-grained and non-replacive, primary dolomite precipitates, not unlike those mentioned by Nadson (1928) about 30 years prior.

A dramatic shift in dolomite research took place in the mid-1990's with the work of Vasconcelos et al. (1995). A more detailed scientific explanation of this study exists below, but at this point it is worth mentioning that this study helped to dramatically change the way scientists approached the Dolomite Problem from then on. By focusing on the role of bacteria in the origin of dolomite, the work of Vasconcelos et al. (1995) brought about what essentially amounted to a paradigm shift in the research into dolomite formation. In the year 2011, many researchers are still working to fully comprehend the implications of the discoveries of Vasconcelos et al. (1995) and other contemporaries (Wright, 1999; Warthmann et al., 2000; Roberts et al., 2004; Bontognali et al., 2010). It is within this context that this current study has been performed, with the intent of further understand the process of the precipitation of dolomite.

The Mineralogy of Dolomite

Before the current understanding of the role of bacteria in the origin of dolomite is to be discussed, a quick introduction into basic dolomite mineralogy is needed. The chemical formula for dolomite is $CaMg(CO_3)_2$, meaning that to a mineralogist an ideal crystal of dolomite would contain equal amounts of $CaCO_3$ and $MgCO_3$, or more specifically a 1-to-1 magnesium to calcium (Mg:Ca) ratio. Mother Nature seems to disagree with this assessment of the term “ideal” in that a perfect 1-to-1 Mg:Ca dolomite crystal is extremely uncommon in modern natural settings. In general, it is more likely for a crystal of dolomite to be rich in calcium ions than in magnesium ions (Tucker and Wright, 1990). The ratio of Mg:Ca in the chemical formula of a given dolomite crystal is referred to as its stoichiometry, where the closer to 1:1 the ratio becomes, the more stoichiometric the crystal.

Dolomite crystals are {101} rhombohedrons that fit into the hexagonal 3 class. A perfectly ordered crystal of dolomite consists of a plane of carbonate anions bounded on one side by a sheet of Mg cations and on the other side by a sheet of Ca cations. The ordering and stoichiometry of dolomite can be used to say something of the origin of the dolomite crystal in question. Modern dolomite crystals tend to be less stoichiometric and more poorly ordered than ancient dolomite crystals. However, in some locales, it has been shown that less stoichiometric and poorly ordered dolomite crystals can change into more stoichiometric and better ordered crystals in a geologically short time frame, as described for the Abu Dhabi sabkhas (McKenzie, 1981).

The Dolomite Problem

The rock record contains an abundance of dolomite. In much of the strata, dolomite is even more common than calcite. For example, the Ellenburger Formation of Ordovician age in central Texas (and the stratigraphically-correlative Knox and Beekmantown formations in the eastern-central US) is over 300 meters thick and composed dominantly of dolomite.

Dolomite has proven to be extremely difficult to synthesize in laboratory settings. One worker (Land, 1998) designed an experiment with solution supersaturated by 1,000-fold with respect to dolomite, ran it for 32 years, and failed to produce any dolomite whatsoever. Until 1995, the only known experiments to successfully produced dolomite in laboratory settings were performed with temperatures in excess of 150°C that did not mimic the conditions of near-surface environments where dolomite is forming currently and has been known to form in the geologic record (Lippman, 1973; Baker and Kastner, 1981). Although the chemical reactions behind dolomitization have been well understood for decades, the best answer for why dolomite is so difficult to synthesize seems to lie in the thermodynamic and kinetic barriers of the reaction (Land, 1998).

Precipitation experiments have revealed much about the inhibitors affecting the dolomitization process. The ratio of Mg^{2+} ions to Ca^{2+} ions serves as an important factor during dolomitization; the higher this ratio is, the more likely dolomitization is to occur (Moore, 1989). The activity of the CO_3^{2-} ion, or carbonate alkalinity, also provides an influence on dolomitization (Slaughter and Hill, 1991). The activity of the CO_3^{2-} ion increases as pH increases, and this tends to favor the dolomitization process (Fig. 1). SO_4^{2-} is a well-known inhibitor to dolomite formation (Tucker and Wright, 1990). An experiment performed by Baker and Kastner (1981) focused on a dilute solution with no SO_4^{2}- which was shown experimentally to precipitate dolomite. When sulphate was added to the solution so that it contained 0.004 molarity SO_4^{2}, calcite precipitated

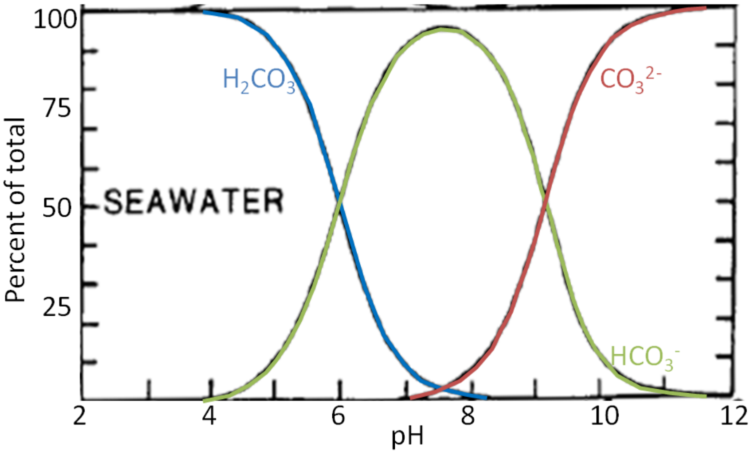

Figure 1. The relationship between the concentrations of carbonic acid (H_2CO_3), bicarbonate ions (HCO_3^-), and carbonate ions (CO_3^{2-}) with pH. As pH increases from 7 into more alkaline values, the concentration of carbonate ions increases relative to those of carbonic acid and bicarbonate ions. (Modified from Slaughter and Hill, 1991)

instead of dolomite, showing that the presence of a slight amount of sulphate may completely inhibit the dolomitization process. Finally, as mentioned above, temperature provides a control over the process of dolomitization; higher temperatures are more favorable to dolomite production (Baker and Kastner, 1981; Land, 1998).

Sabkha dolomitization is one of the most commonly referenced models of dolomitization (Tucker and Wright, 1990). Modern dolomite formation was first recognized in association with evaporites in arid tidal flat sediments in the Abu Dhabi sabkha (Wells, 1962). Literature has considered sabkha-style dolomitization to be the result of increased evaporation of marine waters, which acts to increase the ion concentration of the solution, and the production of gypsum ($CaSO_4 \bullet H_2O$), which decreases SO_4^{2} and Ca^{2+}, and thus locally increases the Mg^{2+}/Ca^{2+} ratio (Tucker and Wright, 1990).

Certain observations about dolomite formed in these environments suggests that perhaps these are not the only reasons why dolomitization is possible in sabkha settings. Dolomitization tends to only take place under reducing conditions in sabkhas, and H_2S is common amongst these dolomitized sediments. However, experiments replicating the precise physicochemical conditions of sabkha environments have failed (Land, 1998).

The idea that bacteria may play a role in the dolomitization process is not a new one (Nadson, 1928; Neher and Roher, 1958) but the idea has been recently rejuvenated thanks to some very important experiments and field observations. In the early eighties, researchers recognized that modern dolomite embedded within deep-sea sediments showed evidence of a microbial origin (Pisciotto and Mahoney, 1981). Vasconcelos et al. (1995) accidentally produced dolomite synthetically at low temperatures in association with sulphate-reducing bacteria collected from a hypersaline lagoon in Brazil. Since this discovery, many different field and laboratory studies have shown that several different types of bacteria are able to mediate the process of dolomite formation (Warthmann et al., 2000; van Lith et al., 2003; Wright and Wacey, 2005; Sanchez-Roman et al., 2008).

This present study is interested in the process of dolomitization as mediated by sulphate-reducing bacteria. The process by which this occurs has been laid out by several researchers (Vasconcelos and McKenzie, 1997; van Lith et al., 2003). First, sulphate-reducing bacteria decrease the sulphate ion concentration because they take up surrounding sulphate ions for metabolization (Eq. 1).

$$Ca^{2+} + Mg^{2+} + 2SO_4^{2-} + 2CH_3COOH \dashrightarrow CaMg(CO_3)_2 + 2H_2S + 2H_2O + 2CO_2$$
Equation 1

Sulphate-reducing bacteria are able to dissociate ion pairs. Typically, magnesium ions (which carry a +2 charge) and sulphate ions (which carry a -2 charge) are attracted to one another ionically while in solution, although they never form an ionic bond between them. Sulphate-reducing bacteria are able to dissociate these ion pairs because the outer sheath of the bacteria is negatively charged which attracts the magnesium ions while repelling the sulphate ions. This negatively charged sheath around the bacteria not only attracts positively charged magnesium ions but also positively charged calcium ions and in doing so changes in the chemical micro-environment around them. The chemical influence of sulphate-reducing bacteria within a solution is not infinitely extensive. Instead, it is strictly relegated to the matrix exo-polysaccharides (EPS), or in other words the “gunk” that the sulphate-reducing bacteria excrete which typically forms a rough sphere around the bacteria that is at most about 30 microns thick (van Lith et al., 2003).

Dolomite formation is further promoted by the increase in carbonate alkalinity of the solution immediately surrounding the sulphate-reducing bacteria. Carbonate ions are eventually released as carbon dioxide (CO_2), which is a product of the metabolism of sulphate-reducing bacteria (Eq.1). The CO_2 mixes with water and spontaneously converts into carbonic acid (H_2CO_3), which can subsequently convert into bicarbonate ions (HCO_3^-) or carbonate ions (CO_3^{2-}) depending on the pH (Fig. 1). Two other chemical reactions occur spontaneously which convert the molecules of carbon dioxide produced as a result of the sulphate reduction process into carbonate ions (Eq. 2 and 3).

$$H_2CO_3 \longleftrightarrow CO_2 + H_2O$$
Equation 2

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$
Equation 3

The increase of concentration of carbonate ions in the solution within the EPS immediately surrounding the sulphate-reducing bacteria favors the precipitation of dolomite because it increases carbonate alkalinity. An influx of hydrogen ions results because of the reactions that ultimately produced the carbonate ions, but also as a dissociation of the hydrogen sulfide that is a product of the original sulphate-reduction equation (Eq. 1 and 4).

$$H_2S \leftrightarrow HS^- + H^+$$
Equation 4

The increase in concentration of hydrogen ions in solution decreases the pH of the solution.

The precipitation of dolomite as mediated by sulphate-reducing bacteria is thought to occur because of the reasons explained above. First, the sulphate-reducing bacteria remove sulphate from the system via metabolization. Secondly, bacteria attract magnesium and calcium cations to their negatively charged surface, and a preferential attraction of magnesium cations occurs because of the ability of the sulphate-reducing bacteria to dissociate the magnesium/sulphate ion pair. Next, carbonate alkalinity is increased because carbonate ions are the eventual result of the sulphate-reduction reaction and because of the increase in pH of the system due to the influx of hydrogen ions.

This model of microbial dolomite precipitation (Vasconcelos and McKenzie, 1997) has been explained and tested by several researchers (Warthman et al., 2000; van Lith et al., 2003; Moreira et al., 2004; Roberts et al., 2004) and in general the model has stood up well; however, there is much work still to be done to further understand this process. For example, although many modern environments seemingly meet the necessary requirements of the model, why do only a few of these environments actually allow for bacterially induced dolomite precipitation? If sulphate-reducing bacteria are able to alter the micro-environment around them so powerfully, why is modern dolomite limited to only a few selected locations.

Also, as alluded to above, different types of bacteria have been shown to result in the precipitation of dolomite, not strictly bacteria of the sulphate-reducing variety (Rivadeneyra et al., 1993; Roberts et al., 2004; Sanchez-Roman et al., 2008). This suggests that perhaps much modern dolomite formed via microbial-influence is the result of a consortium of different types of bacteria, both aerobic and anaerobic, since bacteria is extremely ubiquitous and prolific.

The aim of this study is to help to further understand the microbial model of dolomite formation. Using simple components under chemical conditions that represent more common earth-surface circumstances, the synthesis of dolomite in a laboratory setting has been attempted. Although several studies have been completed which help to better describe this model (Warthman et al., 2000; van Lith et al., 2003, Wright and Wacey, 2005; Bontognali et al., 2010), none have attempted to produce dolomite within non-carbonate sediments and to identify the proximity to which the chemical composition of the dolomitizing solution can mimic normal marine or non-marine conditions. The results of this experiment are reported here.

CHAPTER 2 - METHODS

The goal of the experiment was to attempt to generate simple mini-dolomite-forming environments in different beakers under the influence of sulphate-reducing bacteria. One general experimental set-up was generated, and slight differences were applied to it to test the effects of different factors. The general set-up (Figs. 2-4) simply included a layer of sulphate-reducing bacteria-laden fine siliciclastic sediment bathed in modified seawater. This set-up is designed to be highly simplistic and only contains as many components as were thought necessary to produce dolomite by our understanding of the potential processes of dolomite formation under the influence of sulphate-reducing bacteria.

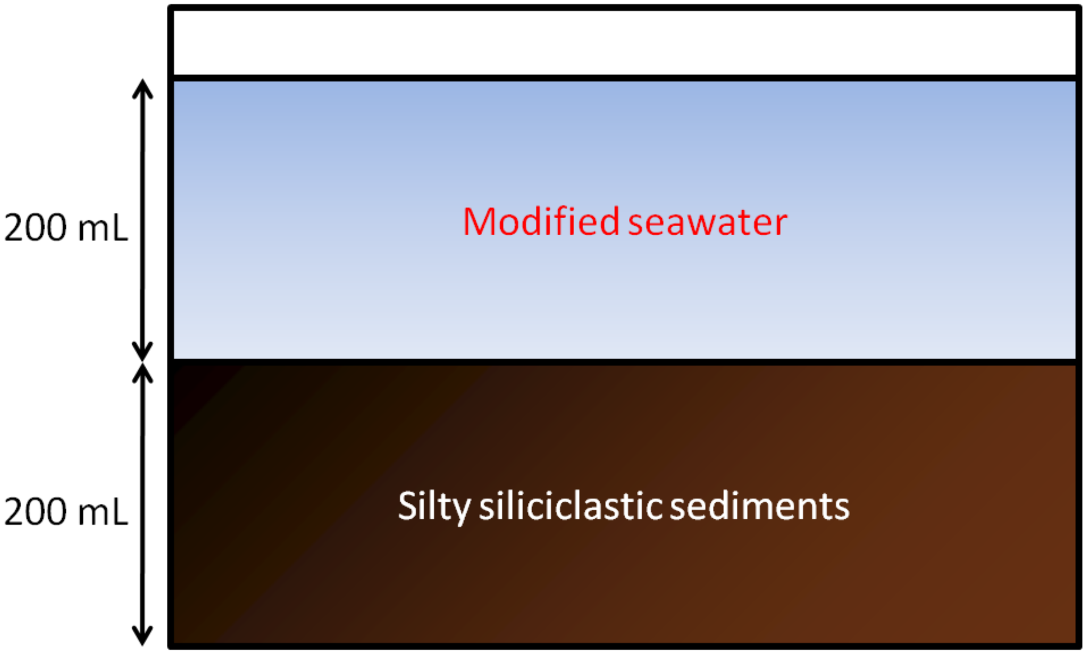

Figure 2. The general experimental set-up for a given experiment in the study. Additional components like ooids, pH buffer, and Mg^{2+} were only added to selected beakers.

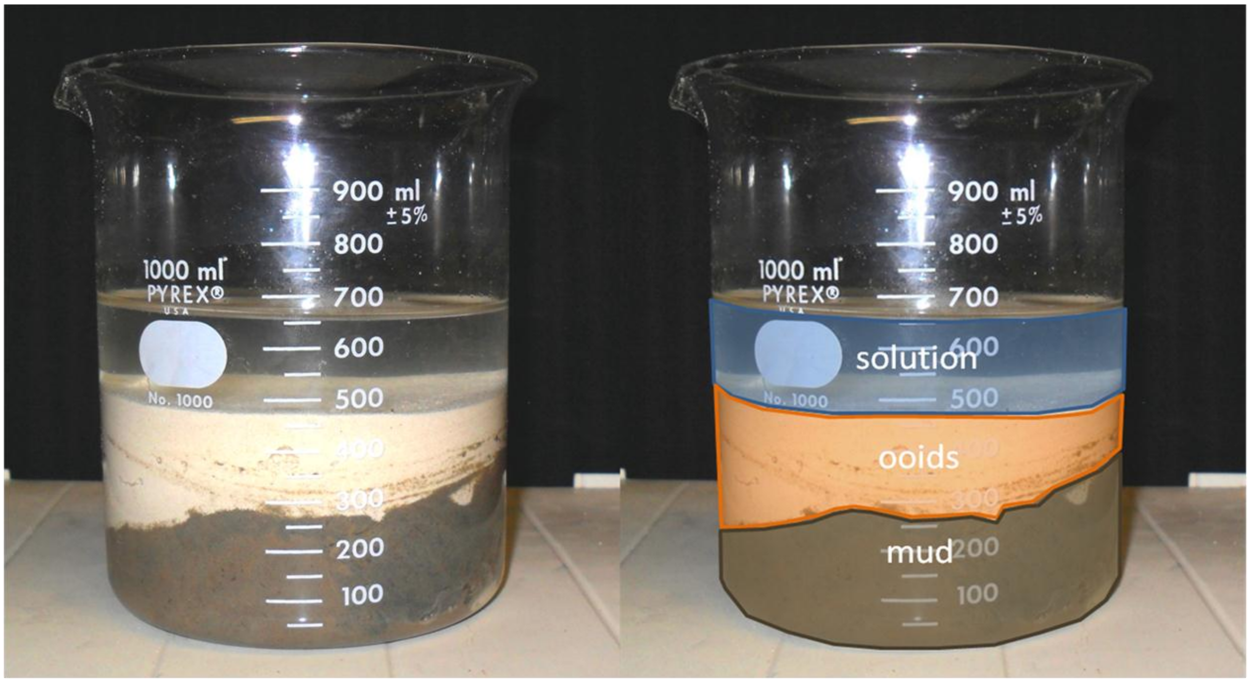

Figure 3. An example of the experimental set-up containing a layer of anoxic sludge at the bottom (mud) overlain by a layer of ooids from the Bahamas (ooids) and bathed by a solution of evaporated seawater (solution).

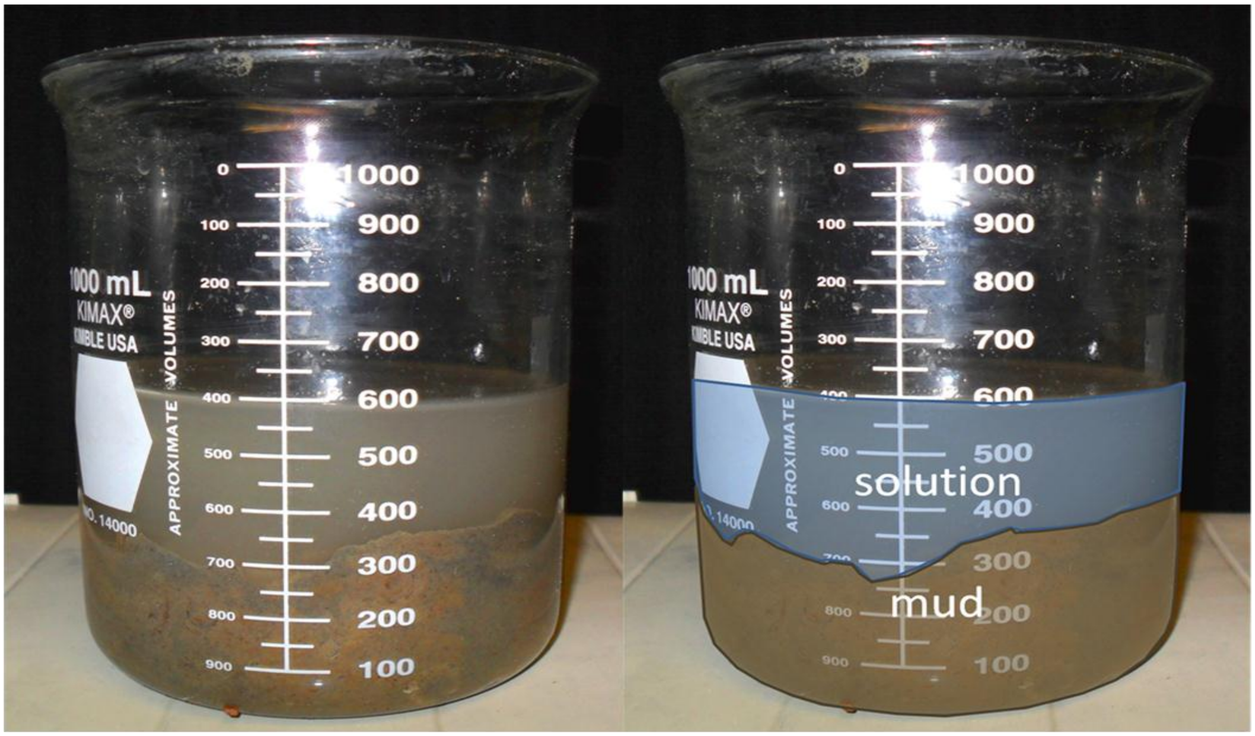

Figure 4. Another example of the experimental set-up, this time containing a base layer of anoxic sludge (mud) from Christmas Bay, Texas bathed in a solution of modified seawater (solution).

In total, 3 experimental runs were performed with each run containing 8 separate and isolated experiments, making a final total of 24 individual and experiments (Table 1).

Experimental Run #	***Individual Experiments Included***	***Length of Experimental Run***	***Mg/Ca Ratio Tested***
1	8	3 weeks	3.14
2	8	3 weeks	3.14
3	8	5 weeks	7.5

Table 1. General outline of experiment.

All 3 experimental runs were performed at 35 degrees Celsius to increase the rate of reaction for these experiments, and because it is easier to overcome some of the kinetic barriers to dolomitization at higher temperatures; it was thought that this relatively higher temperature would speed up the reaction. However, 35 °C is by no means an unusual surface temperature as the sabkhas of Abu Dhabi where dolomite is actively forming today regularly reach up to 50 degrees Celsius (Wells, 1962; Alsharan and Kendall, 2003). The first two experimental runs lasted for 3 weeks while the third was run for 5 weeks. The purpose of this change was to see if the length of time of the experiment dramatically affected the results.

The experiment also attempted in a controlled manner to analyze the effects of different factors thought to play a role in dolomitization (Tables 2 and 3). These factors include: (a) the presence or lack of a carbonate layer, (b) a more alkaline seawater chemistry bathing the system, and (c) an increase in the Mg^{2+}/Ca^{2+} ratio.

It was thought that in addition to the necessary layer of bacteria-laden sediment, a layer of carbonate sediment may change the chemistry in the

Beaker #	Seawater (mL)	Ooids (mL)	10pH Buffer Soln. (mL)	pH (calc.)	MgCl (mg)	Mg^{2+}/Ca^{2+} (calc.)
1	200	200	0	8	0	3
2	200	200	10	12	0	3
3	200	200	10	12	260	3.14
4	200	0	10	12	0	3
5	200	0	10	12	260	3.14
6	200	0	0	8	260	3.14
7	200	200	0	8	260	3.14
8	200	0	0	8	0	4

Table 2. Chemical composition of the experiments included in experimental runs 1 and experimental run 2. The pH of the modified seawater solution and the Mg^{2+}/Ca^{2+} ratio are both approximately calculated (calc.) and accurate to within 15%.

Beaker #	Seawater (mL)	Ooids (mL)	10pH Buffer Soln. (mL)	pH (calc.)	MgCl (g)	Mg^{2+}/Ca^{2+} (calc.)
1	200	200	0	8	0	3
2	200	200	10	12	0	3
3	200	200	10	12	6	7.5
4	200	0	10	12	0	3
5	200	0	10	12	6	7.5
6	200	0	0	8	6	7.5
7	200	200	0	8	6	7.5
8	200	0	0	8	0	3

Table 3. Chemical composition of the experiments included in experimental run 3. As above, the pH of the modified seawater solution and the Mg^{2+}/Ca^{2+} ratio are both approximately calculated (calc.) and accurate to within 15%.

surrounding seawater enough so that microbial dolomitization may be encouraged or sped-up. To test for this, a layer of ooids was added to some experiments while being left out in others. Because it is well-documented that dolomitization occurs favorably in seawater with a more alkaline water chemistry (Land, 1998), we wanted to know whether microbial dolomitzation would be affected by a similar trend. Therefore, to test for this possibility, a pH buffer with a pH value of 10 was added to some experiments and consequently left out in other experiments. It has long been shown that an increased Mg^{2+}/Ca^{2+} ratio could also increase the likelihood of the precipitation of dolomite (Land, 1998). To test how this might affect microbial dolomitization, additional Mg^{2+} was added in some experiments while being left out in others. This additional Mg^{2+} increased the Mg^{2+}/Ca^{2+} ratio of the seawater in the system. Also, the amount of Mg^{2+} added into the experiments included in the third experimental run was much greater than the amount of Mg^{2+} included in the experiments of first two runs which resulted in a much higher Mg^{2+}/Ca^{2+} ratio for those experiments in the third run. This allowed us to see the potential effects of different elevated Mg^{2+}/Ca^{2+} ratios on microbial dolomitization.

Black silty siliciclastic sediment was collected on the island side of Christmas Bay in about 3 feet of water at Follett's Island near Galveston, Texas (Fig. 5). Approximately two feet of overlying sediment, mostly composed of muddy silt, above the collected sediment was removed in order to collect sediment that was more likely to be anoxic for an extended period of time. This black sediment was then shoveled into 5-gallon buckets until they were approximately 80% filled and transported back to the University of Houston campus. The composition of this sediment is approximately 30% clay, 65% silt-sized

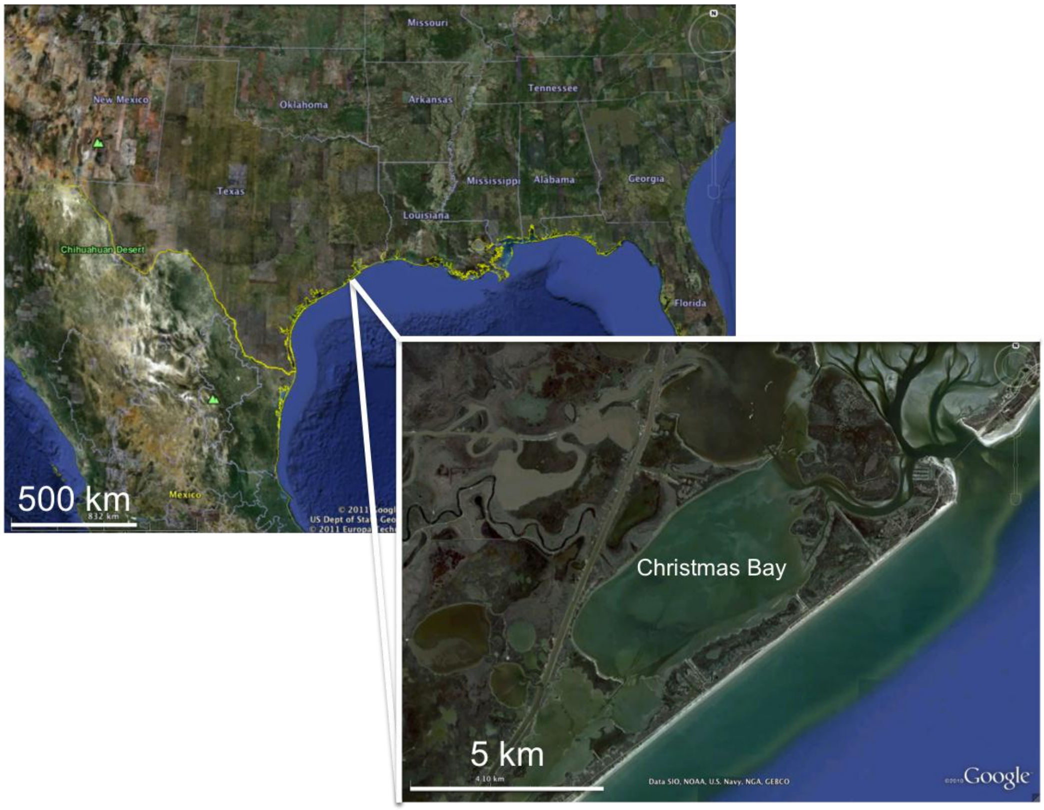

Figure 5. Christmas Bay near Brazosport, Texas where both silty siliciclastic sediment and water samples were collected for experimentation.

grains (almost entirely quartz), 3% sand-sized grains (entirely quartz), and 2% organic matter (plant roots and stems originally buried within the sediment). The plant matter provided food for the bacteria. Each experimental beaker contained approximately 200 mL of this silty sediment.

During this process, it is inevitable that the mud was exposed to oxygen to some degree. This is a potential problem because the total population of sulphate-reducing bacteria, which are strict anaerobes (meaning that not only do they not require oxygen to metabolize but the mere exposure to oxygen can result in their death), may have decreased during sediment acquisition and transportaion. Although the presence of sulphate-reducing bacteria within this mud was never strictly tested for, this researcher does not believe that the integrity of the samples was compromised significantly because, the mud remained black and still emitted the tell-tale smell of hydrogen sulfide (a smell not dissimilar to rotting eggs) when the buckets containing this mud were opened immediately after their transport to the University of Houston campus. This sediment also released a pungent sulfur smell over one year after its acquisition when the same 5-gallon containers in which the sediments were held were opened again suggesting that the anaerobic bacteria within the sediment was able to survive for at least this period of time. For the sulphate-reducing bacteria to survive within a 5-gallon bucket of silt and sandy sediments with limited organic matter for over a year's time they would indeed have to be hardy organisms able to overcome rather dramatic changes in their chemical and physical environment.

The aragonitic ooids used for experimentation were obtained by Dr. Henry Chafetz of the University of Houston. These ooids were originally collected unconsolidated in the Bahamas in a modern ooid-forming shoal environment. They were then transported to the University of Houston campus to be used for the purposes of this study. Each experimental beaker contained approximately 200 mL of ooids.

Seawater was collected from the Gulf of Mexico on the shore of Follett's Island (Fig. 5) in large 5-gallon containers. This seawater was then evaporated to approximately twice salinity by placing the coolers containing the seawater under a heat lamp for a number of days until the volume of water in the coolers was reduced to about half of the starting volume. Each experimental beaker contained approximately 200 mL of evaporated seawater at any given time, and this seawater was changed regularly throughout the duration of the experiment.

After the experiments were run for their duration (either a period of 3 weeks, as in experimental runs 1 and 2, or 5 weeks, as in experimental run 3), the silty sediments (and ooids, when present) were carefully analyzed to determine mineralogy and describe their morphology and chemical composition. The use of X-ray diffractometer (XRD) as a means of identifying bulk mineralogy was considered and even adopted in preliminary stages of the study, but after this preliminary usage of XRD it was shown that any potential dolomite precipitates in the system probably did not pass the threshold abundance necessary for detection via XRD. Furthermore, petrographic analysis revealed at best only hints of authigenic carbonate materials and did not provide much opportunity for any further study either optically or geochemically. Therefore, it was determined that the approach best suited for the identification of very small precipitates as well as a description of their morphology and chemical composition was that of an SEM equipped with energy-dispersive x-ray spectroscopy (EDAX) capabilities. A JEOL JSM-5410 scanning electron microscope (SEM) housed at the Texas Center of Superconductivity at the University of Houston was used in this process while a Seimens GADDS X-ray diffractometer housed at the same location was used for early XRD work. Before undergoing SEM analysis, all samples were coated in a thin carbon film to allow for proper viewing in the SEM as well as trustworthy chemical analysis via EDAX.

To more accurately identify the elemental spectrum of potential dolomite crystals generated in this experiment, 3 dolostones from the rock record were analyzed using the same EDAX instrument that analyzed the results of the experimental runs (Figs. 6-8). The spectrums of the 3 dolostones then served as reference spectrums against which crystals from this experiment were compared. Also, the EDAX employed in this study possesses the ability to approximate relative concentrations in the recognized standards and can therefore generate elemental relative percentages of constituent elements in unknown crystals. Although these elemental percentages are at best approximations, they can be used to better characterize a given crystal.

One aspect of this study that separates it from similar studies performed by other workers in the field (Vasconcelos et al., 1995; Warthmann et al., 2000; Van Lith et al., 2003; Wright and Wacey, 2005; Bontognali et al., 2008; Sanchez-Roman et al., 2008;

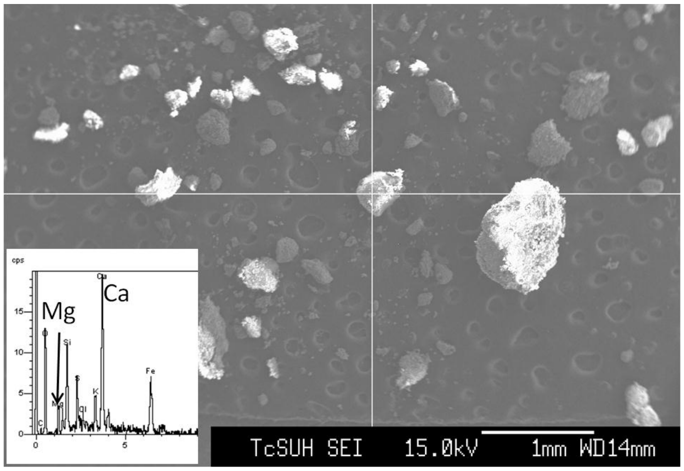

Figure 6. Dolomite standard 1. All grains are composed of dolomite. Although many peaks are present within the spectrum, the large Ca peak and the presence of a Mg peak help to identify the grain as dolomite. Other peaks correspond to impurities in the crystal lattice and indicate the presence of silicon, sulfur, potassium, and iron.

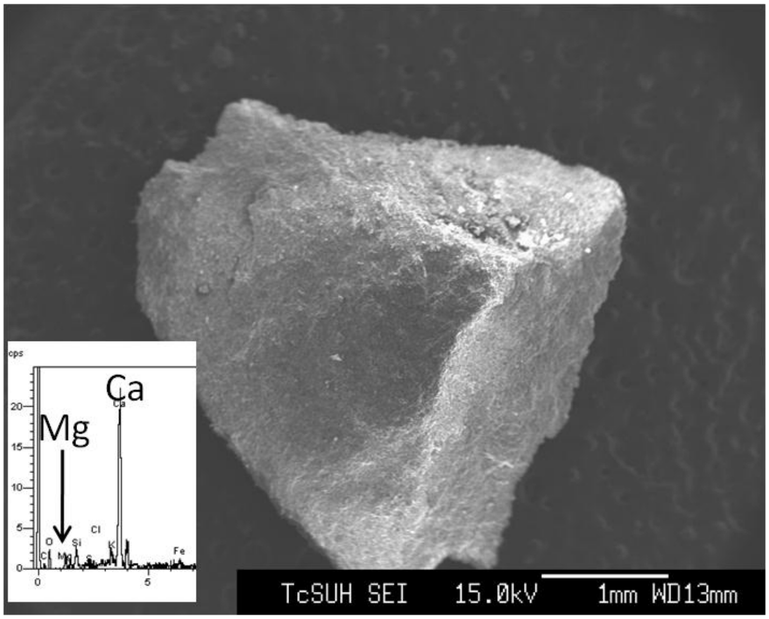

Figure 7. Dolomite standard 2. Even though the Mg peak is relatively small in the spectrum, its presence in conjunction with a Ca peak is indicative of dolomite.

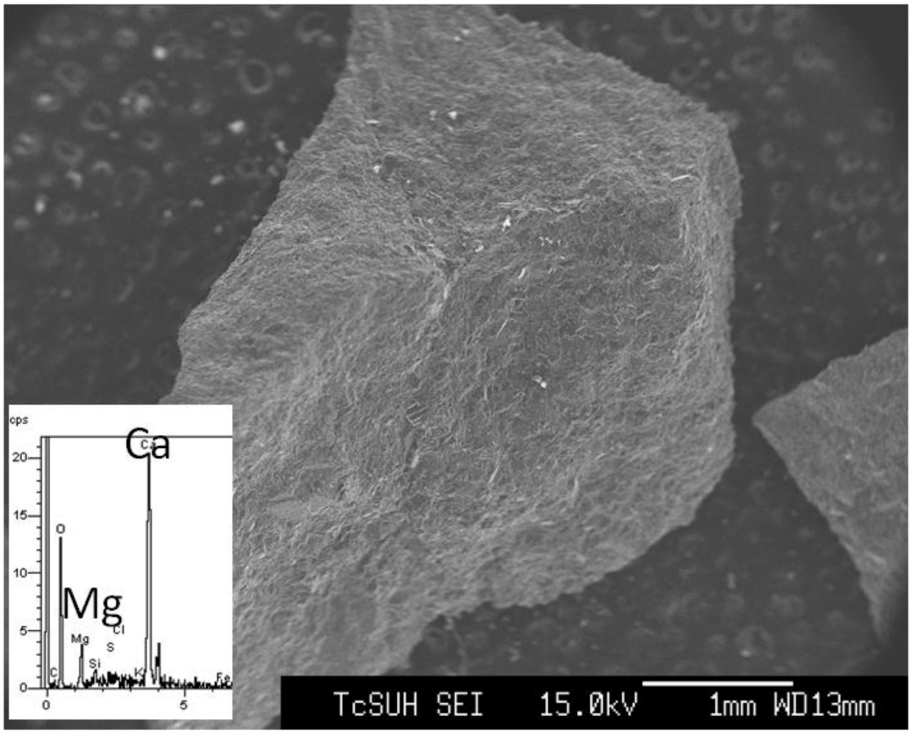

Figure 8. Dolomite standard 3. Significant Ca and Mg peaks indicate that this sample is composed of dolomite.

amongst others) is that this study is not testing whether a specific species of bacteria can induce the precipitation of bacteria. This experimental set-up in which modern sediments and seawater are used, test whether communities of common sulphate-reducing bacteria can induce dolomite precipitation in nature. Although this point may seem rather pedantic at first, it is the opinion of this author that indeed this distinction is geologically significant and will be discussed at length in the Conclusion section.

CHAPTER 3 – RESULTS

Sediments before and after experimentation both show an array of minerals and organic substances. Visual identification via SEM imagery and EDAX analysis allowed for the identification of their components (Table 4). From an analysis of the results of the 24 experimental trials, 3 proved to result in dolomite precipitation in the form of small (5 microns or less) crystals. No similar crystals are identified in sediments that had not undergone experimentation.

Three different types of organic matter were observed: “smooth” organic matter (Fig. 9), “rough” organic matter (Fig. 10), and body fossils (Fig. 11).

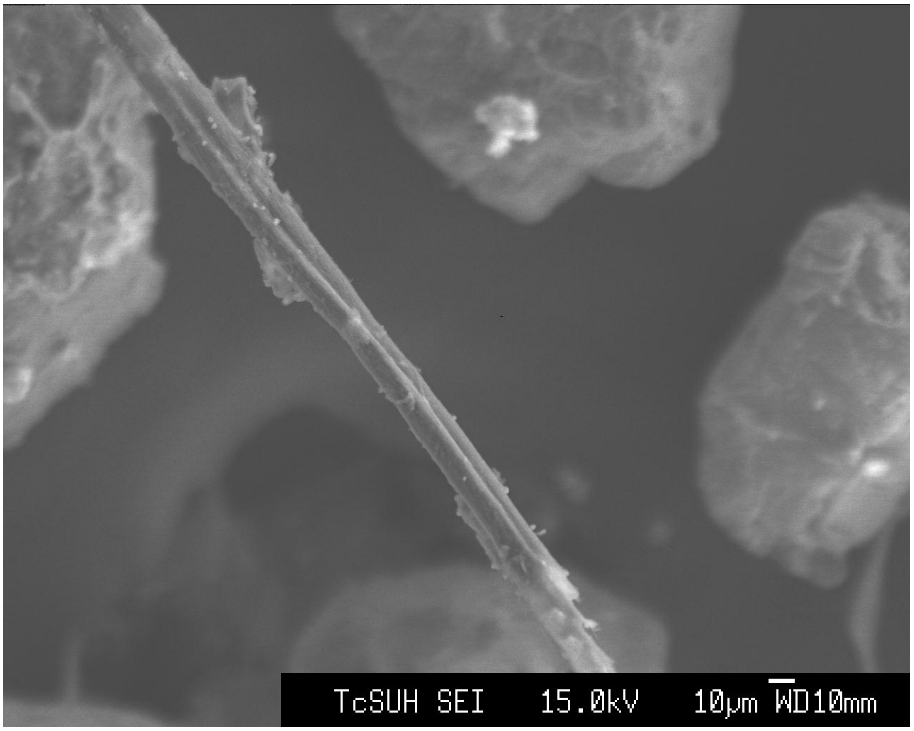

Figure 9. A segment of “smooth” organic matter with small carbonate precipitates and evaporite crystals. Larger silt-sized quartz grains in background.

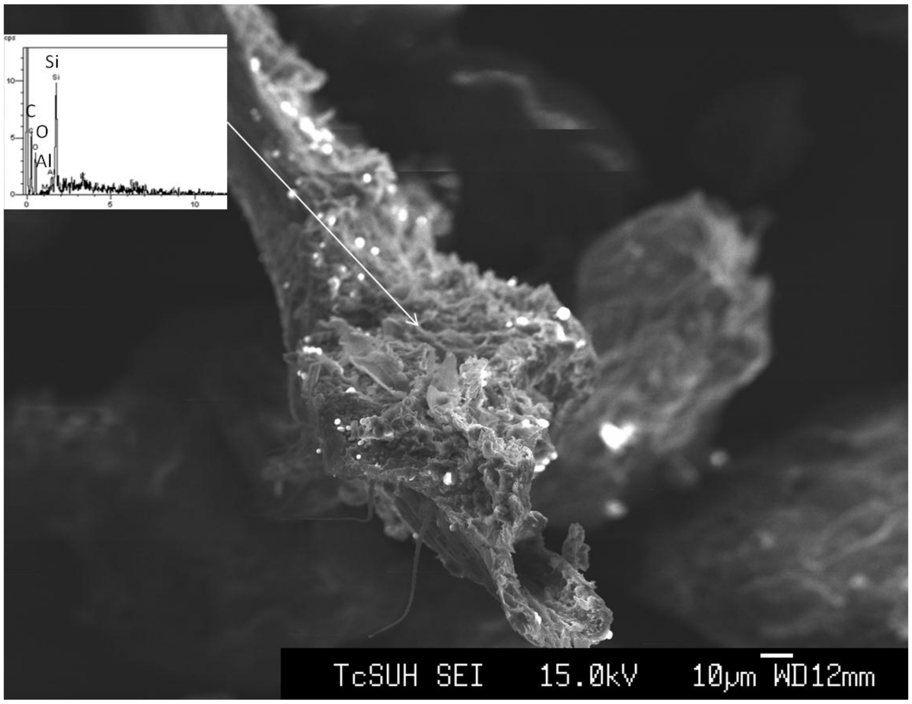

Figure 10. A segment of "rough" organic matter. Arrow points to area of organic matter from which the spectrum was calculated.

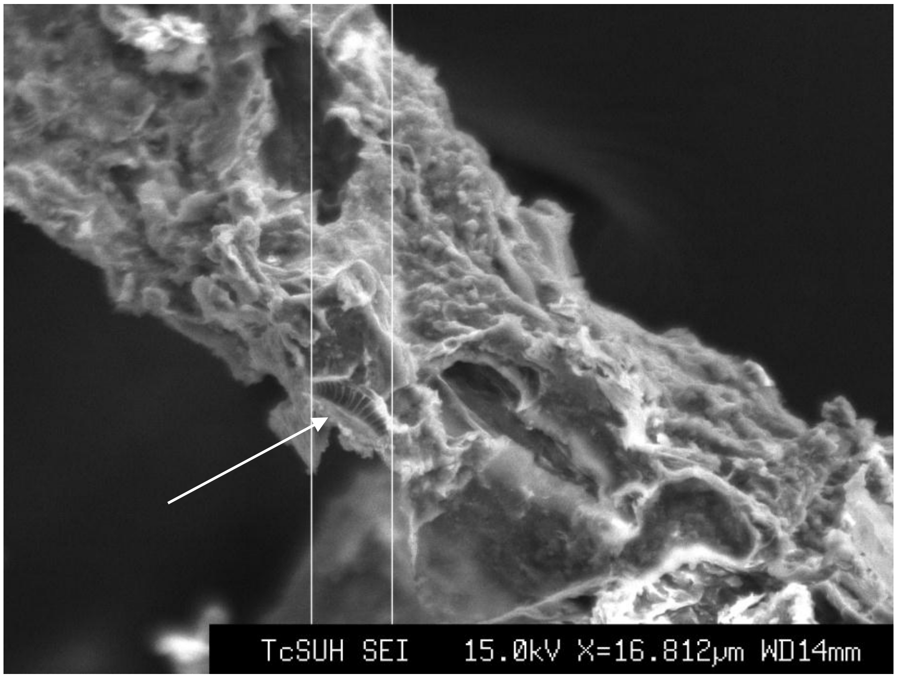

Figure 11. A body fossil (arrow) on a piece of "rough" organic matter. Fossil is about 20 microns in length. Also covering organic matter are evaporite crystals and siliciclastic muds.

The difference between the first two types of organic matter are based on SEM observations where “smooth” organic matter contains relatively few surface markings, usually in the form of a few evaporite or carbonate precipitates. “Rough” organic matter, on the other hand, may be covered with an abundance of mud- or silt-sized grains along with evaporite or iron-sulfide crystals and calcite precipitates. The elemental spectrum of “rough” organic matter shows an abundance of peaks of C, O, and Si (Fig. 10). Preliminary observations suggest that most of the fossils were typical organisms found readily living within the near-shore water column like foraminifera or diatoms.

Many different types of minerals were identified within the samples by comparison with well-established elemental spectrum references (or independently derived references as in the case of dolomite) after the experimental runs had been performed. These include detrital quartz grains (Figs. 12, 16), halite crystals (Figs. 12, 14, 16), gypsum crystals (Figs. 13, 15), iron sulfide (Fig. 17), carbonate ooids (Fig. 18), calcite precipitates (Figs. 19-24, Fig. 28), and dolomite precipitates (Figs. 25-27). An analysis of similar sediments that had not undergone experimentation revealed the presence of detrital quartz grains, halite crystals, gypsum crystals, and aragonitic ooids. Therefore, it follows that the components that were present after the experimental runs took place but were not identified in similar sediments that had not undergone experimentation are: (a) iron sulfide crystals, (b) calcite precipitates, and (c) dolomite precipitates (Table 4).

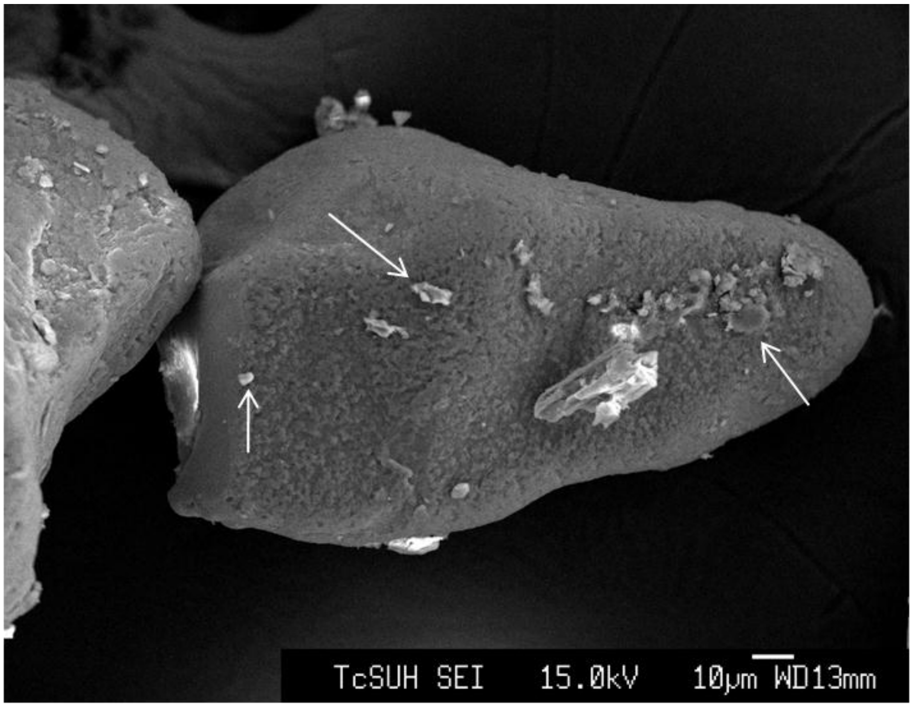

Figure 12. A detrital quartz grain with small evaporite (halite) crystals (arrows).

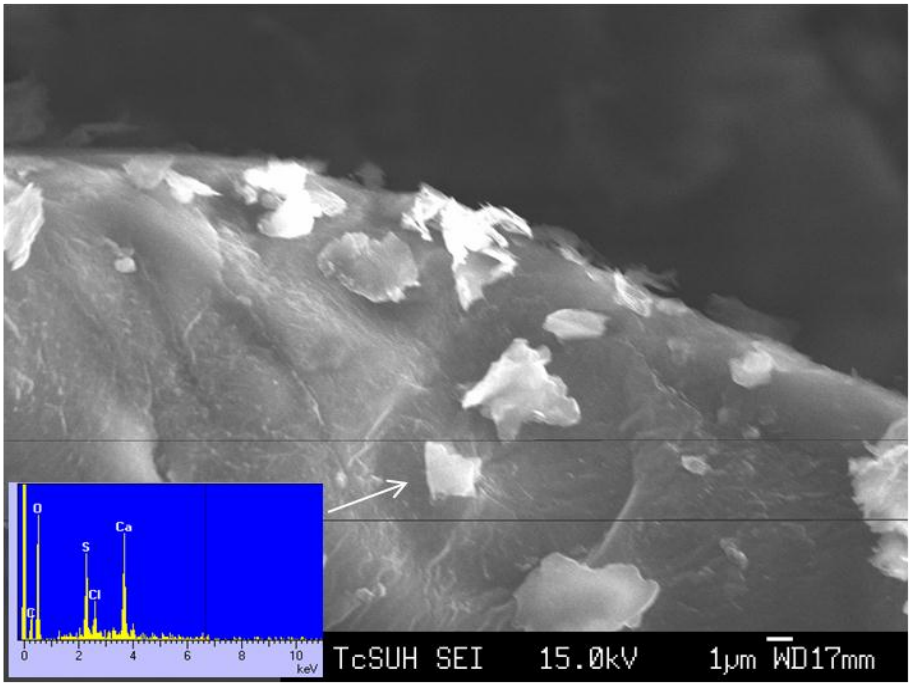

Figure 13. A gypsum crystal (arrow) on “smooth” or “intermediate” organic matter. The surrounding crystals are evaporites (halite) or silica detritus.

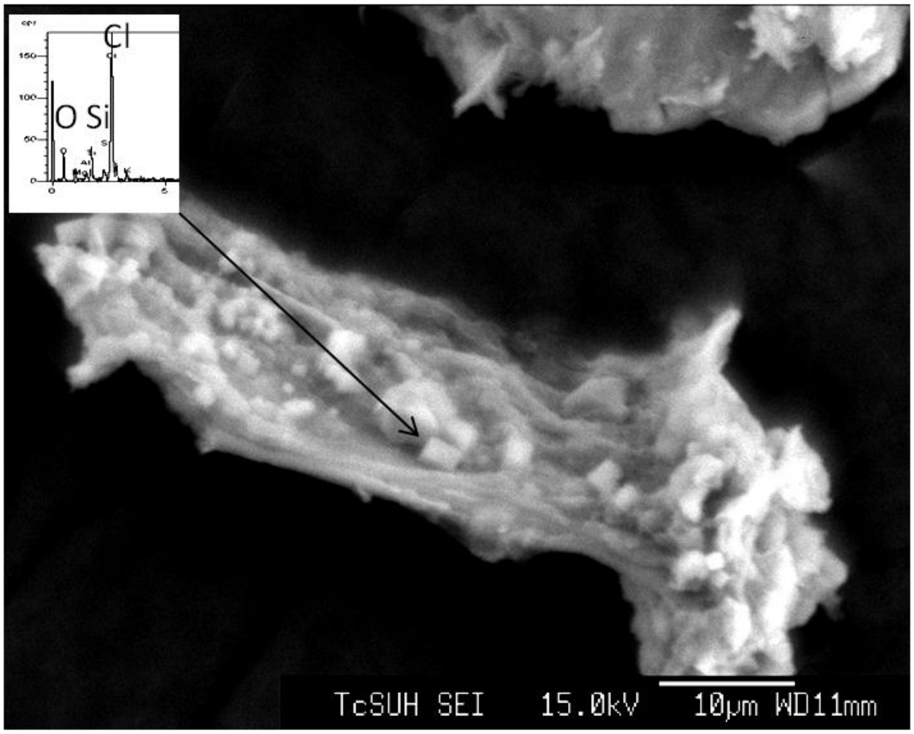

Figure 14. A piece of intermediate (neither exclusively rough nor smooth) organic matter with halite rhombohedrons (arrow).

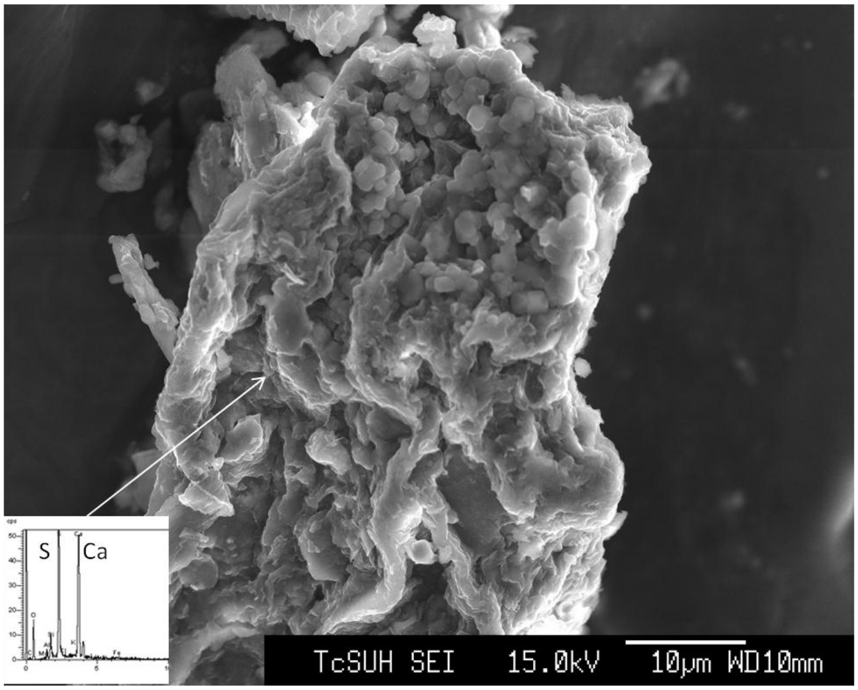

Figure 15. A piece of "rough" organic matter with gypsum crystals (arrow).

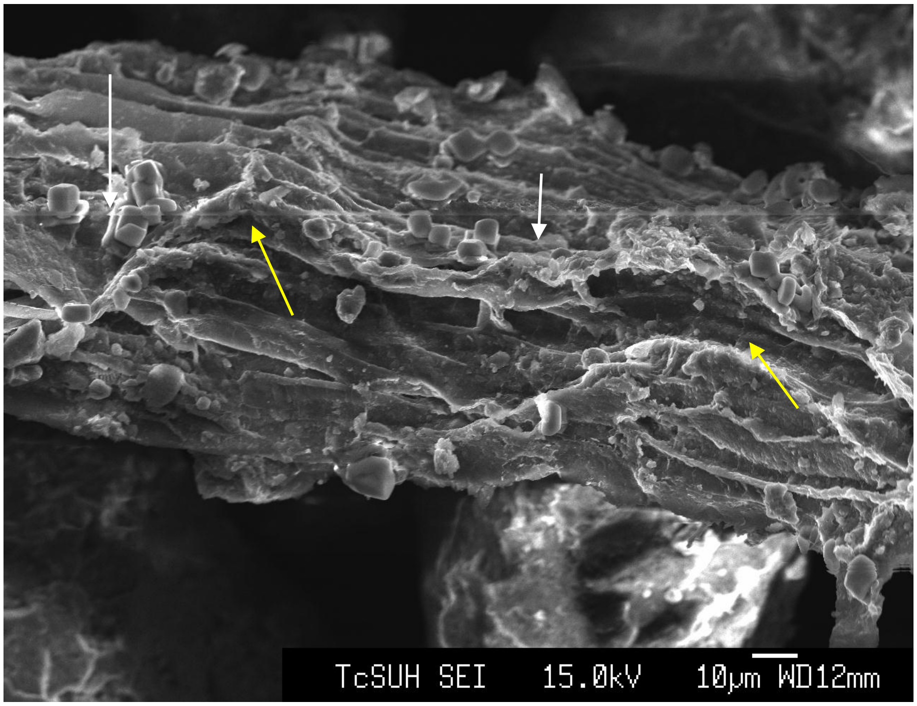

Figure 16. A section of “rough” organic matter with evaporite crystals (rounded, relatively large crystals, halite; white arrow) and quartz detritus (smaller, angular grains; yellow arrows).

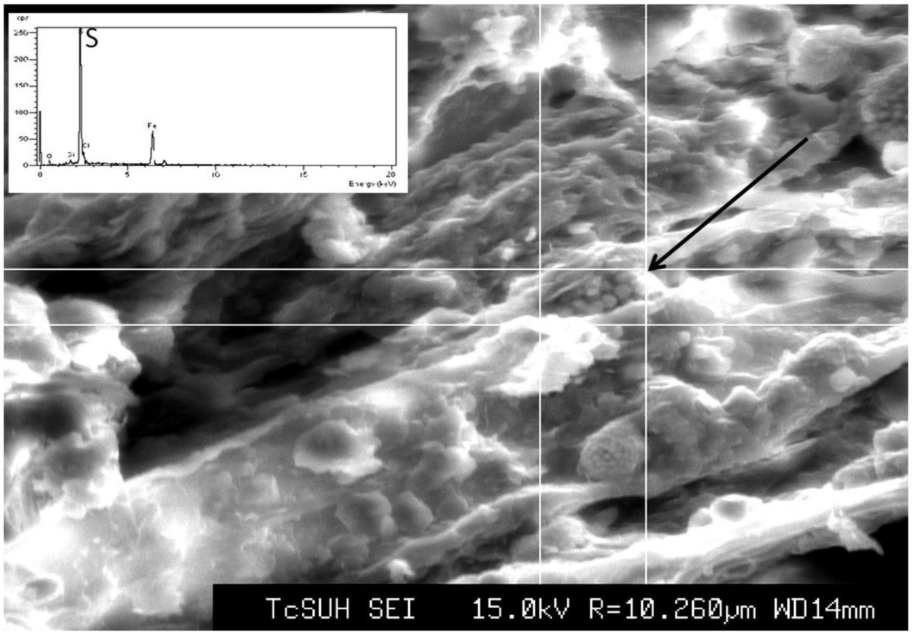

Figure 17. A small group of iron sulfide spheroids (arrow) embedded within a piece of “rough” organic matter that is covered with evaporite crystals and siliciclastic detritus and muds.

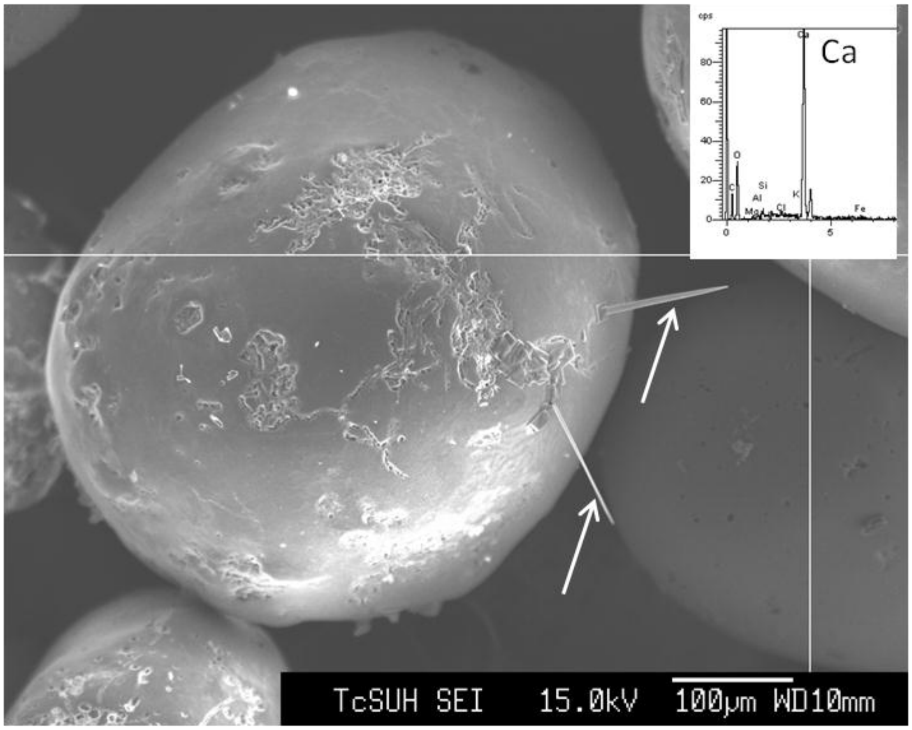

Figure 18. A dimpled aragonitic ooid with sharp-looking halite spikes (arrows) protruding from it.

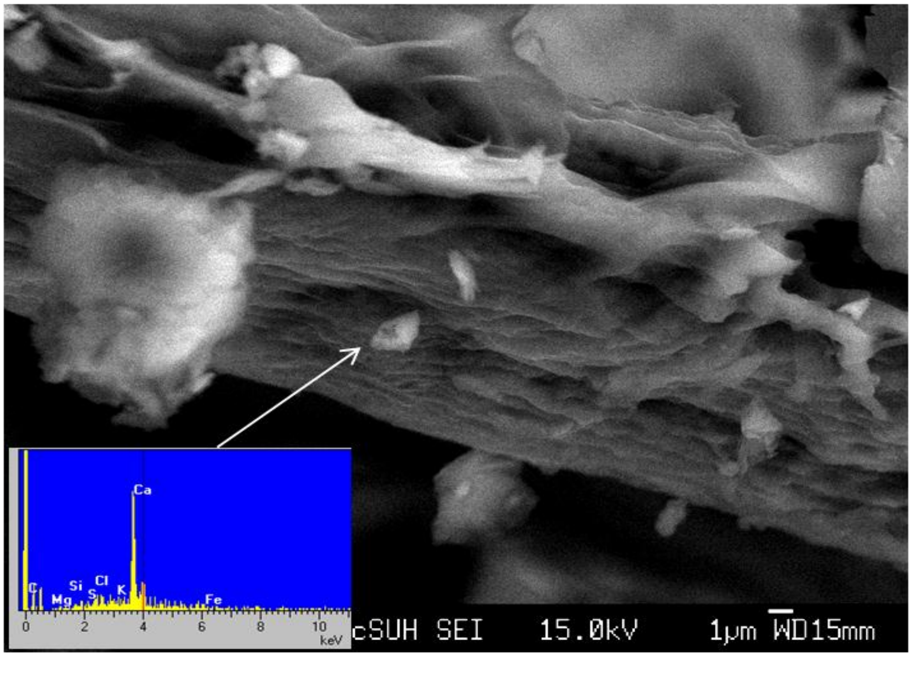

Figure 19. A crystal of calcite (arrow) on “smooth” organic matter. The cloudy mass to the left of the calcite is a mixture of mud, evaporite, and silica detritus.

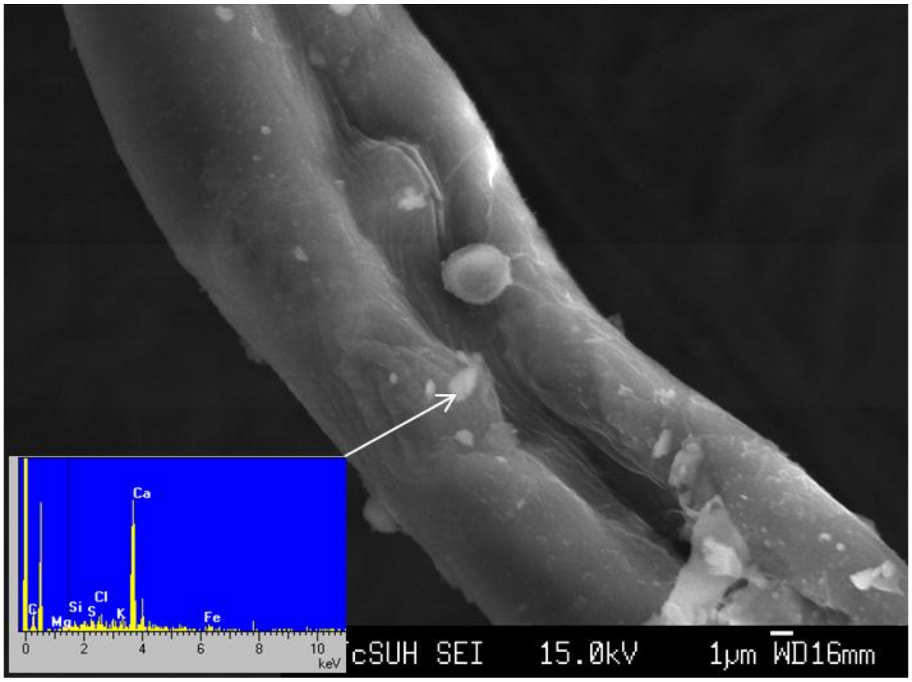

Figure 20. A crystal of calcite on “smooth” organic matter. The larger, circular-shaped crystal above the calcite crystal is a crystal of gypsum.

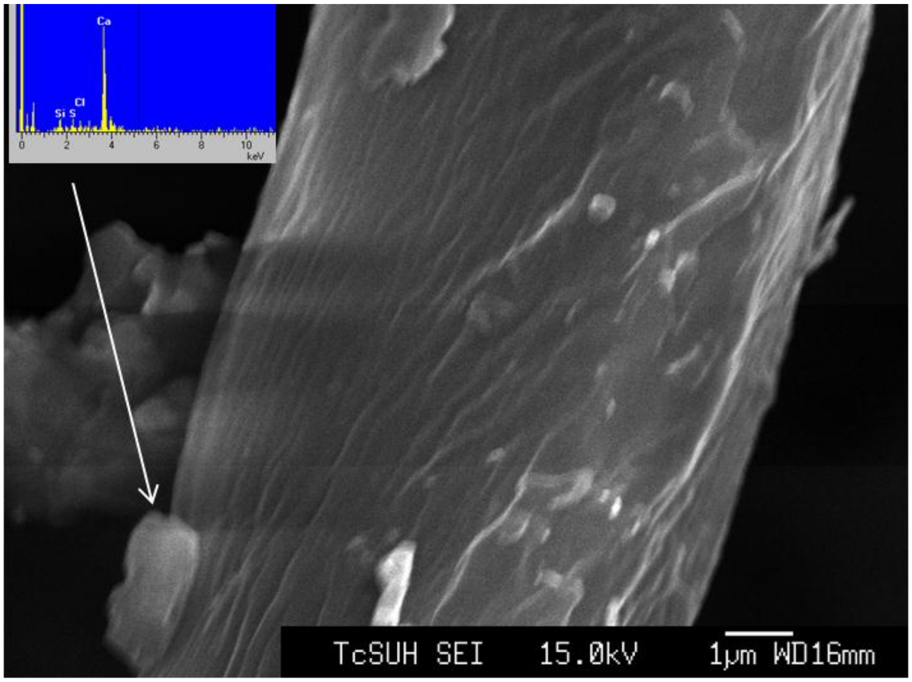

Figure 21. A crystal of calcite (arrow) on “smooth” organic matter. Its irregular shape suggests that it might have a biotic origin. The other crystals and grains on the organic matter are evaporite or silica detritus.

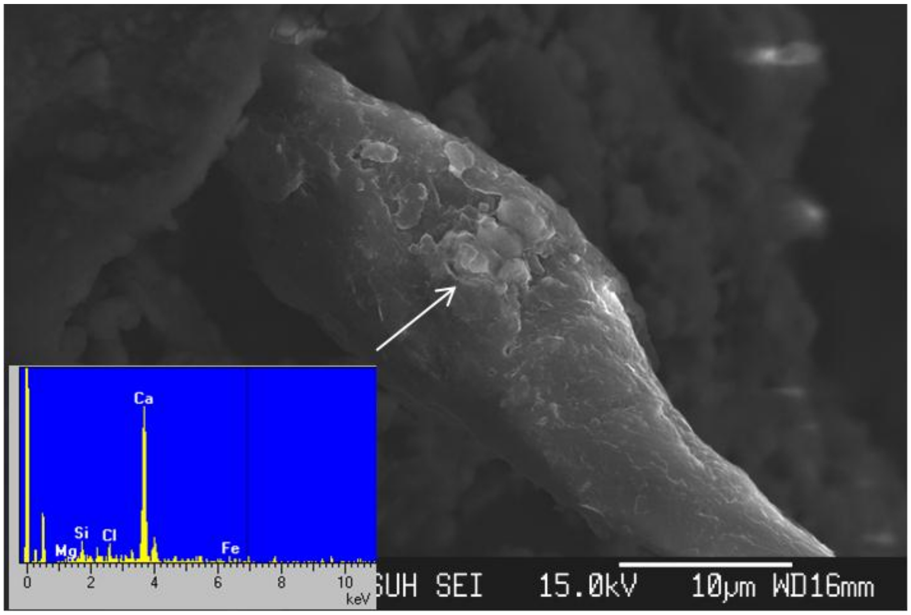

Figure 22. An amalgamation of calcite grains (arrow) on a section of "smooth" organic matter. The amalgamated grains might represent an area of increased bacterial accumulation on the organic matter.

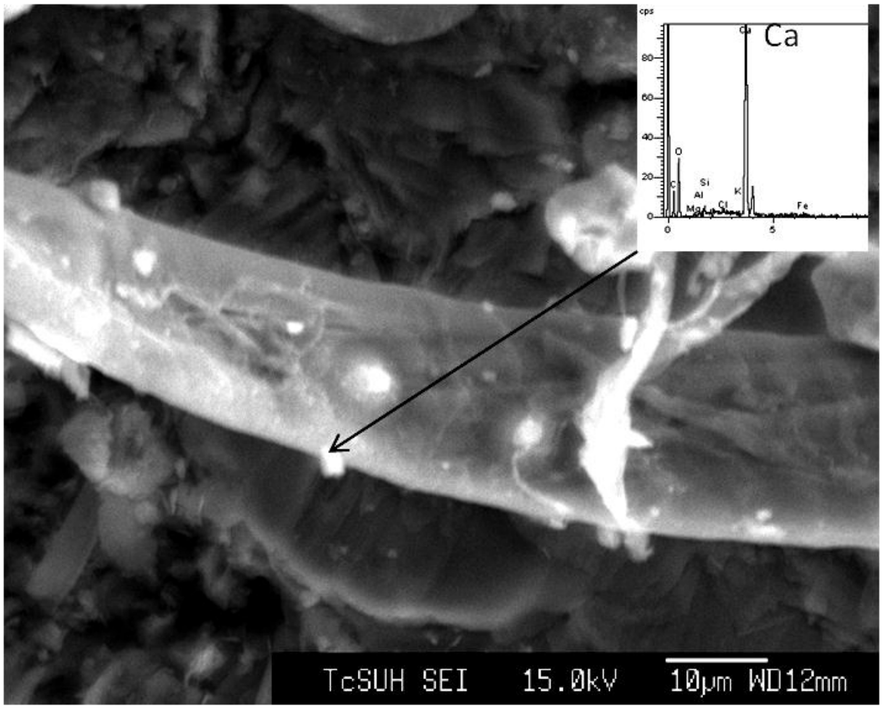

Figure 23. Precipitates of calcite (arrow) showing roughly euhedral crystal habit on "smooth" organic matter

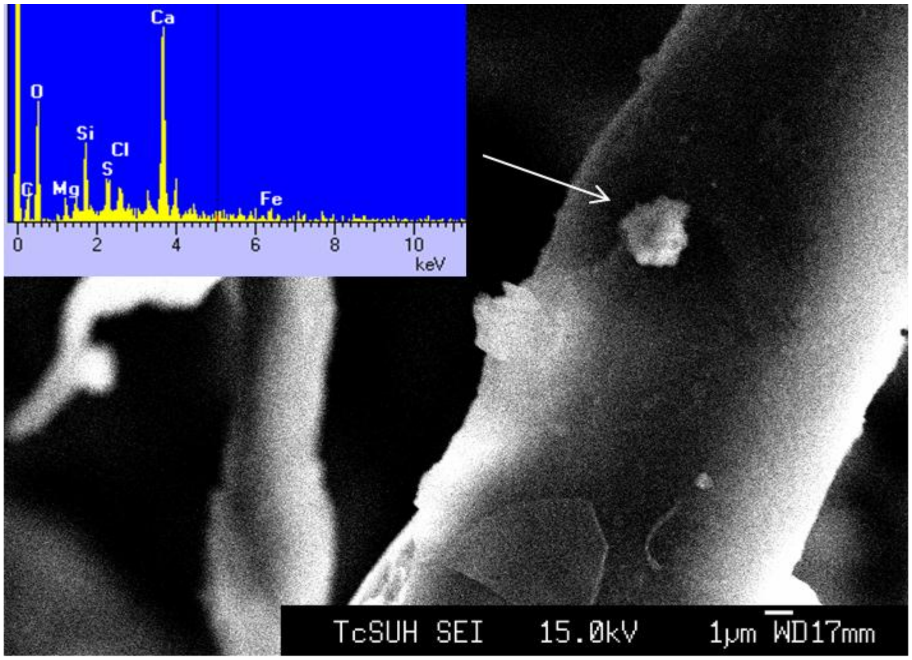

Figure 24. A high-Mg grain of calcite (arrow) on “smooth” organic matter. It contains approximately 23% Mg and 77% Ca.

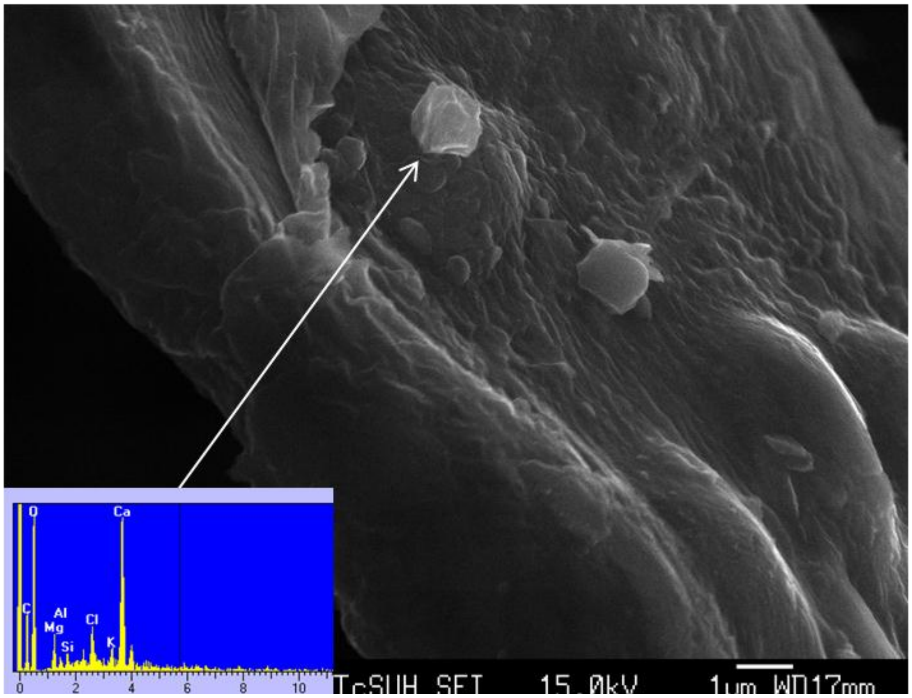

Figure 25. A micron-long precipitate of dolomite (arrow) on “smooth” organic matter. Relatively large, micron-sized crystal to the center-right of the image is an evaporite crystal.

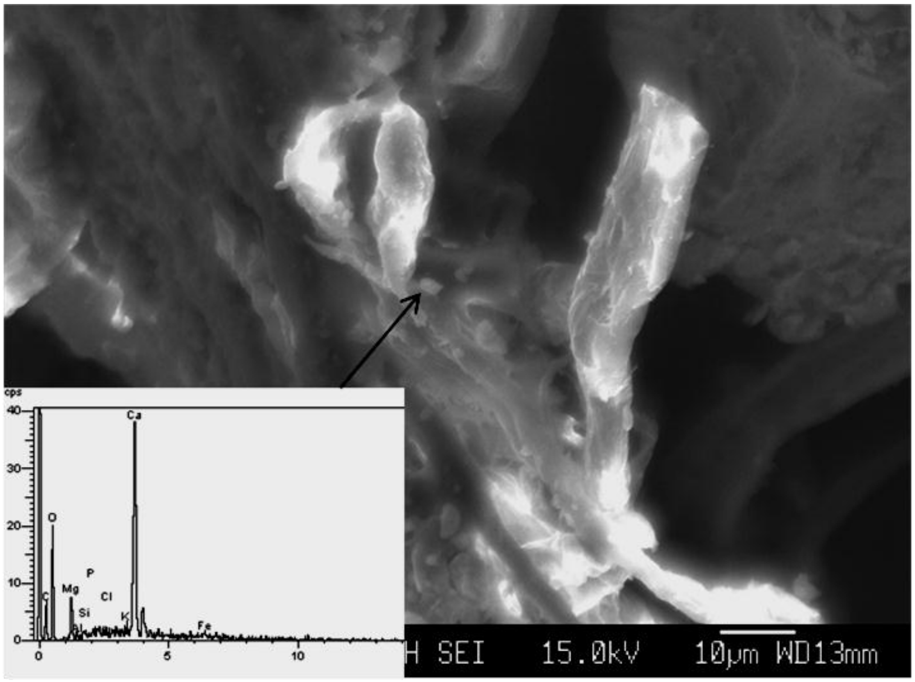

Figure 26. A roughly rhombic dolomite precipitate (arrow) on a piece of "smooth" organic matter from beaker 2.2.

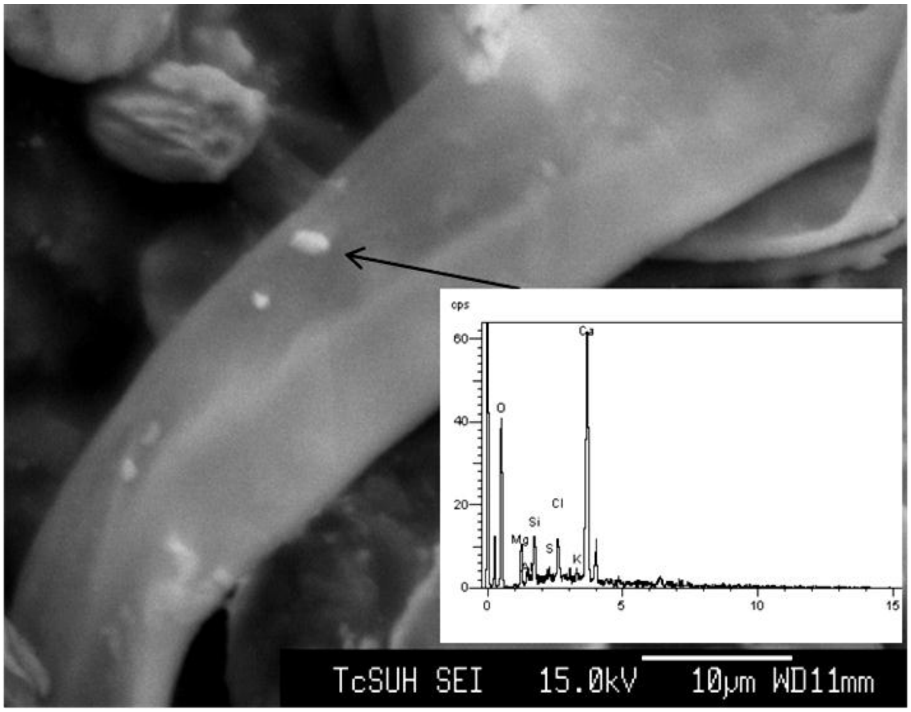

Figure 27. A dolomite precipitate (arrow) on a piece of "smooth" organic matter from beaker 1.7. It shows a roughly rectangular, euhedral morphology

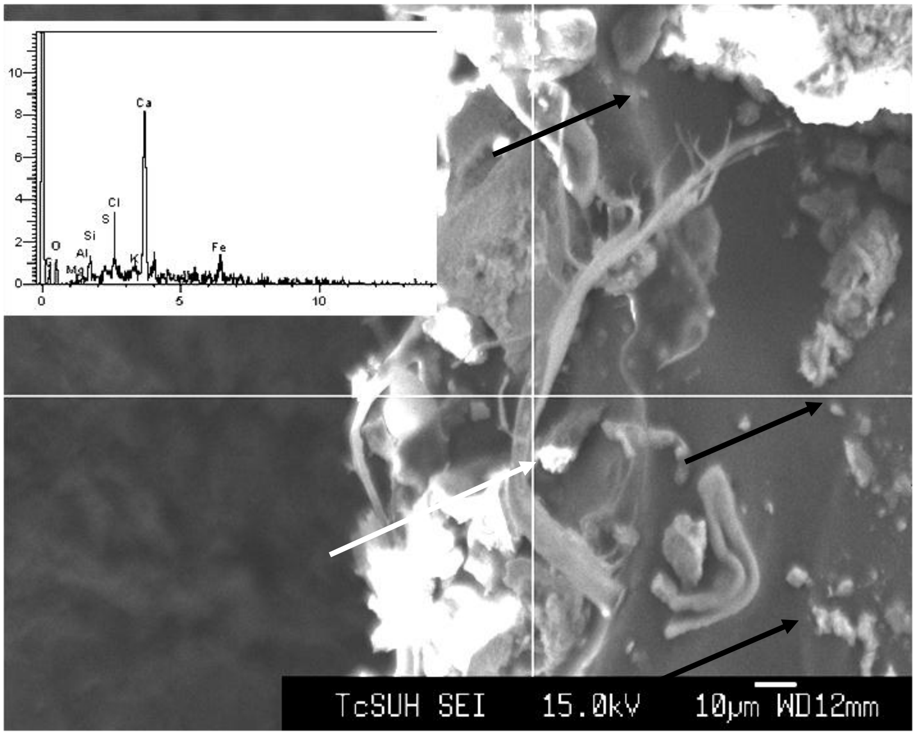

Figure 28. A magnesian-calcite precipitate (white arrow) on “smooth” organic matter from beaker 2.1. Also included are siliciclastic detritus (black arrow).

As mentioned above, dolomite crystals were identified within the sediments in 4 of the experiments (Table 8). In experimental run 1, dolomite was discovered in experimental beakers 3 (beaker 1.3) and 7 (beaker 1.7, Fig. 25). In experimental run 2, dolomite was discovered in experimental beaker 2 (beaker 2.2, Fig. 24). In experimental run 3, dolomite was discovered in experimental beaker 1 (beaker 3.1, Fig. 23). Unfortunately, the image and elemental spectrum of the dolomite precipitate from beaker 1.3 were lost, so this precipitate cannot be compared adequately with the others. Also in experimental run 2, a high-Mg calcite precipitate was discovered in the experimental beaker 1 (beaker 2.1, Fig. 26).

	Seds. Without Experimentation	**Seds. After Experimentation**
“smooth” organic matter	☑	☑
“rough” organic matter	☑	☑
body fossils	☑	☑
detrital quartz	☑	☑
halite	☑	☑
gypsum	☑	☑
iron sulfide		☑
aragonitic ooids	☑	☑
calcite precipitates		☑
dolomite precipitates		☑

Table 4. Comparison of the presence of various components in sediments that had not undergone experimentation and sediments that have undergone experimental runs.

A “back-of-the-envelope” calculation of the ratio between magnesium and calcium in these precipitates was performed which further aided in the interpretation of the mineralogy of these crystal precipitates. As briefly alluded to above, the EDAX employed in this study has the ability to approximate atomic and mass percentages of various elements by comparing their relative spectral magnitudes to previously-analyzed standards. By using this method, the ratio of magnesium to calcium in each of these percentages was determined. The precipitates in beakers 1.7 and 2.2 verge on stoichiometric dolomite with Ca:Mg ratios of 1.07 (Table 5) and 1.03 (Table 6), respectively. The precipitate in beaker 2.1 high-Mg calcite with a

Element	**Mass %**	**Atomic %**
Mg	36.22	48.35
Ca	63.78	51.65
Total	100	100
Ca:Mg Ratio	1.76	1.07

Table 5. Quantitative elemental calculations for precipitate found in beaker 1.7.

Element	**Mass %**	**Atomic %**
Mg	37.06	42.96
Ca	62.94	50.74
Total	100	100
Ca:Mg Ratio	1.70	1.03

Table 6. Quantitative elemental calculations for precipitate found in beaker 2.2.

Ca:Mg ratio of 12.09 (Table 7), with about 8% magnesium included in the crystal structure.

A comparison of the spectra of these magnesian-calcite and dolomite precipitates with the previously-mentioned dolomite standards shows some interesting similarities and differences (Fig. 29). A characteristic and very strong peak in calcium is present in all 6 spectra. A magnesium peak is present in all 6 spectra as well, but its magnitude varies dramatically from one spectrum to another and is the lowest in the magnesian-calcite sample in beaker 2.1. Also, the 3 samples obtained from results of the experiments contain an abundance of elements other than those that constitute pure dolomite, including silicon, chlorine, potassium, and sulfur.

Element	**Mass %**	**Atomic %**
Mg	12.01	7.64
Ca	87.99	92.36
Total	100	100
Ca:Mg Ratio	7.33	12.09

Table 7. Quantitative elemental calculations for precipitate found in beaker 2.1.

The morphology of the carbonate precipitates was determined using visual inspection via SEM imagery. Unfortunately, the precipitates being studied were sometimes obscured by sediments in which they were embedded or overlain, and so a detailed analysis of precipitate morphology cannot be accomplished as part of this study. However, a few very general statements regarding the crystal precipitate shape and size can be made. The crystal precipitates that were identified in the results sampled tend to form the shape of a rectangular prism (Figs. 21-18) and vary in size from about 1 micron or less up to approximately 5 microns (Figs. 24) at their largest.

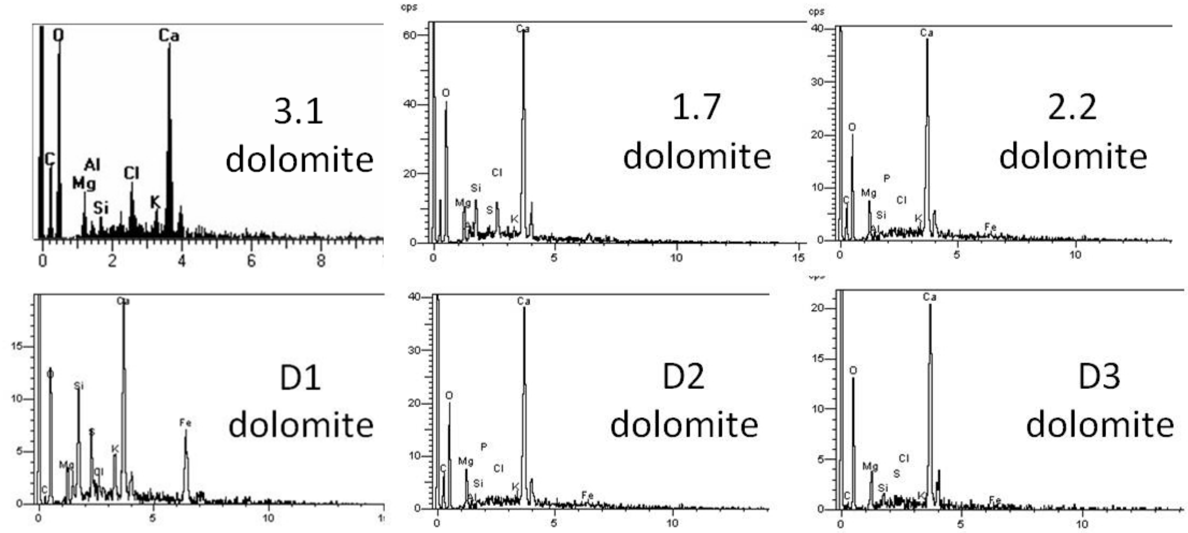

Figure 29. A comparison of the elemental spectra of 6 different substances: dolomite from experimental run 3, beaker 1 (3.1); dolomite from experimental run 1, beaker 7 (1.7); dolomite from experimental run 2, beaker 2 (2.2); dolomite from standard 1 (D1); dolomite from standard 2 (D2); and dolomite from standard 3 (D3)

Carbonate precipitates identified in this study were not randomly scattered throughout the sediments sampled but rather were distributed systematically. They were only found on pieces of organic matter, both “smooth” and “rough” organic matter, they accumulated preferentially on the “smooth” organic matter (Fig. 28). A survey of all carbonate precipitates found shows that 84% of these precipitates were found on “smooth” organic matter (Fig. 25) while only 16% were found on either “rough” organic matter (Fig. 5) or intermediate organic matter (somewhere between “smooth” and “rough”).

“Rough” organic matter was studied more closely to help determine precisely what was accounting for the coarseness of its surface. Elemental spectral analyses via

EDAX reveal that carbonate precipitates are only rarely found on “rough” organic matter. Instead, their surfaces seem to be dominated by silica, carbon, and oxygen with a minor amount of aluminum (Fig. 10). Calcium doesn’t seem to be a significant component in their elemental spectrum.

CHAPTER 4 - DISCUSSION

The results of this study suggest very strongly that the experiment resulted in dolomite precipitation within sediments (a) where no dolomite precipitation (or calcite precipitation) had occurred previously, and (b) that these sediments are considered traditionally to be part of a depositional environment (muddy siliciclastic lagoon/marsh) in which primary dolomite precipitation is unlikely and has not been documented. The precipitation of dolomite was probably accomplished through communites of sulphate-reducing bacteria altering the micro-environments immediately surrounding them such that dolomite precipitation occurred. This study also shows the importance of organic matter in this process.

The Small Sample Sizes of This Study

Only a very small fraction of the sediments that were experimented upon were studied rigorously under the SEM. The experiments were performed with the smallest volume of sediments that was considered appropriate for reacting with the artificial seawater that bathed each beaker. This allowed the running of multiple experiments at once (8 experiments at a time in this case). In total, about 200 mL of muddy silt were used in each beaker. Even with only using 200 mL of this sediment per beaker, a total of approximately 5 L of total muddy silt were experimented upon throughout the duration of all 3 experimental runs. No more than 3 mL of sediment was studied per beaker, meaning that the detailed chemical and morphological analyses of at least 197 mL of sediment *per beaker* were never performed. Although the sample size was indeed small, these samples were deemed representative of the sediments in which they came from as a whole for a variety of reasons: (a) preliminary XRD work performed upon bulk sediment revealed mineralogical uniformity of almost entirely silica-rich silt and clays, and (b) visual inspection reveals no visual changes within the sediment, suggesting much the same processes occurred throughout. The samples that were studied using SEM and EDAX were extracted carefully from two locations per sample, in the middle and towards the top. This helped to account for some vertical variations within the sediment, but since no significant differences could be identified between the two locations for most beakers, it’s assumed that only small vertical variation may have existed within the sediment.

In all likelihood, if a substance can be identified within a representative sample of only 1.5% of the bulk sediment (3 mL extracted of 200 mL total), there is a high likelihook that it exists in the non-sampled portion of sediment. Conversely, if a substance is not observed in the extracted sample, this does not necessarily prove that the substance is not present whatsoever in the greater bulk sediment from which the sample was derived but just that it doesn’t appear within the given sample.

The Identification of Precipitates as Dolomite

Precipitates in several beakers have been identified as primary dolomite using EDAX to determine their elemental spectra (Fig. 29). The similarity of these spectrums with those derived from dolomite standards allows for great confidence in this determination. However, certain variations do exist between these spectra. For example, the precipitate in beaker 1.7 shows a silicon peak as well as a chlorine peak; neither of which are particularly strong evidence that this precipitate is anything other than dolomite. The silicon peak is probably representative of the large amount of silica-rich clays and silts that are essentially ubiquitous within these sediments, and it seems likely that these sediments may serve as some sort of drape over or around the precipitate in question. The chlorine peak is more than likely associated with nearby evaporite crystals as halite is shown to have a very strong chlorine peak that has the ability to obscure the spectrums of nearby crystals. It should also be noted that the elemental spectra of the precipitate in beaker 2.2 is essentially a textbook example of the elemental spectrum of dolomite with absolutely no significant anomalies whatsoever.

Although these crystals are not identical morphologically, these precipitates generally agree with observations of dolomite precipitates identified in previous studies (Vasconcelos et al., 1995; Mastandrea et al., 2006). These crystals range in size from less than 1 micron up to 5 microns (Figs. 25-27). This agrees well with previously published descriptions of the sizes of primary dolomite precipitate crystal sizes which are usually on the scale of a few microns. The shape of these crystals is hard to define in much detail because of the resolution within the sediment, but they are generally euhedral to subhedral which is precisely the morphology observed in other studies (Mastandrea et al., 2006). Also, if these precipitates are indeed the result of bacterial activity, one would imagine that they would encase the bacteria responsible for their formation and thereby form a shape influenced somewhat by the bacterial community itself. Calcite crystals generated in this manner are commonly dumbbell- or rod-shaped (Chafetz and Buczynski, 1992). Bacterially-mediated dolomite crystals formed under the influence of sulphate-reducing bacteria take several different shapes. Some workers observe that upon initial formation it is normally globular or rosette-shaped and with slight diagenetic modifications may develop into more traditional, euhedral-looking dolomite crystals (Vasconelos and McKenzie, 1997; Warthmann et al., 2000; Roberts et al., 2004). Perhaps if the precipitates from this experiment were studied in a more optimal sediment configuration, observations of this type could be made. However, for the purposes of this study, the roughness and complexity of the sediment in which the dolomite crystals were found inhibited the ability to capture detailed morphological information in a systematic manner. When crystals sat upon relatively flat-lying sediment and were not obscured by overlying or nearby grains or organic matter, a clear and detailed photomicrograph of dolomite grains was acquired (Fig. 25). Conversely, when a precipitate is emplaced upon organic matter with irregular topography or is draped and/or nearby other grains, these photomicrographs may have the tendency to be rather poor in quality.

In general, in areas where dolomite precipitation is mediated by bacteria, an abundance of dolomite crystals is generated and is easily identified (Bontognali et al., 2010). However, in this study, only singular isolated dolomite crystals were discovered and no more than one or two 5-micron crystals per about 3 mL of sediment studied. This suggests that their abundance is extremely low. However, it must be kept in mind that these experiments, while attempting to mimic natural environments, are not natural environments themselves, and therefore, one can expect some phenomena which do not precisely imitate nature.

The EDAX also provided an approximation of the ratio of calcium to magnesium within these precipitates. Within the dolomite crystals, this ratio is almost nearly 1 to 1, with there being slightly more calcite than magnesium displayed in the elemental spectra (Tables 5-7). Given that these are approximations of the crystal structure of these precipitates, it seems that these crystals are more or less stoichiometric, ideal dolomite with a roughly equal number of magnesium and calcium ions. This is perhaps one of the most unusual findings of this study because ideal, stoichiometric dolomite is very rare and has proven extremely difficult to synthesize in laboratory settings, especially at low temperatures (Rosenberg and Holland, 1964; Land, 1998). The significance of this unexpected discovery will be discussed below.

The Macro-environmental Settings of Bacterially Mediated Precipitation

Carbonate precipitates seemed to be produced in several of the individual beakers and in all of the experimental runs. In this study, calcite precipitated in a wide variety of macro-environmental settings while dolomite was more restricted to particular ones (Table 8). Calcite precipitates were identified in most of the experiments (75%), and their presence does not show a strong correlation with any particular macro-environmental setting.

Beaker Number	***Added pH?***	***Added Mg?***	***Added ooids?***	***Run 1 precipitates***	***Run 2 precipitates***	***Run 3 precipitates***
1			☑	C	C	C/D
2	☑		☑	C	C/D	C
3	☑	☑	☑	C/D		C
4	☑				C	C
5	☑	☑			C	C
6		☑		C	C	C
7		☑	☑	C/D	C	C
8				C		C

Table 8. Lists the macro-environmental conditions that allowed for the generation of different precipitate types (C = calcite, D = dolomite)

For example, calcite precipitates were found in experimental trials: (a) with no alkalinity increase as well as with a significant alkalinity increase, (b) with a moderate Mg/Ca ratio and also with a much higher Mg/Ca ratio, and (c) with ooids and without ooids. These calcite crystals are found in a plethora of macro-environmental settings and might be the product of bacterial processes. This might be because of the relatively few kinetic barriers that inhibit the reaction that generates calcite. Both calcite and dolomite have been shown to be able to precipitate under the influence of either aerobic (Buczynski and Chafetz, 1991; Roberts et al., 2004; Sanchez-Roman et al., 2007; Sanchez-Roman et al., 2008) or anaerobic (Morita et al., 1980; Vasconecelos et al., 1995; Warthmann et al., 2000) bacteria, but the relative significance of particular genera of bacteria and the precipitates that they generate is still in question, especially in the case of dolomite (Sanchez-Roman et al., 2008). The abundance of calcite precipitates in both oxygenated and anoxic settings within this experiment is evidence of the ability of both aerobic and anerobic bacteria to induce calcite precipitation and to be able to do so more effectively than bacteria responsible for dolomite precipitation.

The macro-environmental settings in which dolomite were found seem to be more restrictive than those in which calcite was found. According to this study, dolomite precipitation seems to occur independently of variations within solution alkalinity and Mg/Ca ratio but the data suggest that it is only able to proceed in the presence of ooids. Dolomite precipitates found in beakers 1.3 and 2.2 were generated in beakers with artificially increased alkalinity while a dolomite precipitate in beaker 1.7 was generated in a beaker with normal alkalinity. This shows that dolomite formation and elevated alkalinity were unrelated in this study. Similarly, dolomite precipitates in beakers 1.3 and 1.7 were generated in beakers with a significantly higher Mg/Ca ratio than normal (7.5) while the dolomite precipitate in beaker 2.2 was produced in a beaker with a more subdued Mg/Ca ratio (3.14), showing the lack of a relationship between elevated Mg/Ca and dolomite formation in this study. All 3 dolomite precipitates, however, were found in beakers that also had ooids present within them, suggesting that the ooids play some role in the precipitation of dolomite. The small sample size limits the confidence with which this statement can be presented but still warrants discussion here.

The fact that well-known variables controlling dolomite formation, like Mg/Ca ratio (Folk, 1974; Land, 1998) and carbonate alkalinity (Slaughter and Hill, 1991), were shown to be unimportant within the context of this study does *not* suggest that either (a) these factors aren't indeed significant to dolomite formation, or that (b) this study somehow failed to illustrate the normal process by which dolomite is formed. Rather, other factors simply were so much more important in the context of this study that the signals from certain variables, like Mg/Ca ratio and alkalinity, were obscured by those other factors. It seems that in this study, the importance of the presence of ooids in dolomite formation heavily outweighed an elevation of either Mg/Ca ratio or alkalinity of the surrounding solution.

Assuming that the correlation between dolomite precipitation and the presence of ooids is not an artifact of sample size, an explanation of this relationship is in order. Early aragonite dissolution is usually accomplished via pore waters with elevated acidity, and the breakdown of organic matter by bacteria has been shown to be an effective means of increasing pore water acidity (Munnecke et al., 1997; Cherns and Wright, 2000; Wright et al., 2003). Subsequently, it has been shown that the dissolved materials from early aragonite dissolution can result in calcite reprecipitation (Preto et al., 2005). A similar process has been inferred as occurring in this experiment. The ooids used in this study are modern aragonitic ooids collected from the Bahamas, and these ooids were surrounded by waters with an elevated acidity as a result of the bacterial decomposition of organic matter taking place immediately below them. These ooids underwent some amount of early aragonite dissolution during the experiment which was facilitated by this increased acidity. The partial dissolution of these ooids contributed excess Ca^{2+} and CO_3^{2-} ions into the bathing solution, and the proximity of these ooids to the underlying mud may have dramatically affected the ion concentrations in the solution within the muddy silt layer of the experiment. For the direct precipitation of dolomite, both Ca^{2+} and CO_3^{2-} (in addition to Mg^{2+}) are reactants:

$$Ca^{2+} + Mg^{2+} + CO_3^{2-} \leftrightarrow CaMg(CO_3)^2$$

Equation 5

In this experiment, the source of the Mg^{2+} is the modified seawater solution and the additional artificial Mg added to select beakers, and the source of the Ca^{2+} and CO_3^{2-} is the modified seawater solution and the ooids undergoing early aragonite dissolution. In general terms, the rate of a chemical reaction is given by the following equation:

$$k = [A]^x [B]^y [C]^z$$

Equation 6

where *k* is the rate of the chemical reaction, [A], [B], and [C] are the concentration of the particular reactant and *x, y*, and *z* are reaction coefficients. If the concentrations of the reactants of a chemical reaction ([A], [B], [C]) increase, then the overall rate of the reaction (*k*) will increase as well. In this experiment, beakers *with* ooids contained a higher concentration of both Ca^{2+} and CO_3^{2-} than in beakers *without* ooids, and as indicated above, an increase in the concentration of reactants will increase the rate of the chemical reaction. As the rate of the dolomitization reaction increases, more dolomite will be produced in a given time period, and therefore more dolomite would be observed in beakers with a higher rate of dolomitization. To put it more succinctly, the presence of ooids is associated with the presence of dolomite precipitates in this experiment because the partial dissolution of these ooids contributed Ca^{2+} and CO_3^{2-} ions into the surrounding solution which resulted in an increase in the rate of the dolomitization reaction which allowed for more dolomite to be produced.

Artificially adding pH buffer to the seawater solution in order to increase its alkalinity did not greatly increase the precipitation of dolomite probably because increasing the alkalinity did not significantly affect the ability of sulphate-reducing bacteria to survive. If sulphate-reducing bacteria are able to survive both with and without an artificial increase of alkalinity, then one should not expect to see a trend between dolomite precipitation and experiments containing added pH buffer.

Sulphate-reducing bacteria are able to induce the precipitation of dolomite because of various processes: decreasing the concentration of SO_4^{2-}, dissociating $MgSO_4$ ion pairs which releases free Mg^{2+} into the system, increasing carbonate alkalinity, and by attracting Ca^{2+} and Mg^{2+} ions to their surface which aid in nucleation (Vasconcelos and McKenzie, 1997; Van Lith et al., 2003; Wright and Wacey, 2005). It is likely that all of these were accomplished by sulphate-reducing bacteria in this experiment because these are well-documented abilities of sulphate-reducing bacteria and because dolomite was indeed precipitated as a result of these experiments. By artificially augmenting these processes experimentally, this experiment hoped to delineate their relative significances, but no clear trend or pattern could be observed.

It is probable that the dolomite precipitates produced as a result of this study were in fact the result of sulphate-reducing bacteria altering their micro-environment in a manner such that dolomite precipitation is favored in the area immediately surrounding them. Although it is logical to assume that the same communities of sulphate-reducing bacteria existed in every experimental run, only those experiments with the right *macro*-environmental settings actually resulted in dolomite precipitation because these macro-environmental settings allowed the *micro*-environmental changes, initiated by the sulphate-reducing bacteria, to break through the kinetic barriers of dolomite formation. In the context of this study, it seems that adding artificial amounts of magnesium or artificially increasing the alkalinity of the solution bathing the sediments did not have any effect on the precipitation of dolomite. The presence or absence of ooids was the controlling factor in dolomite precipitation, probably because these ooids increased the rate of the dolomitization reaction by contributing excess Ca^{2+} and CO_3^{2-} ions into solution.

It is worth noting that these precipitates were all observed within sediments that were gathered in a siliciclastic environment where no carbonate crystals of any kind were previously observed. These lagoonal sediments were composed dominantly of silt-sized and fine sand-sized quartz grains with interstitial clay. Also, no bacteria was added to the sediments during the experiments (except for bacteria potentially associated with other experimental components, like bacteria contained within the seawater or surrounding the ooids). It seems likely that within these sediments many different bacterial species existed and lived in diverse bacterial communities. These observations allow for two important conclusions to drawn from this experiment: (a) the host sediment mineralogy is not particularly important to carbonate, particularly dolomite, precipitation as long as the necessary macro-environmental conditions are met, and (b) a consortium of bacteria living together in bacterial communities can result in the precipitation of dolomite.

The Role of Organic Matter in the Bacterially Mediated Precipitation of Dolomite

One of the most interesting discoveries of this study was that both dolomite and calcite precipitation took place *strictly* on the organic matter. No carbonate precipitate was found either in the matrix of the sediments, mixed together with the silts and clay, or on top of either the much larger, sand-sized detrital quartz grains or the aragonite ooids. Furthermore, “smooth” organic matter seemed to be preferentially suited to carbonate precipitation rather than the “rough” organic matter. These observations have implications for the understanding of how communities of bacteria are able to mediate the precipitation of dolomite as well as the precipitation of calcite.

Organic matter has been shown to be important in the precipitation of dolomite as supported by primary dolomite’s well-recognized relationship with stromatolites (Wright, 1999; Dupraz and Visscher, 2005; Mastandrea et al., 2006; Meister et al., 2007; Bontognali et al., 2010; Spadafora et al., 2010). In this study, 100% of all carbonate precipitates discovered, both calcite and dolomite, were on the surface of organic matter (Figs. 9, 19-28). This organic matter is generally some sort of plant stem or root which was transported with the sediment when originally collected. It is believed that the reason why organic matter always served as a substrate in this study for carbonate precipitation is two-fold: (a) the organic matter is used as food for communities of bacteria and thereby develops into a locus of bacterial activity. These bacterial communities eventually result in the precipitation of carbonate minerals. (b) Any carbonate precipitates formed within the water column or within pore waters may have been flushed out when the system was drained for sample preparation. It is probable that the former is more important than the latter because the concentration of bacteria on organic matter is much greater than the concentration of bacteria floating in the water column, often by orders of magnitude (Donderski and Wilk, 2001), such that the amount of carbonate precipitates generated by these free-floating bacteria is much less than the amount of carbonate precipitates generated by bacterial communities feeding upon organic matter.

Carbonate precipitates were dominantly found on “smooth” organic matter as opposed to “rough” organic matter, with 84% of all precipitates being discovered on “smooth” organic matter while only 16% on either intermediate or “rough” organic matter (Fig. 30). As mentioned before, “smooth” organic matter contains relatively few

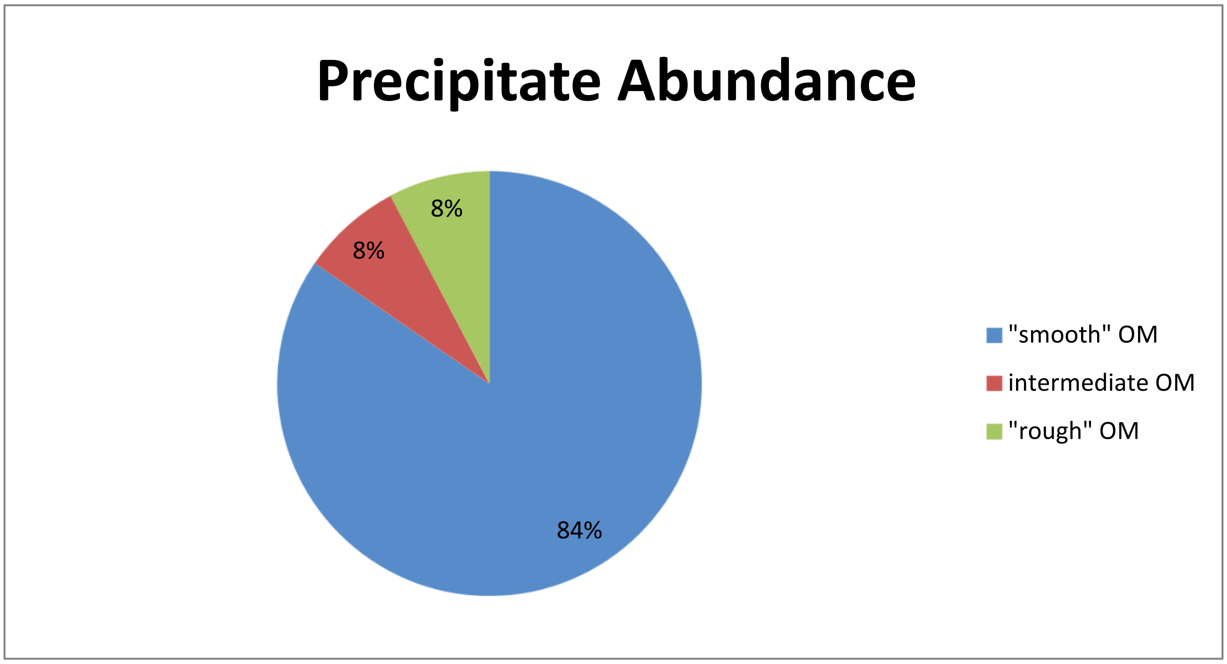

Figure 30. The abundance of precipitates as a function of where they were found. Eighty-four percent of all precipitates were found on “smooth” organic matter, while 8% were found on intermediate organic matter and 8% on “rough” organic matter.

surface markings (Figs. 9, 13, 19-28, 31) while its “rough” counterpart looks like normally shaped organic matter that has since been almost entirely covered with silt, clay, precipitated crystals, or fossils (Figs. 10, 11, 15-17, 32). The elemental spectrum of “smooth” organic matter shows that it is composed mostly, if not entirely, of carbon and oxygen, and this suggests that “smooth” organic matter is nothing more than dead organic matter that has retained, to a great extent, its original appearance, with very few crystals or detrital grains on its surface. Conversely, the elemental spectrum of “rough” organic matter (Fig. 10) shows large amounts of carbon and oxygen, as one would expect for organic matter, but also a strong silicon peak. This suggests that “rough” organic matter is perhaps just regular organic matter (originally was probably “smooth” to begin with) that has since been entirely enveloped with detrital sediments like silts and

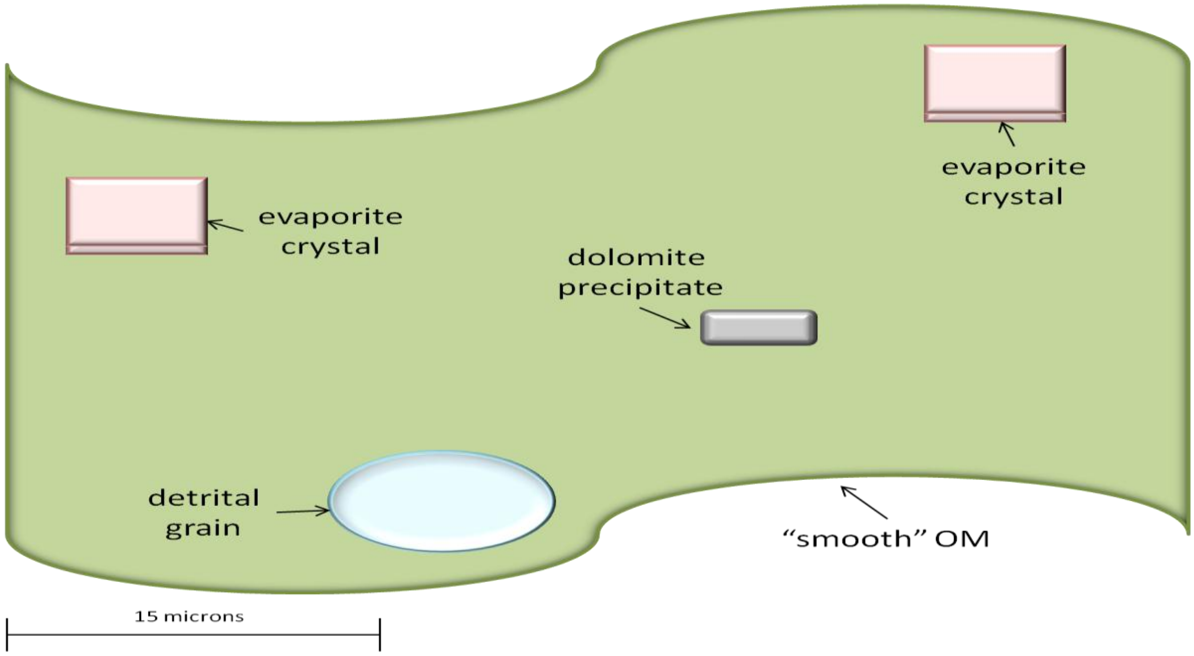

Figure 31. The surface of “smooth” organic matter contains relatively few surface features in the way of evaporite crystals, siliciclastic detritus (in this case a detrital silt grain), and carbonate precipitates (in this figure, dolomite).

clays as well as potentially serving as a substrate for the growth of evaporite, sulfur, or rarely, carbonate precipitates (Figs. 31-32).

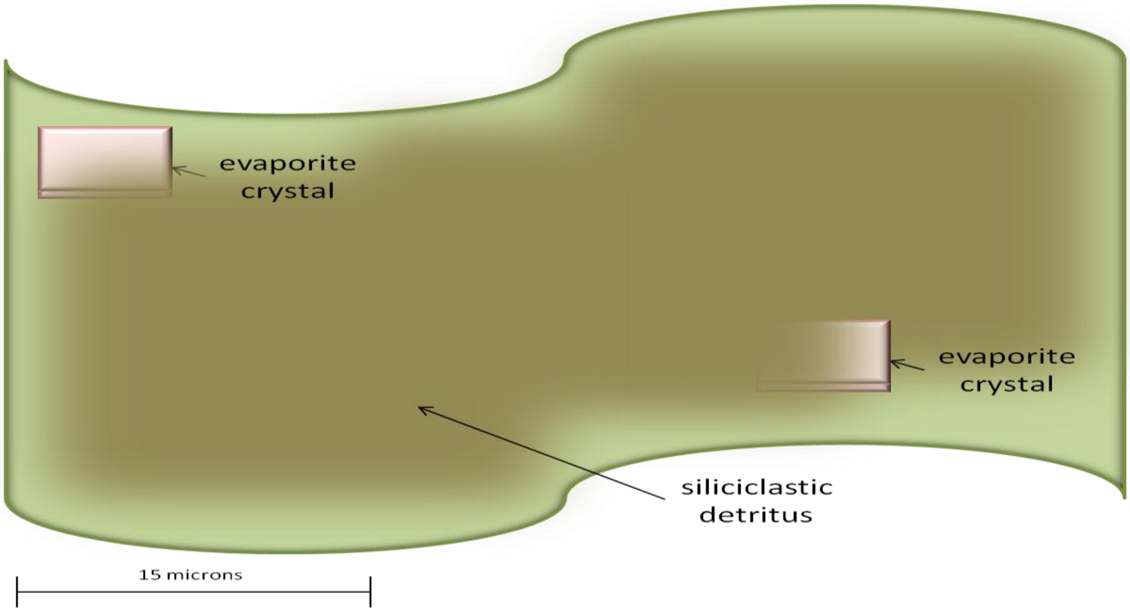

Figure 32. The surface of “rough” organic matter is almost entirely covered with siliciclastic detritus in the form of silts and clay and also partially covered with evaporite crystals or other secondary precipitates like sulfur. It usually does not contain carbonate precipitates (as illustrated) but it is by no means impossible for carbonate precipitates to found on “rough” organic matter.

In many studies, the organic matter associated with sulphate-reducing bacteria is in the form of exo-polymeric or extracellular polymeric substances (EPS), a broad term that encompasses many generic polymers secreted by bacteria (Decho and Kawaguchi, 1999; Mastandrea et al., 2006; Meister et al., 2007; Sanchez-Roman et al., 2007; Bontognali et al., 2010). In this study, dolomite and calcite were discovered precipitating on top of organic matter in the form of plant fragments or root stems, while no EPS was observed. There are several possible reasons for this. First, it is entirely possible that EPS was not observed because of resolution limits due to the nature of the sediments being studied; perhaps the EPS is so insubstantial that they were either too small to be observed or were completely obscured by nearby or overlying grains and organic matter.

EPS typically comes in the shape of a thin (commonly less than 1 micron thick) matrix that surrounds bacteria and resultant precipitates (Bontognali et al., 2008) and can be difficult to see because of its small size and wide dispersal. Furthermore, EPS tends to form a fragile matrix around bacterial cells and precipitated crystals that can easily be disturbed (Decho and Kawaguchi, 1999; Bontognali et al., 2008). The sediments in this study were subjected to several possible periods of shaking and transportation in which this EPS matrix could have been broken and subsequently moved from its original location. Communities of bacterial cells regularly secrete EPS immediately around them, and it is within this EPS that precipitation of carbonate crystals is most likely because EPS represents the limit of the chemical influence of the bacterial communities (Stolz et al., 2001; Tichet et al., 2001). The presence of microbially mediated calcite and dolomite precipitates in this study suggests that EPS must have been secreted by bacterial communities even though there is no direct evidence of the EPS itself.

Early vs. Late Precipitate Growth

It is not difficult to imagine a scenario in which sulphate-reducing bacteria (or really bacteria of any kind) could thrive on dead organic matter that is bathed in nutrient-rich waters while in a reducing environment. This is what this author believes occurred with the "smooth" organic matter observed in this study. It is less obvious how carbonate precipitates, the result of bacterial activity, can form on organic matter that is currently covered in siliciclastic detritus and/or evaporite crystals. There are two scenarios in which this can occur that seem most likely, and the difference between these two is derived directly from the timing of the precipitate growth: (a) early precipitate growth, and (b) late precipitate growth (Fig. 33).

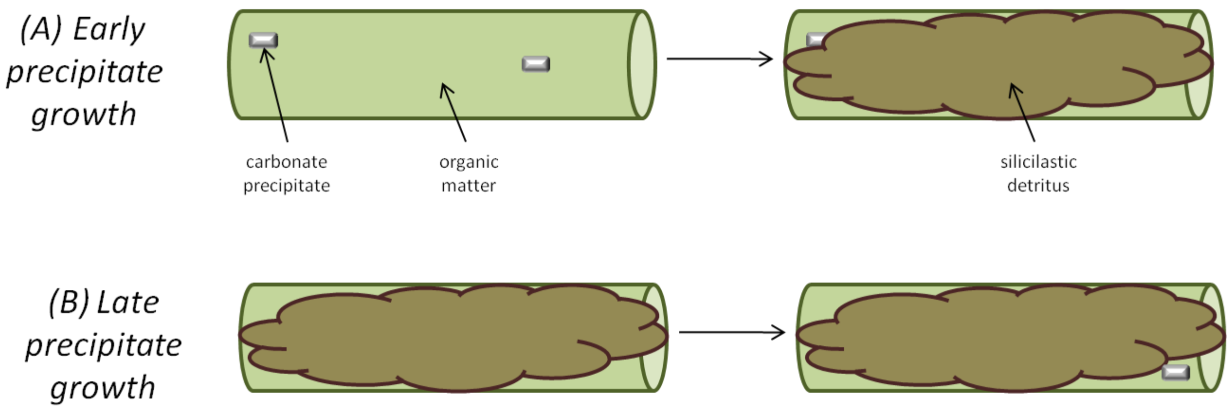

Figure 33. Two processes by which carbonate precipitates can appear on "rough" organic matter. In early precipitate growth, precipitates pre-date the siliciclastic covering of the organic matter. In late precipitate growth, the precipitates post-date the siliciclastic covering of the organic matter.

In early precipitate growth, it is assumed that the organic matter was previously not covered by siliciclastic detritus or secondary precipitates like evaporites or sulfur. While bare, bacteria feasted upon its surface and resulted in the precipitation of carbonate precipitates, be they calcite or dolomite. At some later point, a large amount of siliciclastic clays and silts enveloped the organic matter, covering to some degree any previously formed bacterial precipitates. Enough siliciclastic detritus would need to affix to the organic matter to obscure any underlying calcium or magnesium peaks, as the elemental spectra of all analyzed "rough" organic matter in this study failed to show any peaks of either element. In early precipitate growth, the formation of carbonate precipitates by bacterial mediation must occur in a short amount of time such that these precipitates are already in-place by the time the siliciclastic clay and silts are fully deposited.

In late precipitate growth, the bacteria responsible for mediating the precipitation of carbonate are only able to thrive in areas where the organic matter is exposed and not covered with sediment. Because uncovered organic matter seems to represent a small fraction of the overall surface area of the “rough” organic matter as observed by SEM imagery (Figs. 10, 11, 14-17), it follows that only a small fraction of the surface should show carbonate precipitation. In late precipitate growth, the “rough” organic matter is never required to have been “smooth” in an earlier stage. Instead carbonate precipitates are generated on the areas of “rough” organic matter that is uncovered.

Of these two alternating ideas for the origination of carbonate precipitates on “rough” organic matter, the latter is favored. Late precipitate growth does not require “rough” organic matter to have been bare of detritus for an extended period of time and does not force carbonate precipitation to occur in an unreasonably short time span. Higher resolution SEM work could reveal conclusive evidence as to which theory is correct if it could be demonstrated clearly that either the carbonate precipitates or the siliciclastic sediment was superimposed upon the carbonate. Unfortunately, the rough, irregular nature of the sediments in this study does not allow for such resolution.

The Relationship between Microbially Mediated Dolomite and Stromatolites

A relationship between primary dolomite precipitated through the mediation of bacteria and stromatolites has been observed for decades (Sarin, 1962; Wright, 1999; Rao et al., 2003; Mastandrea et al., 2006; amongst others). Upon first inspection this study may seem to contain very little pertaining to the nature of this relationship. However, the observations of the interaction between dolomite precipitation and organic matter made during this study suggest that perhaps this relationship can be imitated in a laboratory setting.

This author argues that this study shows unequivocally that dolomite precipitation should be expected in areas where communities of sulphate-reducing bacteria tend to gather. In this particular study, the area of greatest bacterial accumulation happened to be upon stalks of dead organic matter that had not yet been covered with siliciclastic detritus. It is not difficult to imagine a natural setting that is essentially identical to the experimental set-up employed in this study except that the concentration of organic matter is higher and therefore precipitates of dolomite are more common. In this hypothetical case, dolomite precipitates would accumulate in layers where dead organic matter was most common. Within a relatively short time this layer of organic matter would be covered by a layer of sediment, and much of this organic matter would be either dissolved or compacted while most of the dolomite precipitates that formed within this layer would remain essentially unaltered. In this manner, one can imagine how small layers of organically-related microbially mediated dolomite can accumulate in a layered fashion (Fig. 34). This method of microbial lamination formation is essentially the same as that suggested by Chafetz and Buczynski (1992) where instead of dead cyanobacteria serving as a substrate for bacterially-mediated carbonate precipitation, dead plant material (like plant stems or roots) serve as the substrate. If macro-environmental conditions are conducive to dolomite formation and long-lasting, these microbial laminations could potentially develop into dolomitized stromatolites with time. Since the experiments involved in this study contained very small dolomitized volumes of sediment when compared to natural environments of dolomite formation, it is difficult to make far-fetching generalizations about depositional environments and sedimentary structures from the results gathered, but the strong association between carbonate precipitation and organic matter demonstrated in this study certainly suggests that a relationship not unlike the one described above may very well exist and could lend itself to further study.

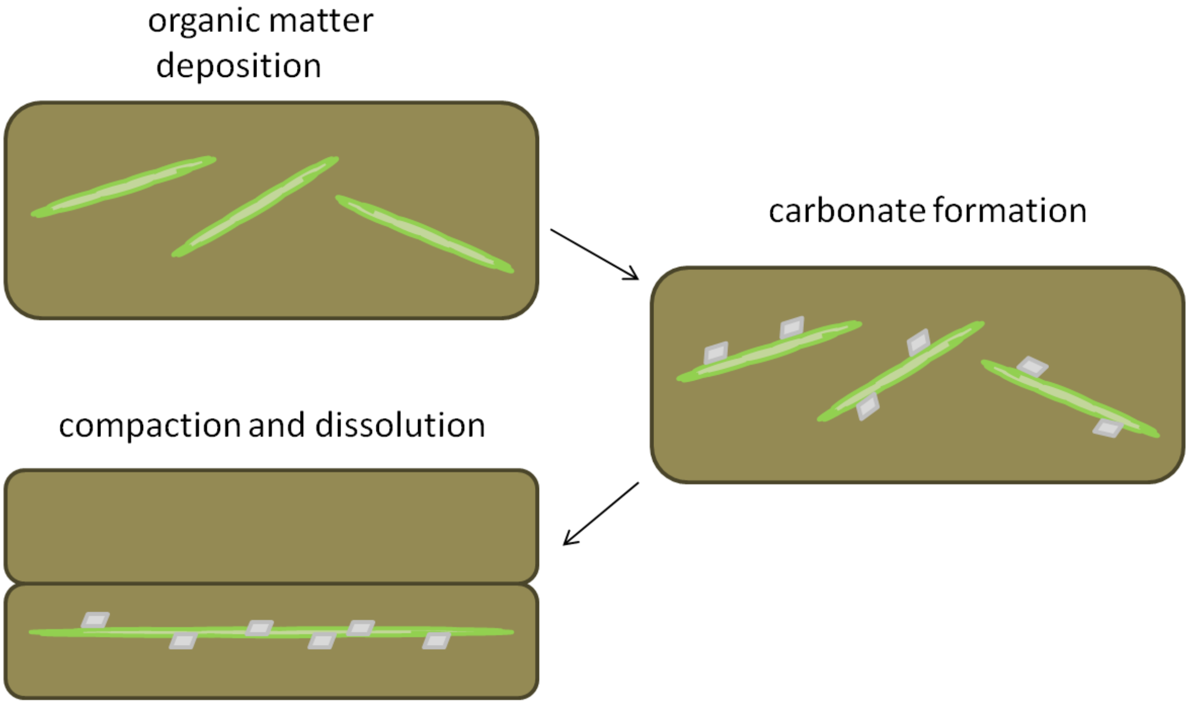

Figure 34. A hypothetical example of how carbonate precipitate formation, occurring in a similar fashion to this study, could ultimately lead to microbial laminations. First, the organic matter is deposited amongst sediment. Then, carbonate precipitates are formed via microbial mediation. Finally, upon compaction and/or subsidence, organic matter is dissolved while the carbonate precipitates remain roughly the same size and are reorganized in a layered fashion.

Both ancient and modern dolomites are commonly found in association with stromatolites (Pratt and James, 1982; Amthor and Friedman, 1992; Rao et al., 2003; McKenzie and Vasconcelos, 2009), and this study may help partially explain this relationship. Two components that are extremely important to the precipitation of dolomite, according both to the literature and the results of this study, are sulphate-reducing bacteria and organic matter. It has been shown that sulphate-reducing bacteria are common in active microbial mats (Teske et al., 1998) and that microbial mats have existed as far back as the Archean (Schidlowski, 1987). Since these mats contain both sulphate-reducing bacteria as well as an abundance of organic matter (in the form of cyanobacteria, microbes, as well as other organic matter detritus like plant fragments), they provide both of these necessary components for dolomite precipitation, and since these mats are so extensive both geographically and temporally, it is not hard to imagine how they may be able to be the loci of large amounts of dolomite.

CHAPTER 5 - CONCLUSION

The main conclusions and observations of this study may be summarized as follows:

- An experimental set-up containing silty/muddy sediments gathered from Christmas Bay near Brazosport, Texas and a modified seawater solution was capable of producing dolomite precipitates within a few weeks. Other authigenic crystals formed during experimentation include calcite, iron sulfide, gypsum, and halite.
- A comparison of the elemental spectra of the precipitates with the spectra of dolomite standards suggests strongly that the precipitates are indeed dolomite. The scale of the precipitates is in agreement with similar dolomite precipitates found in other studies.
- Calcite precipitates were much more abundant than dolomite precipitates and their presence does not seem to be controlled by any of the macro-environmental conditions tested for including alkalinity differences, Mg/Ca ratio changes, and the presence or absence of ooids. Dolomite seemed to precipitate independently of alkalinity changes or Mg/Ca ratio variations but was only found in experiments which contained ooids, suggesting that the primary dolomite produced in this study required the presence of incipient carbonate material for precipitation to occur. Early aragonite dissolution contributed excess Ca^{2+} and CO_3^{2-} into solution which increased the likelihood and rate of dolomitization.

- Sulphate-reducing bacteria living on the surface of the organic matter changed the chemical conditions in their microenvironment such that dolomite precipitation became favored in the following ways: (a) by decreasing the concentration of SO_4^{2-}, (b) by disassociating $MgSO_4$ ion pairs, and (c) by attracting Ca^{2+} and Mg^{2+} ions to their surface.

- Carbonate precipitates were only found in directly on or slightly embedded within organic matter. Of the different types of organic matter observed in this study, “smooth” organic matter contained significantly greater amounts of carbonate precipitates than “rough” organic matter. “Smooth” organic matter is that which is not overwhelmed with siliciclastic detritus whereas “rough” organic matter has.

REFERENCES

Alsharan, A.S., and Kendall, C.G..St.C., 2003, Holocene coastal carbonates and evaporites of the southern Arabian Gulf and their ancient analogues. Earth-Science Reviews, vol. 61, pg. 191-243.

Amthor, J.E., and Friedman, G.M., 1992, Early- to late-diagenetic dolomitization of platform carbonate: Lower Ordovician Ellenburger Group, Permian Basin, West Texas. Journal of Sedimentary Petrology, vol. 62, no. 1, pg. 131-144.

Baker, P.A., and Kastner, M., 1981, Constraints on the formation of sedimentary dolomite, Science, vol. 213, no. 4504, pg. 214-216.

Bontognali, T.R.R., Vasconcelos, C., Warthmann, R.J., Dupraz, C., Bernasconi, S., and McKenzie, J.A., 2008, Microbes produce nanobacteria-like structures, avoiding cell entombment. Geology, vol. 36, pg. 663-666.

Bontognali, T.R.R., Vasconcelos, C., Warthmann, R.J., Bernasconi, S.M., Dupraz, C., Stromhenger, C.J., and McKenzie, J.A., 2010, Dolomite formation within microbial mats in the coastal sabkha of Abu Dhabi (United Arab Emirates). Sedimentology, vol. 57, pg. 824-844.

Buczynski, C., and Chafetz, H.S., 1991, Habit of bacterially induced precipitates of calcium carbonate and the influence of medium viscosity on mineralogy. Journal of Sedimentary Petrology, vol. 61, pg. 226-233.

Burns, S.J., McKenzie, J.A., and Vasconcelos, C., 2000, Dolomite formation and biogeochemical cycles in the Phanerozoic. Sedimentology, vol. 47, pg. 49-61.

Chafetz, H.S., and Buczynski, C., 1992, Bacterially induced lithification of microbial mats. Palaios, vol. 7, pg. 277-293.

Cherns, L., and Wright, V.P., 2000, Missing mollusks as evidence of large-scale, early skeletal aragonite dissolution in a Silurian sea. Geology, vol. 28, pg. 791-794.

de Dolomieu, D., 1791, Sur un genre de pierres calcaires trespeu effervescentes avec les acides et phosphorescentes par la collision. Journal de Physique, vol. 39, pg. 3-10.

de Saussure, N.T., 1792, Analyse de la dolomite. Journal de Physique, vol. 40, pg. 161-172.

Decho, A.W., and Kawaguchi, T., 1999, Confocal imaging of in situ natural microbial communities and their extracellular polymeric secretions using nanoplast resin. BioTechniques, vol. 7, pg. 1256-1252.

Donderski, W., and Wilk, I., 2001, Bacteriological studies of water and bottom sediments of the Vistula River between Wyszogrod and Torun. Polish Journal of Environmental Studies, vol. 11, pg. 33-40.

Dupraz, C., and Visscher, P.T., 2005, Microbial lithification in marine stromatolites and hypersaline mats. Trends in Microbiology, vol. 13, pg. 429-43.

Folk, R.L., The natural history of crystalline calcium carbonate: effect of magnesium content and salinity. Journal of Sedimentary Petrology, vol. 44, no. 1, pg. 40-53.

Illing, L.V., Wells, A.J., and Taylor, J.C.M., 1965, Penecontemporary dolomite in the Persian Gulf. In: Dolomitization and Limestone Diagenesis (Ed. L.C. Pray and R.C. Murray), SEPM Special Publication, vol., 13, pg. 89-111.

Land, L.S., 1998, Failure to precipitate dolomite at 25C from dilute solution despite 1000-fold oversaturation after 32 years. Aquatic Geochemistry, vol. 4, pg. 361-368.

Lippmann, F., 1974, Sedimentary Carbonate Minerals: New York, Springer-Verlag, 228 pg.

Lokier, S., and Steuber, T., 2009, Large-scale intertidal polygonal features of the Abu Dhabi coastline. Sedimentology, vol. 56, pg. 609-621.

Mastandrea, A., Perri, E., Russo, F., Spadafora, A., and Tucker, M.E., 2006, Microbial primary dolomite from a Norian carbonate platform: northern Calabria, southern Italy. Sedimentology, vol. 53, pg. 465-480.

McKenzie, J.A., 1981, Holocene dolomitization of calcium carbonate sediments from the coastal sabkhas of Abu Dhabi, UAE: a stable isotope study. Journal of Geology, vol. 89, pg. 185-198.

McKenzie, J.A., and Vasconcelos, C., 2009, Dolomite Mountains and the origin of the dolomite rock of which they mainly consist: historical developments and new perspectives. Sedimentology, vol. 56, pg. 205-219.

Meister, P., McKenzie, J.A., Vasconcelos, C., Bernasconi, S., Frank, M., Gutjahrs, M., and Schrag, D.P., 2007, Dolomite formation in the dynamic deep biosphere: results from the Peru Margin. Sedimentology, vol. 54, pg. 1007-1031.

Moore, C.H., 1989, Carbonate Diagenesis and Porosity: Amsterdam, Elsevier Science Publications, 338 pg.

Moreira, N.F., Watler, L.M., Vasconcelos, C., McKenzie, J.A., and McCall, P.J., 2004, Role of sulfide oxidation in dolomitization: Sediment and pore-water geochemistry of a modern hypersaline lagoon system. Geology, vol. 32, pg. 701-704.

Morita, R.Y., 1980, Calcite precipitation by marine bacteria: Geomicrobiology Journal, vol. 1, pg. 63-82.

Munnecke, A., Westphal, H., Reijmer, J.J.G., and Samtleben, C., 1997, Microspar development during early marine burial diagenesis: a comparison of Pliocene carbonates from the Bahamas with Silurian limestones from Gotland (Sweden). Sedimentology, vol. 44, pg. 977-990.

Nadson, G.A., 1928, Beitrag zur Kenntnis der bakteriogenen Kalkablagerungen. Arch. Hydrobiol., vol. 19, pg. 154-164.

Neher, J., and Roher, E., 1958, Bakterien in tieferliegenden gesteinslagen. Eclogae Geologicae Helvetiae, vol. 52, pg. 619-625.

Nesse, W.D., 2000, Introduction to Mineralogy: Oxford, Oxford University Press, 442 pg.

Pisciotto, K.A., and Mahoney, J.J., 1981, Isotopic survey of diagenetic carbonates. In: Initial Reports of the DSDP (Ed. R.S. yeats and B.U. Haq), pg. 595-609. US Government Printing Office, Washington, DC.

Pratt, B.R., and James, N.P., 1982, Cryptalgal-metazoan bioherms of early Ordovician age in the St. George Group, western Newfoundland. Sedimentology, vol. 29, pg. 543-569.

Preto, N., Spotl, C., Mietto, P., Gianolla, P., Riva, A., and Manfrin, S., 2005, Aragonite dissolution, sedimentation rates and carbon isotopes in deep-water hemipelagites (Livinallongo Formation, Middle Triassic, northern Italy). Sedimentary Geology, vol. 181, pg. 173-194.

Rao, V.P., Kessarkar, P.M., Krumbein, W.E., Krajewski, K.P., and Schneider, R.J., 2003, Microbial dolomite crusts from the carbonate platform off western India. Sedimentology, vol. 50, pg. 819-830.

Rivadeneyra, M.A., Delgado, R., Delgado, G., Del Moral, A., Ferrer, M.R., and Ramons-Cormenzana, A., 1993, Precipitation of carbonates by Bacillus sp. Isolated from saline soils. Geomicrobiology Journal, vol. 11, pg. 175-184.

Roberts, J.A., Bennett, P.C., Gonzalez, L.A., Macpherson, G.L., and Milliken, K.L., 2004, Microbial precipitation of dolomite in methanogenic groundwater. Geology, vol. 32, pg. 277-280.

Rosenberg, P.E., and Holland, H.D., 1964, Calcite-dolomite-magnesite stability relations in solutions at elevated temperatures. Science, vol. 145, pg. 700-701.

Sanchez-Roman, M., Vasconcelos, C., Schmid, T., Dittrich, M., McKenzie, J.A., Zenobi, R., and Rivadeneyra, M.A., 2008, Aerobic microbial dolomite at the nanometer scale: implications for the geologic record. Geology, vol. 36, pg. 879-882.

Sarin, D.D., 1962, Cyclic sedimentation of primary dolomite and limestone. Journal of Sedimentary Petrology, vol. 32, no. 3, pg. 451-471.

Schidlowski, M., 1987, Evolution of the early sulphur cycle. In: Geochemistry and Mineral Formation in the Earth Surface (Ed. R. Rodriguez-Clemente and Y. Tardy), pg. 29-49, Consejo Superior de Investigacions Cientificas, Madrid.

Slaughter, M., and Hill, R.J., 1991, The influence of organic matter in organogenic dolomitiziation. Journal of Sedimentary Petrology, vol. 61, pg. 296-303.

Spadafora, A., Perri, E., McKenzie, J.A., and Vasconcelos, C., 2010, Microbial biomineralization processes forming modern Ca:Mg carbonate stromatolites. Sedimentology, vol. 57, pg. 27-40.

Stolz, J.F., Feinstein, T.N., Salsi, J., Visscher, P.T., and Reid, R.P., 2001, TEM analysis of microbial mediated sedimentation and lithification in modern marine stromatolites. American Mineralogist, vol. 86, pg. 826-833.

Teske, A., Ramsing, N.B., habicht, K.S., Fukui, M., Kuver, J., Jorgensen, B.B., and Cohen, Y., 1998, Sulphate-reducing bacteria and their activities in cyanobacterial mats of Solar Lake (Sinai, Egypt). Applied Environmental Microbiology, vol. 64, pg. 2943-2951.

Trichet, J., Defarge, C., Tribble, J., Tribble, G., and Sansone, F., 2001, Christmas Islands lagoonal lakes, models for the deposition of carbonate-evaporite-organic laminated sediments. Sedimentary Geology, vol. 140, pg. 177-189.

Tucker, M.E., and Wright, V.P., 1990, Carbonate Sedimentology: Oxford, Blackwell Scientific publications, 482 pg.

van Lith, Y., Warthmann, R., Vasconcelos, C., and McKenzie, J.A., 2003, Sulphate-reducing bacteria induce low-temperatuer dolomite and high Mg-calcite formation. Geobiology, vol. 1, pg. 71-79.

Vasconcelos, C., McKenzie, J.A., Bernasconi, S., Grujic, D., and Tien, A.J., 1995, Microbial mediation as a possible mechanism for natural dolomite formation at low temperature. Nature, vol. 377, pg. 220-222.

Vasconcelos, C., and McKenzie, J.A., 1997, Microbial mediation of modern dolomite precipitation and diagenesis under anoxic conditions (Lagoa Vermelha, Rio de Janeiro, Brazil). Journal of Sedimentary Research, vol. 67, no. 3, pg. 378-390.

von der Borch, C.C., 1965, The distribution and preliminary geochemistry of modern carbonate sediments of the Coorong area, South Australia. Geochimica Cosmochimica Acta, vol. 29, pg. 781-799.

von Morlot, A., 1847, Ueber Dolomit und siene kunstliche Darstellung aus Kalkstein. In: Naturwissenschaftliche Abhandlungen (Ed. W. Haidinger), Wien, vol. 1, pg. 305-315.

Warthmann, R., van Lith, Y., Vasconcelos, C., McKenzie, J.A., and Karpoff, A.M., 2000, Bacterially induced dolomite precipitation in anoxic culture experiments. Geology, vol. 28, pg. 1091-1094.

Wells, A., 1972, Recent dolomite in the Persian Gulf. Nature, vol. 194, pg. 274-275.

Wright, D.T., 1999, The role of sulphate-reducing bacteria and cyanobacteria in dolomite formation in distal ephemeral lakes of the Coorong region, South Australia. Sedimentary Geology, vol. 126, pg. 147-157.

Wright, D.T., and Wacey, D., 2005, Precipitation of dolomite using sulphate-reducing bacteria from the Coorong Region, South Australia: significance and implications. Sedimentology, vol. 52, pg. 987-1008.

Wright, V.P., Cherns, L., and Hodges, P., 2003, Missing mollusks: field testing taphonomic loss in the Mesozoic through early large-scale aragonite dissolution. Geology, vol. 31, pg. 211-214.