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Enhanced Resolution of the Paleoenvironmental and Diagenetic Features of the Silurian Brassfield Formation

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ENHANCED RESOLUTION OF THE PALEOENVIRONMENTAL
AND DIAGENETIC FEATURES OF THE SILURIAN
BRASSFIELD FORMATION

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science

By

LISA MARIE OAKLEY
B.S., Wright State University, 2009

2013
Wright State University
I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Lisa Marie Oakley ENTITLED Enhanced Resolution Of The Paleoenvironmental And Diagenetic Features Of The Silurian Brassfield Formation BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science.

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ABSTRACT


The Brassfield Formation is an early Silurian (Aeronian, Llandoverian) unit of limestone and dolostone with excellent preservation of early reef communities and a diverse invertebrate fauna. A well-preserved outcrop occurs in southwestern Ohio at the Oakes Quarry Park in Fairborn; it contains abundant corals and stromatoporoids that are co-dominant in reef and reef-affected settings. This research provided an enhanced perspective of the Brassfield Formation to better reconstruct its paleoenvironment and better understand its diagenetic features.

The depositional and diagenetic features of the Brassfield are described and interpreted using histologic methods and light microscopy. Selected thin sections were treated with carbonate stains to reveal the mineral interactions and possible microbial influence that led to the dolomitization present. These stains also revealed banding patterns that may indicate seasonal events.
Features visible in the thin sections provided evidence for dolomite crystallization mediated by microbial activity and for both oxic and anoxic environments. Oxic environments are indicated by increased hematite precipitate and little organic carbon. Anoxic environments are indicated by increased pyrite precipitate and micritic or microbial associations. Dolomite associated with oxic characteristics appears unstable, with patches of dedolomitization. Dolomite associated with anoxic characteristics appears more intact, with larger mosaics and with larger crystal size.

Growth patterns for all coral specimens have detectable high density (HD) and low density (LD) banding, most have growth interruption bands, and some have absent or breakage bands. Patterns indicate seasonal events (HD banding) that led to disruption of the coral viability, increased internal sedimentation, increased carbonate accumulations, and increased precipitates (namely pyrite and dolomite). Some events were marked by sediment infills and breakage bands at the probable point of organism death, suggesting a period of major environmental stress on the coral. Periods between events (LD banding) showed marked cementation, porosity, ferrous precipitation, and dolomite instability.

This research suggested an important link between reducing environments and dolomite formation. Additionally, a relationship is probable between increased organic content, pyrite precipitation, and dolomite nucleation. Given that microbial evidence has been detected in past research examining carbonate and pyrite deposits, a link between microbial activity and dolomite formation is likely. Continued research into the geologic record may prove that indicators for specific microbial forms are marked by distinct phases of dolomite formation and degradation.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.  INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II. OBJECTIVES</td>
<td>3</td>
</tr>
<tr>
<td>III. BACKGROUND</td>
<td>4</td>
</tr>
<tr>
<td>Previous Work on Dolomitization</td>
<td>4</td>
</tr>
<tr>
<td>Previous Work on the Brassfield Formation</td>
<td>14</td>
</tr>
<tr>
<td>IV. METHODS</td>
<td>20</td>
</tr>
<tr>
<td>V.  RESULTS</td>
<td>30</td>
</tr>
<tr>
<td>Specimen 1A</td>
<td>30</td>
</tr>
<tr>
<td>Specimen 1B</td>
<td>35</td>
</tr>
<tr>
<td>Specimen 2A</td>
<td>39</td>
</tr>
<tr>
<td>Specimen 2B</td>
<td>44</td>
</tr>
<tr>
<td>Specimen 3A</td>
<td>47</td>
</tr>
<tr>
<td>Specimen 3B</td>
<td>53</td>
</tr>
<tr>
<td>Specimen 4A</td>
<td>57</td>
</tr>
<tr>
<td>Specimen 4B</td>
<td>62</td>
</tr>
<tr>
<td>Specimen 5A</td>
<td>66</td>
</tr>
<tr>
<td>Specimen 5B</td>
<td>70</td>
</tr>
<tr>
<td>Specimen 6A</td>
<td>74</td>
</tr>
</tbody>
</table>
VI. INTERPRETATION OF RESULTS

Specimen 1 ................................................................. 84
Specimen 2 ................................................................. 85
Specimen 3 ................................................................. 86
Specimen 4 ................................................................. 87
Specimen 5 ................................................................. 88
Specimen 6 ................................................................. 90

VII. CONCLUSION ......................................................... 92

REFERENCES ........................................................ 95

APPENDICES ......................................................... 99

A. The Art of Staining ............................................... 99
B. Detailed Methods ............................................... 101
LIST OF FIGURES

Figure                                      Page

1. Dolomite crystal classification (Warren, 2000) ........................................4
2. Schematic representation of Dolomite SRB-mediated precipitation
   (Corzo et al. 2005) ..........................................................................................6
3. Carbonates and their response to staining (modified from Dickson, 1966) ........9
4. Rock slabs produced from initial cuts to specimen 3 ....................................24
5. Rock slabs produced from initial cuts to specimen 6 ....................................24
6. All rock sections in order (from 1 on right to 6 on left), curing overnight .......25
7. Thin section 1a; Stromatoporoid with Alizarin Red S and Potassium
   Ferrocyanide staining .....................................................................................26
8. Thin section 1a; Stromatoporoid with Alizarin Red S and Potassium
   Ferrocyanide staining .....................................................................................26
9. Thin section 2a; Tabulate coral with Alizarin Red S and Potassium Ferrocyanide
   Staining .........................................................................................................26
10. Thin section 2b – Tabulate coral with Alizarin Red S staining only ...............26
11. Thin section 3a; Colonial Rugose coral with Alizarin Red S and Potassium
    Ferrocyanide staining ....................................................................................27
12. Thin section 3b; Colonial Rugose coral with Alizarin Red S staining only……..27

13. Thin section 4a; Fossiliferous packstone with Alizarin Red S and Potassium Ferrocyanide staining.............................................................27

14. Thin section 4b; Fossiliferous packstone with Alizarin Red S staining only……27

15. Thin section 5a; Reef coral with Alizarin Red S and Potassium Ferrocyanide Staining.................................................................28

16. Thin section 5b; Reef coral with Alizarin Red S staining only.....................28

17. Thin section 6a; Tabulate coral with Alizarin Red S and Potassium Ferrocyanide Staining.................................................................28

18. Thin section 6b; Tabulate coral with Alizarin Red S staining only..................28

19. Thin section 1c; Stromatoporoid unstained..............................................29

20. Thin section 5c; Reef coral unstained.......................................................29

21. Thin section 6c; Reef coral unstained.......................................................29

22. Thin section 6d; Reef coral unstained.......................................................29

23. Enlargement of Figure 5...........................................................................30

24. Patch of blue staining (with dolomite) in upper left lobe; digital zoom .........33

25. Planar-e dolomite patch on left side of thin section; digital zoom...............33

26. Planar-e and planar-s dolomite on left side of thin section; evidence of pore space; digital zoom.........................................................33

27. Blue stain cross-cuts at right side of thin section; digital zoom....................33

28. Planar-e dolomite on right side of thin section..........................................34

29. Enlargement of Figure 6...........................................................................35

viii
30. Dolomite exhibiting grid-like zonation and crystal-moldic porosity; digital zoom…38
31. Dolomite exhibiting darkened, medium to large centers; digital zoom………………38
32. Dolomite exhibiting zonation; replacement along lamina infilling; digital zoom…..38
33. Enlargement of Figure 7……………………………………………………………………39
34. Dolomite crystals within micritic areas; evidence of crystal-moldic porosity;
    digital zoom………………………………………………………………………………42
35. Micritic infilling of corallite chambers; digital zoom……………………………………42
36. Vertical corallite pattern; digital zoom…………………………………………………42
37. Transition from pink corallite divisions to darker brown, thicker, micritic
    divisions; digital zoom……………………………………………………………………43
38. Enlargement of Figure 8…………………………………………………………………44
39. Micritic infilling of corallite; digital zoom………………………………………………46
40. Polygonal corallite structure; digital zoom………………………………………………46
41. Subtle traces of dolomite crystals within micritic area of corallite chamber;
    digital zoom………………………………………………………………………………46
42. Enlargement of Figure 9……………………………………………………………………47
43. Orange staining on corallite; digital zoom………………………………………………51
44. (left) Completely micritic interior of corallite, (right) beginning stages of
    micrite infilling of corallite; digital zoom………………………………………………51
45. Evidence of pore space or crystal-moldic porosity; digital zoom………………………51
46. Large rhombic dolomite crystals associated with sparry calcite cement; smaller
    dolomite clusters associated with micrite; digital zoom……………………………..51
47. Xenotypic mosaic dolomite; digital zoom.................................52
48. Crinoidal debris, arm segments at arrows; digital zoom........52
49. Peloid within space between corallites; digital zoom.............52
50. Crinoid stem from left to right end of section; digital zoom....52
51. Enlargement of Figure 10......................................................53
52. Planar-e dolomite within micritic areas between corallites; digital zoom.....56
53. Crinoid debris, peloids, and some crystal-moldic porosity; digital zoom........56
54. Enlargement of Figure 11......................................................57
55. Fracture porosity (a) xenotypic mosaic dolomite, (b) unimodal planar-e
dolomite, (c) only 3 dolomite crystals present, unimodal planar-e;
digital zoom.................................................................61
56. Unidentified grains; peloids; digital zoom..............................61
57. Bryozoan fragment; digital zoom..........................................61
58. Enlargement of Figure 12......................................................62
59. Large crinoid stem with a crude isopachous layer of cement, polymodal
planar-s dolomite, and some pore space; digital zoom...............65
60. Patches of dolomite, peloidal fragments and crinoidal debris; digital zoom......65
61. Enlargement of Figure 13......................................................66
62. Fenestral porosity; micrite and calcite cement within corallite chambers;
planar-e dolomite, lower left chamber; digital zoom...............69
63. Fabric selective porosity; possible dolomite presence in upper right pore space;
digital zoom.................................................................69
64. Unidentified grains; smooth, rounded, dark centers with white surrounding; digital zoom………………………………………………………………………………………….69
65. Enlargement of Figure 14…………………………………………………………………………………..…70
66. Fabric selective porosity; digital zoom…………………………………………………………….……73
67. Thickened corallite walls with orange staining; digital zoom…………………………………73
68. Two distinct forms of dolomite within a single corallite chamber; digital zoom……73
69. Indistinct patch of non-fabric selective dolomite; digital zoom……………………………….73
70. Enlargement of Figure 15………………………………………………………………………………………….74
71. Transition from polygonal corallites to longitudinal chambers; yellow-brown-
   infillings at bottom are associated with dolomite crystals, and more intense ferroan calcite above; opaque material is clumped along walls at the center of the plate; digital zoom………………………………………………………………………78
72. Corallite walls (thicker, gray towards bottom of plate), “dripping” of dark opaque material from top of corallites; digital zoom………………………………………………………………….78
73. Large rhombohedral dolomite, with dedolomitization, crystal moldic porosity,
   and associations with densely opaque material; digital zoom……………………………………78
74. Enlargement of Figure 16…………………………………………………………………………………..…79
75. Crystal moldic porosity; digital image…………………………………………………………………82
76. Variation in color of micritized areas, evidence of dark opaque matter,
dedolomitization and dolomite crystals; digital image………………………………………………82
77. Dolomite rounded, without center inclusions; digital image……………………………………82
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I. INTRODUCTION

The Silurian Period was a time of global reef building and divergence of species. The previous continental glaciers that marked the end of the Ordovician Period melted and led to a rise in sea level. As a result, epicontinental seas created new marine habitats for a diverse invertebrate fauna. Corals were especially suited for the warm, shallow, near-surface waters and thrived in complex reef communities. The “Age of Corals” was a title associated with the Silurian ecosystems that contributed to a tropical ecology and promoted diversification of species.

This “age,” which is generally agreed to have lasted from about 443 to 417 mya, occurred at a time when present-day Ohio was contained in the landmass of Laurentia. A vast polar ocean was situated to the north of this landmass and Gondwana bordered the south. The Taconic Orogeny of the Ordovician Period had subsided, but left the uplifted Cincinnati Arch in its wake. East of this arch, the distinctive Brassfield Formation was deposited during the Llandovery Epoch approximately 435 mya (Kleffner, 1998).

A well-preserved outcrop of the Brassfield Formation is accessible in southwestern Ohio at the Oakes Quarry Park in Fairborn. This exposure reveals seven distinct units composed mostly of limestone, dolostone, and shale. The site also yields a wide variety of invertebrate fossils, including those from the phyla Cnidaria, Spongæ, Echinodermata, Bryozoa, and Mollusca. In particular, the co-dominance of
Silurian corals and stromatoporoids is evident by their fossil abundance and persistent co-
ocurrence in reef and reef-affected settings. It is this fossil abundance, diversity and
preservation that led to the consideration of the Brassfield Formation as a key resource
for understanding the paleoenvironment and faunal success of the Silurian. This
research provided further understanding of this period and the processes that influenced
the deposition and diagenesis of the Brassfield formation.
II. OBJECTIVES

The purpose of this research was to better understand and reconstruct the paleoenvironment of the Brassfield Formation by using histologic methods. This will lead to greater insight into the development of the invertebrate fauna and their accompanying paleoenvironment and better characterization of the diagenetic processes that occurred. Careful examination of selected thin sections treated with iron and calcite stains revealed the mineral interactions and possible microbial influence that led to the presence of dolomite. Histological methods were an effective tool for studying the carbonate rocks and their fossil and mineral constituents.
III. BACKGROUND

PREVIOUS WORK ON DOLOMITIZATION

Carbonate rocks are typically composed of mostly calcite (CaCO$_3$) and/or dolomite CaMg(CO$_3$)$_2$, the latter of which is able to replace calcite in a magnesium-rich environment. The ratio of these two minerals, and how they are expressed within a rock, are key indicators of a rock’s diagenetic history. Properties such as primary or replacive dolomite, crystal texture and size (Figure 1) are all clues to the sequence of environments that created them. Through past analyses of carbonate rocks it has been inferred that most dolomite occurrences are a result of specialized marine ecosystems, specifically anoxic, sulfate-rich environments (Alonso-Zarza and Martin-Perez, 2008).

Figure 1. Dolomite crystal classification (Warren, 2000)
Typically, dolomite is readily precipitated in a setting that provides a magnesium (Mg) source, a system of flow (for bringing in the surrounding Mg, and flushing out the retained calcium, Ca), and favorable kinetics. This combination of processes operates in nature today; however, it rarely produces the quantity or structure of dolomite deposited in ancient formations. Even the most thermodynamically stable forms are rarely precipitated in modern marine environments. Non-ideal, calcium-rich dolomite is typically what dominates ancient sediments, leading to the enigmatic “dolomite problem” (Zhang et al., 2012).

For years, researchers have attempted to recreate the environment and chemistry of developing dolomite in order to understand why the observed dolomitic forms differ from what is expected. These numerous laboratory tests have failed to produce stoichiometrically similar dolomite at normal earth surface conditions. Ideal dolomite, which is both well-ordered and stoichiometric, is also underrepresented despite its thermodynamic stability. New research is attempting to create a better understanding of dolomite by developing a more applicable stoichiometric model.

Teedumae et al. (2003) investigated dolomitic processes from three different areas of genesis. They concluded that secondary (replacive) dolomite exhibited greater order; the most stoichiometric of which was the most altered. This highlighted the correlation of crystal growth rate to stoichiometric composition. The most pure composition resulted from slowly-growing crystals.

Following this research, Liu et al. (2005) compared the rate-determining mechanisms of dissolution between limestones and dolostones. The authors determined
that rates of dissolution were significantly lower among dolomitic composition. This was due primarily to dolomite’s surface reaction controlling mechanism. Also, the dolomite dissolution was discovered to be less reactive to surrounding hydrodynamics.

More recent attention, however, has been given to the role of bacteria in mediating dolomite precipitation. Despite the prevailing marine conditions of a certain locality, bacteria encompass an area of increased pH, magnesium, and carbonate within the cellular envelope. This boundary layer is a result of bacteria consuming organic substrates that prompt a series of chemical reactions leading to changes in the micro-environment. Increased negative charges accumulated by the cell increase its affinity for calcium and magnesium ion binding, while sulfate-reducing activities ultimately initiate dolomite nucleation on extracellular polymeric extensions (Figure 2). This process of microbial dolomite mediation by sulfate reducing bacteria (SRB) broadens the dolomite model to include not just areas of hypersaline marine environments, but a variety of environments including perhaps non-marine and aerobic.

Figure 2. Schematic of dolomite SRB-mediated precipitation (Corzo et.al., 2005).
It is only through microbial influence that experimental dolomite has ever been produced at near earth-surface temperatures. Sanchez-Roman et al. (2008) proposed that dolomite nucleation begins on nanoglobules that protrude from the cell surface of a microbe, or nanobacterium. When equal amounts of Ca\(^{2+}\) and Mg\(^{2+}\) accumulate within the bacterial cell envelope, a change in the micro-environment occurs, allowing for the precipitation of dolomite. This micro-environment alteration surrounding the nanobacteria ultimately lowers the kinetic barrier that prevents dolomitization. A typical process involves the addition of sulfate-reducing bacteria that elevate pH levels. These same bacteria produce CO\(_2\) that eventually dissolves to HCO\(_3^-\) or CO\(_3^{2-}\). Within this altered local environment, a supersaturation to dolomite occurs in the presence of Ca\(^{2+}\) and Mg\(^{2+}\).

Krause et al. (2012) expanded on the idea of microbial influence by further investigating the effects of kinetic barriers. This research highlighted the increased hydration energy of Mg\(^{2+}\). The extra-cellular environment created by bacterial polymeric substances lowers this hydration energy, thereby increasing solubility of Mg and Ca ions. This indicates that a hypersaline environment is not crucial for dolomitization as was previously believed, but rather bacterial mediation in modern marine salinities may still favor the production of dolomite at the nano level.

The geologic record supports this study because dolomite formations of the past typically developed during periods of low oxygen levels. These anoxic conditions led to increased activity of anaerobic organisms, which continued the process of organic degradation in the absence of oxygen. This process of anaerobic decay was not only
dominant, but mostly consisted of sulfate-reducing bacteria. Microbial biofilms are also able to flourish under these conditions because deposit-feeding benthic fauna, which compete with bacterial colonies, are limited or absent in anoxic waters (Krause, 2012).

More recently, Zhang et al. (2012) examined the process of dolomite nucleation and the lowering of kinetic barriers. This research demonstrated that Mg\(^{2+}\) is only partially dehydrated when absorbed into the dolomite nucleus. It is the remaining water present that ultimately prevents nuclear growth. However, once the pH rises due to the activities of sulfate-reducing bacteria, the dielectric constant is lowered and dehydration of Mg\(^{2+}\) is increased. This underscores the important role that bacteria may have in the dolomitization process.

For better microscopic resolution of the subtle features within ancient rocks, scientists have applied the art of carbonate staining used in the field of histology. Histological staining is a routine practice applied to laboratory analysis of human tissue. The application of this staining practice has found much success in studies of fossil vertebrates. During this process, chemical stains are added to the specimen to enhance the appearance of specific features. For instance, hard materials such as bones and teeth are very receptive to the calcium mineral stain.

Gerald M. Friedman (1959) first developed the basic method of identifying calcium and other carbonate minerals through staining. Each histological stain was applied and tested for its permeability to particular minerals, then catalogued for future use in sedimentary petrology. From this research scientists learned the importance of Alizarin Red S for calcite staining, Potassium Ferrocyanide for iron staining, Feigl’s
Solution for aragonitic staining, and the resistance of dolomite to accepting any of these colors (Figure 3). Additional information on this staining art is provided in Appendix A.

Figure 3. Carbonates and their response to staining (modified from Dickson, 1966)

Chemical stains are most valuable in the interpretation of calcite and dolomite crystals. These crystals, when etched with hydrochloric acid, exhibit different reliefs under light microscopy. Calcite is reduced in relief, while dolomite is unaffected, allowing for a raised “3-D” appearance of the dolomite crystal. The uptake of the standard Alizarin Red S stain further distinguishes the pink-red calcite from the unstained dolomite (Dickson, 1966).

The second most common carbonate stain, Potassium Ferrocyanide, is useful in differentiating crystals containing iron from crystals without (Dickson, 1966). The Turnbull reaction, which occurs when Potassium Ferrocyanide reacts with ferrous iron,
specifically targets ferroan deposits, whether in pore spaces, along fracture lines, or within crystals themselves. Staining is also represented in ranges; therefore, slightly ferroan accumulations appear lighter (lavender) in comparison to highly ferroan accumulations (bright blue). The ability to follow a precipitate trail and its crystal associations is beneficial for diagenetic and environmental analysis. From the minerals detected and their placement and concentration, it can be determined if the environment was oxic or anoxic, marine or fresh water, and near shore or at depth.

Additionally, staining enhances features that normally are more difficult to detect. Pore space, fractures, and moldic porosity are augmented by the surrounding color. Banding patterns of corals are also enriched with greater resolution following chemical staining. Combined with the mineral analysis mentioned earlier, evaluation of enhanced features provides supplementary evidence for environmental reconstruction.

More recently, staining has been tested on invertebrate fossils with similar successes. Layers deposited by ancient cyanobacteria, the mineral trail of diagenesis, and even banding patterns occurring within stromatoporoids and corals have all been made visible with the addition of selective stains. Recent research has identified coral banding characteristics associated with changes in environmental conditions (Hubbard and Scaturo, 1985; Taylor et al., 1993; Lough and Cooper, 2011) that, with the addition of histological staining, can be compared to banding patterns in ancient fossil corals (Barnes and Lough, 1993). These recognizable patterns can be classified and used to interpret possible controls on stromatoporoid and coral growth in the geologic past (Young and Kershaw, 2005).
Internal banding is classified into one of four visible features: absence of banding, density banding, growth interruption banding, and post mortem banding. Typically, stromatoporoids have either no banding or banding that ranges from variable to unrecognizable. Therefore, stromatoporoids are not dependable models for paleoenvironmental reconstructions based on these distinct bands. The four classifications listed above, however, are especially identifiable in rugose and tabulate corals. Accurate paleoenvironment analysis requires comparison of internal banding within corals of the same taxonomic class, but for the purpose of diagenetic history, individual banding patterns may indicate levels of sediment, organic composition, and available oxygen (Young and Kershaw, 2005).

Coral bands may be high density (HD) or low density (LD) deposits, as determined by the thickness of the skeletal elements, spacing between these elements, and development of additional structures. Principally, these bands indicate annual growth increments. Growth, however, is subject to environmental stresses and is therefore reflected in the arrangement of HD and LD bands. The thinner, greatly spaced, LD bands reflect periods of decreased environmental stress and are later subject to post mortem lithostatic compaction, referred to as breakage bands. The presence of thicker, minimally spaced, HD accumulations is typically attributed to increased carbonate secretions, increased sedimentation, and/or reduced light while the colony maintains constant linear growth rates (Young and Kershaw, 2005).

The presence of growth interruption bands, occurring as sediment inclusions or marginal notching, adjacent to or above the HD bands, further implicates increased
sedimentation as the most likely cause. This type of characteristic may be patterned within a coral, thus signifying a seasonal event. When HD bands are evident right before growth interruption bands and death of the coral, it presents a strong indication that sedimentation was greatly increased (a possible severe event) and significantly affected the viability of that coral (Young and Kershaw, 2005). This idea is further supported by the lack of banding present in corals from deeper marine environments (Archer and Feldman, 1986).

The availability of oxygen following coral mortality can be estimated using banding presence and staining. In the presence of greater oxygen (oxic conditions) there is rapid decomposition and most organic matter is removed. For this reason, the highest rates of decay result from freely-flowing seawater or coverage by permeable, sandy sediments. In contrast, lack of oxygen (anoxic conditions) yields increased putrefaction and resynthesize that favors the preservation of organic material. Therefore, marine environments at depth (merely 3 cm below the sediment/water interface) and/or within mud might produce lesser degrees of decay. If the coral is retained in a reducing environment for some time, pyrite is commonly formed as a product of bacterial sulfate reduction (Scoffin, 1992). Greater preservation of banding, organic composition, and presence of pyrite are just some of the additional features highlighted by carbonate staining that aid in paleoenvironmental analysis.

These methods of mineral staining have not been previously used in great detail in the study of diagenetic processes within the Silurian-aged Brassfield Formation. It is likely that studies of the Brassfield would be enhanced with the addition of stains
that are selective for dolomite, calcium and other diagenetic precipitates. Evidence for microbially-affected environments and microbially induced dolomite might be better identified with the addition of mineral stains and thin section analysis.

The research presented here will expand the knowledge of dolomitic processes and their relation to the diagenetic and paleo-environment. Through carbonate staining techniques, specific dolomite characteristics are identified from thin section and staining analysis. Crystal size, texture and mode of replacement are described, along with color presentation, coral banding and any other details of importance. This research is provided to complement prior studies and further advance the understanding of the “dolomite problem.”
PREVIOUS WORK ON THE BRASSFIELD FORMATION

The Brassfield Formation is an early Silurian (Aeronian, Llandoveryan) sedimentary unit composed mainly of high-purity limestone with minor amounts of dolostone and shale. It has been described in Ohio, Indiana, Kentucky, Tennessee, and West Virginia and occurs in varying degrees of thickness and dolomitization. The paleontology and stratigraphy of the Brassfield has been the subject of numerous studies. Previously named the Clinton (Orton 1871), the unit was later renamed the Brassfield (Foerste 1906) and a description of the formation was subsequently given by the same author (Foerste 1935).

Foerste (1935) interpreted the physical nature of the descending beds of the Brassfield to be:

1. 1.5 ft of ferruginous limestone (overlaying a crinoidal bead bed)
2. 2 ft. of irregularly bedded (mostly) limestone and clay
3. 3.3 ft. (mostly) clay with interbedded thin limestone
4. 8.2 ft. irregularly bedded limestone with thin clay
5. 6 ft. of unfossiliferous limestone

In total, Foerste described 21 feet of Brassfield thickness exposed in east-central Kentucky. He went on to determine its extent and thickness in additional regions. Other researchers (Berry and Boucot, 1970; Cooper, 1975) concentrated on conodont taxonomy in order to assign a precise age to the formation. It wasn’t until 1998, with conodont
research headed by Kleffner, that the age was constrained to between 438.6 and 432.6 mya (1998).

The studies of the Brassfield from the 1960s and 1970s concentrated on the major characteristics of the formation, such as its regional extent, mineralogy, and paleontology. Ehlers and Hoover (1961) recorded the clay occurrences in the formation, which were determined to be illite, chlorite, and combinations of the two as kaolinite. Horvath (1967) determined the Brassfield Formation extends as far north in Ohio as Sandusky and as far east as the occurrence of the Clinton Sandstone. Gauri and Boucot (1970) highlighted the variation in morphology and abundance of growth stages within the brachiopod communities of the Brassfield. New species were described, as well as new questions posed about the mode of calcification they exhibited. Harrison and Harrison (1975) later interpreted the paleo-environment of the Brassfield to be shallow, marine conditions subjected to the turbid currents of a nearshore locality.

The 1980’s introduced a wealth of crinoidal research led by William I. Ausich. The morphological diversity that was previously described within the Brachiopoda was similarly described within the Echinodermata (specifically the Crinoidea). New species were introduced, as well as others restudied with new insight (Ausich, 1984; 1986a; 1986b; 1986c; 1987).

Schneider and Ausich (2002) investigated the paleoecological effects of the coral framebuilders in the Brassfield reef communities. These authors recorded the top three contributors to be (in order of descending abundance) Favositids, Stromatoporoids, and colonial Rugose corals. Classified as framebuilders and binders, these organisms
exhibited a random distribution in their paleosetting, which was at an area 28° south paleolatitude in southern Laurentia. In addition, the microbial fabric of *Wetherdella* was identified in specimens from Oakes Quarry Park, Fairborn, Ohio.

The following year Friedrich and Carney (2003) undertook a thorough analysis of the depositional and diagenetic history of all exposed facies of the Brassfield Formation in Fairborn, Ohio. This study provided a more complete understanding of the cementation and dolomitization processes within the Brassfield. Further studies included maps constructed by Bayless and Carney (2004) and the research collaboration project of Carney, Bayless and Bonham (2004) in preparation for the establishment of Oakes Quarry Park as a public facility.

The transformation of Oakes Quarry into a park freely available for research and education led to excellent opportunities for graduate students in the area. A thesis project was performed by McDonough (2006) as a more thorough investigation of an anomalous marker bed within the quarry park that contains an unusual concentration of cephalopods and gastropods. McDonough’s research provided a clear description of the marker bed’s variable thickness, extent, and composition. McDonough also described microbial fossils and preferential dolomitization within the marker bed.

The subject of dolomitization was revisited in work by Klosterman (2006) to determine the possibility of fabric selectivity. The greatest amounts of dolomitization were present in the lowest facies, with a fine crystals of subhedral shape and cloudy cores. Similar crystal shapes followed in the overlying crinoidal grainstones, though in a coarser, crystalline matrix. Further, the mollusk-rich beds exhibited clear, zoned, euhedral
dolomite crystals with cloudy centers that typically replaced the micrite within fossil organisms. Finally, in the overlying fossiliferous grainstones and packstones, the least amount of dolomitization was evident. A fine crystalline dolomite with euhedral shape and zonation exhibited the first evidence of some clear cores amongst the cloudy cores. This evidence suggested multiple dolomitization events, or at minimum, multiple sources of dolomitization. In addition, microbial fabrics were again identified.

The various hints of microbial influence led to further research in the role of bacteria within the Brassfield’s depositional environments. Schmidt (2004) interpreted the Brassfield limestone to have been influenced by benthic and cryptic microbial organisms such as cyanobacteria. Hand samples and acetate peels were examined for both direct and indirect evidence of microbial activity. Products of microbial carbonate mediation were detected, such as:

1. Micropeloids
2. Micrite halos around skeletal grains
3. Stromatolitic and thrombolytic microtextures
4. Microbial fabrics adjacent to primary, fibrous calcite
5. Isopachous fibrous calcite

Both photosynthetic and heterotrophic bacteria were surmised to be joint contributors to calcite cementation.

Also of interest in Schmidt’s research were cavities and voids that were formed in an oxygen rich environment. This was deduced by the abundance of red coloration within hand samples and thin sections from the Brassfield. This coloring was determined to have resulted from an abundance of hematite, which is a mineral
precipitated in oxic environments. Water circulation then decreased following an increase in internal sedimentation of micrite and microbial coatings. This led to an anoxic environment that was suggested by the presence of pyrite precipitate (Schmidt, 2004).

Framboidal aggregates of pyrite are typical in lower, anaerobic layers associated with cyanobacterial activity. It can also be an indication of iron and sulfuric deposits in the presence of bacterial metabolism. As bacterial presence increases, the formation of precipitated minerals increases as well. Additional evidence of bacterial activity may occur as microscopic biofilms on sedimentary particles. Hard surfaces, such as grains, peloids, and fossil fragments, tend to collect and concentrate food that bacteria can consume when attached externally (Rozanov and Astafleva, 2009).

In accordance with this association of pyrite and microbial presence, most mineral accumulations are located in body chambers or areas of organic decay. Raspberry-shaped pyrite aggregates are commonly embedded in ancient organic slime within limestones of reducing environment origins. Nanobacterial cells examined in thin sections from these limestones occur in sizes similar to the pyrite associated with them. This suggests these cells are not just laying atop the minerals, but are involved in the precipitation of them (Folk, 2005).

Sedimentary pyrite was determined by Schieber (2002) to be a significant indicator of microbial presence. SEM was used to locate bacterial remains within the pyrite framboid aggregates, which is a difficult task with light microscopy due to the opaque nature of the mineral. It is suggested from Schieber’s research that greater
microbial evidence can be found in ancient rocks if pyrite formations are investigated closer.

Previous research by Berner (1984, 1985) highlighted three important constituents controlling the formation of sedimentary pyrite: iron, dissolved sulfate (by sulfate reducing bacteria), and organic matter. Throughout time a shift in carbon deposition has created a carbon to pyrite sulfur ratio (C/S) that differs from today. The Paleozoic C/S ratio was very low due to lack of organic accumulations from land to marine waters. This decrease in carbon availability is supported by the evidence of a decrease in microbial communities within coral reefs at that time (Riding 2006).

Furthering this research into the processes of mineral precipitation and the carbonates associated with them is crucial to understanding the local environmental influence. Collective evidence of organic content, mineral associations, skeletal characteristics, and carbonate staining can provide enough evidence to satisfy the likely paleoenvironment and resulting pathway for diagenesis. Ancient environment reconstructions are therefore possible with a combined approach that includes both macroscopic and microscopic analysis of ancient structures.
IV. METHODS

For this study, rock samples were collected from the Oakes Quarry Park in Fairborn, Ohio. All samples were from the Brassfield Formation, an exposed unit within the quarry that dates to approximately 435 million years ago. Rock samples were chosen based on texture, representative lithology, good preservation of stromatoporoids and corals, and reef-like characteristics.

Of the collected rocks, six samples were selected for further analysis. Five of the samples were identified by the organism preserved and one was identified by its lithologic texture. The six samples were identified as follows:

Sample 1. Stromatoporoid

Sample 2. Tabulate Coral

Sample 3. Colonial Rugose Coral

Sample 4. Fossiliferous Packstone

Sample 5. Colonial Coral

Sample 6. Tabulate Coral

Microscopic thin sections were produced from each sample in a laboratory at Wright State University’s Lake Campus in Celina, Ohio.
Each rock specimen was first reduced to manageable palm-sized chunks with a specialized rock cutter (Figure 4, Figure 5). Multiple chunks, in varying amounts, were produced from the six specimens. Afterwards, the side of each slab that was to be adhered to a slide was smoothed along a series of sandpapers. Eight papers, decreasing in coarseness, were aligned on a laboratory table. Sandpaper grit size began at 80 (coarsest paper with largest particle diameter) and continued through 120, 200, 400, 600, 800, 1000 and finally 2500 (finest paper with smallest particle diameter). Additional information on the sanding procedure is provided in Appendix B.

Sanding was considered complete after the rock type underwent each step of the sandpaper line and had a smooth texture along the polished surface. Following completion of hand sanding, each polished sample was briefly held against an automated buffer to produce a more smoothed, finished appearance. Polished, buffed rock slabs were grouped according to sample number and two sections from each sample were chosen to be affixed to glass slides. In addition, an extra section from specimens 1 and 5, as well as two extra sections for specimen 6, were selected. A total of 16 sections were prepped for continued laboratory analysis.

A rectangular 3 x 2 inch glass slide was chosen for each section. Identifying information (i.e., location and specimen number) was etched into the glass using a diamond-tipped engraving tool. Next, an epoxy mixture was prepared unclear (a blue-tinged mixture is typically used for easy identification of pore space, but for this experiment the blue color might create confusion with the blue color of the iron stain). The clear mixture was then applied to the polished, buffed surface of a chosen section
and that surface was subsequently pressed against its accompanying slide. The section was pressed firmly against the glass slide for a full minute to ensure proper adhesion. Once completed, each adhered section/slide was placed on a laboratory table with the slide facing down and allowed to complete the drying process. Specimens were left to cure overnight, and the first full day of laboratory work was complete (Figure 6).

The next laboratory work day began with a general inspection of the slides to make certain the adhesion process was successful. All slides were considered to be satisfactory and the thin section process was continued. A Microtec Micro-sectioner (MARK II) was used for both cutting and sanding. Though this micro-sectioner did not indicate the exact measured thickness of each section produced, it is by the preparer’s professional opinion that all sections were at or below the standard petrographic thickness of 30 micrometers. Additional information on the cutting procedure is provided in Appendix B.

After examination of each specimen’s integrity, two slides of each specimen were chosen for preferential staining. An Alizarin Red S with Potassium Ferrocyanide stain was prepared for the first stain as follows:

Beaker 1. 1.5% HCL
Beaker 2. 3:2 ratio Alizarin Red S: Potassium Ferrocyanide (made by dilution of .2g Alizarin Red S in 100ml 1.5% HCl and 2.0g Potassium Ferrocyanide in 100ml 1.5% HCl)
Beaker 3. 0.2g Alizarin Red S per 100ml 1.5% HCl

One slide from each of the six specimens was stained using a procedure that detailed the timing and placement of slides within the three beakers. First, slides were placed in
Beaker 1 to be etched in HCl for approximately 10 seconds. Care was taken not to exceed this time because prolonged exposure would have deteriorated the sample.

Next, slides were dipped in Beaker 2 for about 20 seconds. Prolonged exposure in this solution would intensify the stain. It was critical to maintain identical times in this solution for each slide so staining results were comparable and not skewed. Finally, slides were counterstained for 15 seconds in Beaker 3 and briefly rinsed with deionized water. The second slide of each specimen was stained with Alizarin Red S only (in Beaker 1 and Beaker 3) for comparison. All slides exhibited successful and comparable uptake of the stains. Each slide was then photographed using a digital camera attached to a microscope and backlight (Figure 7- Figure 22). Properties resulting from slide staining, as well as other characteristics of the thin sections are detailed in the following section.
Laboratory Images

Figure 4. Rock slabs produced from initial cuts to specimen 3

Figure 5. Rock slabs produced from initial cuts to specimen 6
Figure 6. All rock sections in order (from sample 1 on right to sample 6 on left), curing overnight
Digital Images

Figure 7. Thin section 1A; Stromatoporoid with Alizarin Red S and Potassium Ferrocyanide staining

Figure 8. Thin section 1B; Stromatoporoid with Alizarin Red S and Potassium Ferrocyanide staining

Figure 9. Thin section 2A; Tabulate coral with Alizarin Red S and Potassium Ferrocyanide staining

Figure 10. Thin section 2B; Tabulate coral with Alizarin Red S staining only
Figure 11. Thin section 3A; Colonial Rugose coral with Alizarin Red S and Potassium Ferrocyanide staining

Figure 12. Thin section 3B; Colonial Rugose coral with Alizarin Red S staining only

Figure 13. Thin section 4A; Fossiliferous packstone with Alizarin Red S and Potassium Ferrocyanide staining

Figure 14. Thin section 4B; Fossiliferous packstone with Alizarin Red S staining only
Figure 15. Thin section 5A; Reef coral with Alizarin Red S and Potassium Ferrocyanide staining

Figure 16. Thin section 5B; Reef coral with Alizarin Red S staining only

Figure 17. Thin section 6A; Tabulate coral with Alizarin Red S and Potassium Ferrocyanide staining

Figure 18. Thin section 6B; Tabulate coral with Alizarin Red S staining only
Figure 19. Thin section 1C; Stromatoporoid unstained

Figure 20. Thin section 5C; Reef coral unstained

Figure 21. Thin section 6C; Reef coral unstained

Figure 22. Thin section 6D; Reef coral unstained
Figure 23. Enlargement of Figure 7; Alizarin Red S and Potassium Ferrocyanide Stain
A. Gross Description

Specimen 1A is a laminar stromatoporoid exhibiting wavy, horizontal laminae. Lamination occurs in undulations of thin, ferroan latilamina alternating with thicker, calcitic infilling. Vertical pillars are evident, but they are not as prominent as the horizontal latilamina. Extensive occurrences of dense, reddish black matter, identified as organic in origin and associated with pyrite precipitation, dot the latilamina, with many instances of fracture porosity.

Areas of orange-pink calcite are evident from the lower left to lower middle of specimen (arrow 1). From the bottom, this coloring fingers upward. Two small tinges of orange-pink calcite are also present in the top left and top middle portions of the thin section. The organic matter with pyrite associations present in these areas is more spaced, less dense, and redder in tint than in most other areas of the sample.

Ferroan staining, intermixed with dolomite crystals, finger together on both the left and right side of the specimen. Each instance is associated with thin fractures in the sample. Blue-black (red-tinted) dolomicritic fabric trends along each fracture, lining the uppermost portion of the calcite infilling (bottommost portion of dark latilamina). Dolomite crystals associated with this fabric are large and exhibit zonation with cloudy centers and clear rims.

Extensively zoned pink calcite fills the spaces within the laminaions. A concentrated patch of ferroan stain is also present in the upper left lobe of the specimen (Figure 24), as well as small spots that dot the interior. Two projections along the right edge appear to cross-cut the laminaions (Figure 27).
B. Dolomite

Dolomite crystals occur along the entire left edge and in patches along the right edge. Crystal size is mostly unimodal, though variation in size is represented. Crystal texture is planar-e entirely on right (Figure 28), planar-e mostly on left (Figure 25), and planar-s within 3 patches on the left side. The middle of the 3 planar-s patches is a precursor to a pore space that is entirely outlined in planar-e dolomite (Figure 26). This replacement dolomite is also evident within pore space on the right. All dolomite is associated with a dolomitic fabric beneath the relief of the crystals when examined with light microscopy.

Zonation is complex and grid-like in dolomite to the right. To the left, dolomite crystals house enlarged darkened, square centers and limpid rims. Much of the dolomite has incorporated red matter in its crystal centers and/or outlined the outer clear surface. Pore space at left represents possible dedolomitization. Other areas represent possible calcitization.

Under reflective light metallic flecks of pyrite are evident within much of the dolomitic areas and crystals.

C. Skeletal Fragments and Other Grains

None noted
Figure 24. Patch of blue staining (with dolomite) in upper left lobe; digital zoom

Figure 25. Planar-e dolomite patch on left side of thin section; digital zoom

Figure 26. Planar-e and planar-s dolomite on left side of thin section; evidence of pore space; digital zoom

Figure 27. Blue stain cross-cuts at right side of thin section; digital zoom
Figure 28. Planar-e dolomite on right side of thin section
Figure 29. Enlargement of Figure 8; Alizarin Red S stain only
A. Gross Description

Specimen 1B is an additional sample of the laminar stromatoporoid. It exhibits wavy lamination of thin, ferroan latilamina and thick, calcitic infilling. Dense, reddish-black organic material, with pyritic associations, outlines the horizontal latilamina. Fracture porosity is present, but this is not as prominent as in Specimen 1A. Areas of faded orange-colored calcite are evident on most of the left flank, and one concentration on the right. Within these areas the dense collections of matter occur less often and with increased spacing. Resolution decreases and associated calcite is clear to lightly stained. Ferroan staining is not represented in this section, though tiny spots of blue color are randomly distributed.

B. Dolomite

Dolomite crystals occur on the left outer edge within the area of orange, and extend along the edge (past the boundary of orange) to the upper middle portion, fingerling inward. Crystals also occur on the right side, adjacent to the area of orange, and extend downward (past the boundary of orange), though none are actually within the orange patch. All dolomite is polymodal, planar-e. Arrows on the left, from left to right, indicate areas of: (a) grid-like zonation (Figure 32); then (b) darkened, medium sized centers; followed by (c) more grid-like zonation. Arrows on the right, from left to right, indicate areas of: (a) large, grid-like zonation (Figure 30); then (b) darkened, medium to large sized centers (Figure 31); followed by (c) some grid-like zonation.
Dedolomitization is also present towards the bottom-most portion of the thin section. Much of the dolomite throughout incorporates the dark red-black matter into its cloudy centers or as outlines of the clear rims. Under reflected light metallic flecks of pyrite are evident within dolomitic areas and crystals.

C. Skeletal Fragments and Other Grains

None noted
Figure 30. Dolomite exhibiting grid-like zonation and crystal-moldic porosity; digital zoom

Figure 31. Dolomite exhibiting darkened, medium to large centers; digital zoom

Figure 32. Dolomite exhibiting zonation; replacement along lamina infilling; digital zoom
Figure 33. Enlargement of Figure 9; Alizarin Red S and Potassium Ferrocyanide stain
A. Gross Description

Specimen 2A is a tabulate reef coral cut longitudinally and exhibiting columnar corallite growth patterns. Corallites have intermediate to highly ferroan walls with a darkened calcite center line flanked by altered micrite. Within the micrite are dark concentrations of organic material mostly confined to the outer edges. Equant calcite lines the corallite chambers and large, blocky calcite cement fills the center, creating a drusy mosaic. Nearly all calcite is ferroan. Some partial to full non-ferroan calcitic infilling is also present in patches along the perimeter. Darker, thicker segmentation is evident in areas toward the top and bottom (Figure 37), with both incorporating increased brownish hues. At the top and bottom of the thin section, fine-grained micrite or mud partially to fully fills some chambers. Many of these infillings exhibit a dolomicritic fabric with reddish granular outlines. HD and LD bands are evident, with growth interruptions manifested by extensive marginal raggedness and sediment inclusions (Figures 35, 36, 37).

Fractures are evident and associated with ferroan staining, which in some spaces leaches out into the inter-crystalline calcite spaces. Some ferroan staining is also associated with the dark material lining the micritic corallite walls. This staining is more pronounced along the left and right edges, fading inward.

Under reflected light, metallic flecks and cubes of pyrite are present throughout the specimen.
B. Dolomite

Light and dark brown micritic infillings are present in lower left sections (Figure 34). To the right are light gray/brown partial infillings with polymodal, singular planar-e dolomite. Farther right are both partial and complete micritic infillings of darkest brown. Partial infillings trend towards a triangular shape protruding from the upper right corner of the section (Figure 35). An isolated patch of dark brown micrite is also present at the specimen interior. Polymodal, planar-e dolomite accompanies this patch. Also, a half-filled patch of dark brown micrite without the presence of dolomite occurs at the specimen center. Single to few dolomite crystals are present along the top left corner and inward. Some dolomite crystals exhibit specks of red coloring, suggesting hematite origin. All dolomite crystals are associated with the dolomicritic fabric evident beneath the dolomite relief (as revealed with light microscopy).

Dedolomitization was evident at the top left corner of the thin section.

C. Skeletal Fragments and Other Grains

Dark sediment infills contain skeletal debris consisting of mostly ostracods and crinoid columnals. Worm tubes were also present in several infills.
Figure 34. Dolomite crystals within micritic areas; evidence of crystal-moldic porosity; digital zoom

Figure 35. Micritic infilling of corallite chambers; digital zoom

Figure 36. Vertical corallite pattern; digital zoom
Figure 37. Transition from pink corallite divisions to darker brown, thicker, micritic divisions; digital zoom
Figure 38. Enlargement of Figure 10; Alizarin Red S stain only
A. Gross Description

Specimen 2B is a second representation of the tabulate reef coral, cut transversely with a surface view of the tightly packed polygonal corallites. Corallite walls contain a gray calcification center within a large septum of altered micrite and concentrations of brown/yellow material (Figure 40). Corallites are filled with pink to lavender drusy mosaic cement and some septal stubs are visible. Less distinct features occur toward the upper portion of the specimen, and greater resolution occurs toward the left. Ferroan staining is not present in this section.

One micritic infilling of note is dark yellow to brown in color with subtle dolomite crystals (Figure 39). Fracture lines are located at five positions around the micritized corallite and dedolomitization is present within. A semi-circle of corallites to the left, surrounding this infilling, are lined with red-brown color facing the infilling (possible ferroan calcite).

B. Dolomite

Possible dolomite crystals are present in a patch toward the bottom and within the muddy inclusion; however, precise identification is not possible due to indistinct features (Figure 41).

C. Skeletal Fragments and Other Grains

None noted
Figure 39. Micritic infilling of corallite; digital zoom

Figure 40. Polygonal corallite structure; digital zoom

Figure 41. Subtle traces of dolomite crystals within micritic area of corallite chamber; digital zoom
SPECIMEN 3A

Figure 42. Enlargement of Figure 11; Alizarin Red S and Potassium Ferrocyanide stain
A. Gross Description

Specimen 3A is a colonial rugose coral cut in horizontal cross section and characterized by relatively large corallites and visible septa. Grossly the section is dominated by these lavender corallites and septa, with mostly lavender-stained, micritic infilling at the outer edges and ferroan to non-ferroan sparry calcite infilling trending inwards. A possible three generations of cement is present within corallites: first a calcitic, coarse-grained microspar, then a bladed clear to pink non-ferroan calcite extending inwards, and finally, large, ferroan mosaic calcite slabs completely filling the interior. Several examples of prismatic, calcite spar cement are also present.

Areas between corallites are brown and micritic; these areas are more red-brown towards the top of the thin section and black-brown to the right. Ferroan staining between corallites is most evident in spaces longitudinally from top left to bottom left. Three large corallites encompass the center horizontally, surrounded by smaller corallites (which mostly dominate the left side of the specimen). In addition, a longitudinal section occurs at the bottom right and mid right of the thin section, as well as a transverse tabulate (mid-right).

Also notable is orange calcitic staining occurring within the septa at the center of a partial corallite and at the top of a smaller corallite in the upper left corner of the plate (Figure 43). One small corallite contains a completely brown, micritic center with mostly crinoidal fragments. The interior skeleton is markedly less visible and septa partially branch inward before also diminishing in resolution. Clear, sparry cement fills the left with some ferroan tabulae still obvious. Iron staining mostly dominates the right
with tabulae indistinguishable. A neighboring small corallite appears to be at the beginning stages of the same development (Figure 44).

An area of pore space, or perhaps extensive crystal-moldic porosity, occurs at the bottom left of the plate (Figure 45).

B. Dolomite

Single rhomboid dolomite crystals, planar-e, occur throughout the specimen and within nearly all brown, micritic infillings. Larger crystal size tends to be associated with or near blue stained areas, whereas clusters of dolomite crystals (exhibiting more distortions in shape) tend to be associated with micritic areas between corallites (Figure 46). Two prominent patches of dolomite occur within this specimen. A patch of xenotypic mosaic dolomite is evident (arrow 1) with larger, rhomboid crystals within and around the blue stained cement; then adjacent to medium, less rhomboidal dolomite at the edge of the micrite. Farther into the micritic area the dolomite crystals are smaller, fewer, and mostly planar-s. An additional patch of mostly xenotypic mosaic dolomite, some planar-s, occurs left of the first (arrow 2) (Figure 47).

All areas associated with dolomite retain the dolomicritic fabric beneath the dolomite relief. Reddish tint is associated with many dolomitic areas, and reddish material, most likely hematite, is incorporated into most of the dolomite crystals. Many occurrences of dedolomitization and possible calcitization are represented. Some mimetic characteristics, of original fabric, are evident in the remaining dolomite. Numerous small, black rhombohedral crystals of pyrite are scattered among dolomitic areas, all exhibiting metallic luster under reflected light.
C. Skeletal Fragments and Other Grains

Skeletal debris is mostly crinoidal and is present within micritic areas of the specimen. Several crinoid arm segments (which are used in the movement of food to the body) are visible (Figure 48). Also, a long section of crinoid stem is twisted within an area of micrite (Figure 50). Crinoid disks and peloids are the most abundant grains (Figure 49). Two unidentified objects occur at arrow 3. They have an irregular, rounded shape and are filled with ferroan stained, scored cement. An outer ring of gray-brown-lavender encompasses the shapes; the outline retaining the dolomicrite associated with previous dolomite occurrences (though no crystals are present). The right object has four protruding extensions at the bottom and an unusual star shaped figure (most likely a crinoid grain) occurring in the uppermost section.

Worm holes (possibly Trypanites borings) were evident within the mostly micritized smaller corallite.
Figure 43. Orange staining on corallite; digital zoom

Figure 44. (left) Completely micritic interior of corallite, (right) beginning stages of micrite infilling of corallite; digital zoom

Figure 45. Evidence of pore space or crystal-moldic porosity; digital zoom

Figure 46. Large rhombic dolomite crystals associated with sparry calcite cement; smaller dolomite clusters associated with micrite; digital zoom
Figure 47. Xenotypic mosaic dolomite; digital zoom

Figure 48. Crinoidal debris, arm segments at arrows; digital zoom

Figure 49. Peloid within space between corallites; digital zoom

Figure 50. Crinoid stem from left to right end of section; digital zoom
Figure 51. Enlargement of Figure 12; Alizarin Red S stain only
A. Gross Description

Specimen 3B is an additional sample of the rugose, colonial coral, cut in an oblique downward direction from the coral’s upper surface. Corallites appear in cross section with some additional longitudinal visibility. Corallites are composed mostly of lavender walls, with two generations of cement present and extending into the chamber space. Smaller, coarse microspar outlines the perimeter of the chamber space and blocky calcite cement fills the interior. Orange calcite staining is present at several locations (arrows at 1). Micritic areas between occur between corallites and are lighter brown to the right, and darker brown to the left. A possible artifact of sample preparation is indicated by arrow 2.

Numerous manifestations of fracture porosity are present. Some of these are associated with lavender staining, whereas others are light or dark brown color. Larger porous areas also cross-cut the corallites.

Several instances of absent banding are present, particularly along the outer rings of the corralites, with increased spacing between elements. Possible breakage bonds are likely, but banding overall is variable and lacks resolution.

B. Dolomite

Dolomite is not widespread, but large, rhomboid crystals (planar-e) occur in micritic sections to the right (Figure 52). Dolomitic areas within the left portion of the sample are somewhat indistinguishable; in these areas dolomite is grayish in color and mottled.
C. Skeletal Fragments and Other Grains

Crinoid debris and peloids occur in sections within micritic areas to the right that house the indistinguishable, grey dolomite (Figure 53). The crinoid debris includes a large, central columnal and other associated ossicles.
Figure 52. Planar-e dolomite within micritic areas between corallites; digital zoom

Figure 53. Crinoid debris, peloids, and some crystal-moldic porosity; digital zoom
Figure 54. Enlargement of Figure 13; Alizarin Red S and Potassium Ferrocyanide stain
A. Gross Description

Specimen 4A is a fossiliferous packstone that is composed mostly of crinoidal debris. The overall brownish color of the specimen is darkest near the top and intermixes with ferroan staining towards the bottom. Under crossed polars the specimen grossly reflects colors of red, brown, orange and yellow.

Many skeletal grains have developed an indistinct, peloidal microtexture and are surrounded by micritic matrix. Grains exhibit evidence of compaction and possible pressure solution (grains are overpacked and pushed against each other and portions of grains are missing, distorted, and broken). Three main fractures are present, with each having larger cavities toward one end that have been partially filled with ferroan calcite and dolomite crystals. Ferroan staining is scattered throughout, both within fossil grains and former pore space.

Under standard light microscopy grains are difficult to distinguish, but with the aid of crossed polars grains are more abundant and identifiable. Peloids, pellets, and partly-identifiable skeletal fragments are visible, with dark micritic envelopes (micritic halos). Most debris is infilled with calcitic microspar. Some occurrences of infills with large, blocky clear-pink non-ferroan calcite are present in grains of least discernable features.

Dense, red-black material occurs throughout the specimen, most prevalent in peloids with echinoderm fabric, and within some dolomite centers. Dolomicrite centers and single dolomite crystals are also present in the lumens of many peloids.
B. Dolomite

Three occurrences of fracture porosity are indicated at arrows 1 (Figure 55). Each of these features contain partial dolomitic infillings at its farthest right and include a vein that leads from the dolomite towards the left specimen edge. The largest of the three extends to make contact with the left edge. The dolomite surrounding the largest pore space is most likely xenotypic mosaic. The other two spaces are surrounded by unimodal planar-e, the smallest space containing only 3 crystals. Most concentrated dolomite occurs within the upper-right portion of the thin section. Moldic crystal porosity is present at mid-bottom of the thin section and is associated with the same dolomicritic fabric that characterizes the rest of the dolomite within the specimen. Crystals throughout the specimen also enclose center inclusions of bluish-black color (ferroan, pyritic), as well as red color (possible hematite).

Both clear and cloudy centered dolomite are present; cloudy dolomite (characteristic of inclusions) is mostly associated with crystals invading grains and crystals within a thick patch of dolomite.

C. Skeletal Fragments and Other Grains

Crinoid ossicles dominate this specimen. A longitudinal segment of crinoid stem is indicated by arrow 2. Some planar-e to planar-s dolomite crystals with cloudy centers and zonation are commonly located within these crinoid fabrics. Crinoid columnals occur throughout the sample as discs with micritic centers. Oblong peloids and unidentifiable square-shaped grains also occur throughout the section (Figure 56). Bryozoans are present in several locations. They show no extinction under crossed polars.
and tend to exhibit ranges of ferroan shades (Figure 57). Two fabric-selective infillings of ferroan, sparry cement appear to have filled former moldic porosity resulting from the previous dissolution of skeletal grains (arrow 3). Most grains are outlined with thin rims of micrite that appear with greatest resolution under crossed polars.

Echinoderms exhibit a more red-brown honeycomb fabric with dense, dark red accretions throughout. The crinoidal discs retain darkened lumens and spongy fabrics. All other debris is infilled with microspar. Possible bivalves and brachiopods are present, with bladed calcite emerging from one of the large skeletal fabrics.
Figure 55. Fracture porosity; (a) xenotypic mosaic dolomite; (b) unimodal planar-e dolomite; (c) only 3 dolomite crystals present, unimodal planar-e; digital zoom

Figure 56. Unidentified grains; peloids; digital zoom

Figure 57. Bryozoan fragment; digital zoom
Figure 58. Enlargement of Figure 14; Alizarin Red S stain only
A. Gross Description

Specimen 4B is an additional thin section from the fossiliferous packstone. It consists of a non-ferroan to slightly ferroan matrix and scattered crinoid ossicles that have undergone varying stages of micritization, including complete alteration to a peloidal microtexture. Grains exhibit evidence of compaction and possible pressure solution (grains are overpacked and pushed against each other; portions of grains are missing, distorted, and broken). Some grains exhibit dark outlines with associated non-ferroan calcitic microspar; centers are also composed of larger, coarser non-ferroan calcite, dolomite crystals, or red inclusions. Grain resolution increases under crossed polars. Many fracture traces are present as thin, dark lines without any associated pore space. Scattered ferroan staining is evident throughout and four primary patches of dolomite are noted at arrows 1.

B. Dolomite

Planar-e dolomite occurs in the patches to the left in the thin section (Figure 60), whereas planer-s dolomite dominates the patch to the right. Scattered dolomite crystals are also present throughout the specimen. Dolomitic infilling occurs within the large crinoid stem at arrow 2. Towards the left this dolomite rings the interior of the ossicles, interspersed between non-ferroan calcitic cementation at the ossicle edges and centers. Toward the right the dolomite penetrates farther, occupying the center space that is calcite at the left. This dolomite is polymodal planar-s and farther right is pore space. All dolomite present occurs in a blue-black dolomicritic fabric. The inner ossicle edges
are outlined with a blocky isopachous cement layer throughout (Figure 59). Grain-to-grain contact is evident, with micritic halos distinguishing the boundaries.

C. Skeletal Fragments and Other Grains

A prominent longitudinal section of crinoid stem is present (Figure 59; arrow 2). To the left, the interior of the crinoid stem exhibits several generation of cement. An outer area of non-distinct, fibrous (non-ferroan) calcite outlines the inner ossicle, followed by a thin line dolomicritic fabric. Entirely filling the central cavity is large, blocky, non-ferroan calcite. Moving along the stem to the right, the thin line of dolomicritic fabric enlarges, and accompanies an increased occurrence of dolomite crystals. Porosity occurs in this area and increases farther to the right. At the end of the large crinoids stem this porosity widens into a large open space that is adjacent to a large patch of blocky calcitic cement. A line of fracture extends from above the blocky calcite at the open end of the stem at the right, to the large pore space at the left. Immediately adjacent to the right of the stem section is an abundance of crinoid columnals and peloids. Peloids and scattered crinoid ossicles occur in low concentrations throughout the specimen. (Figure 60).
Figure 59. Large crinoid stem with a crude isopachous layer of cement, polymodal planar-s dolomite, and some pore space; digital zoom

Figure 60. Patches of dolomite, peloidal fragments and crinoidal debris; digital zoom
Figure 61. Enlargement of Figure 15; Alizarine Red S and Potassium Ferrocyanide stain
A. Gross Description

Specimen 5A is a longitudinal section of a colonial reef coral characterized by intermediately ferroan corallites and infilling from center to bottom of the sample. Nearly non-ferroan corallites with highly ferroan infilling occur from center to top. Corallite walls consist of a dark, central calcite line surrounded by a dolomicritic fabric. Extending inwards is a drusy mosaic of equant calcite spar, with the chambers completely filled with large, blocky calcite cement. Calcite ranges from non-ferroan to ferroan towards the walls and intermediate to highly ferroan towards the corallite center.

Micritic infillings dot the top left portions of the specimen and fill larger areas to the top right. These areas consist of a dolomicritic fabric that is typically paired with dolomite crystals. These infillings tend to begin in a lower left triangle formation within the corallite chamber and extend inward (Figure 62). Fabric-selective porosity is evident towards the bottom of the thin section. Pore spaces are confined to the interior of the corallite chambers, and mostly occur in the same triangular pattern as do the micrite infillings within the uppermost chambers. This geometry may represent moldic porosity resulting from the dissolution of coarse calcite crystals (Figure 63).

Areas of intense ferroan staining and red precipitate are present. Thicker elements are associated with the uppermost portions of the specimen that exhibit greater ferroan staining. HD and LD banding are both represented, with pore space and dolomite crystals obvious along the denser bands. Growth interruption banding is also present, manifested by extensive sediment inclusions and some marginal disturbances.
B. Dolomite

Large, rhomboid, planar-e dolomite crystals occur in several infillings on the top left and right micritic areas of the specimen (Figure 62). Dolomitic fabrics and crystal moldic porosity are associated with many corallite walls.

C. Skeletal Fragments and Other Grains

Two circular, white objects of unknown affinity with dark, circular centers are noted at arrow 1 (Figure 64).
Figure 62. Micrite and calcite cement within corallite chambers; planar-e dolomite, lower left chamber; digital zoom

Figure 63. Fabric-selective porosity; possible dolomite presence in upper right pore space; digital zoom

Figure 64. Unidentified grains; smooth, rounded, dark centers with white surrounding; digital zoom
Figure 65. Enlargement of Figure 16; Alizarin Red S stain only
A. Gross Description

Specimen 5B is an additional longitudinal section of the colonial reef coral with intermediately ferroan corallites and slightly ferroan infilling throughout, grading into non-ferroan toward the top. Fabric-selective pore spaces occur from the center to the bottom of the thin section; calcite cement has filled some corallite chambers (Figure 66). Areas of orange calcitic stain are present within the thick, fibrous walls at top left and top center; dolomite patches are associated with each (Figure 67). Coarse, crystalline texture becomes increasingly coarser downward from the top. The central line of dark calcite within the corallite walls that was present in specimen 5A is also present here, but is not as thick or prominent. Coarse, non-planar, subhedral fabric is also less prominent.

B. Dolomite

Dolomite is mainly planar-e and occurs in large rhomboid crystals. Most dolomite occurs in micritic infillings toward the top of the specimen (Figure 68). Fabric-selective, clear dolomite occurs mostly within corallite walls throughout the specimen; one large, non-distinct patch is non-fabric selective (arrow 1) (Figure 69). This non-selective area consists of rough, non-planar fabric with associated dolomite crystals. Crystals contain inclusions, but have clear, limpid rims. This patch is within an area of HD banding, roofed by breakage bands.

HD banding is less prominent, though still detectable, and LD bands are faint to possibly absent in areas. Dolomite crystals are still associated with HD banding patterns, but a correlation between pore space and bands is not discernable.
At arrow 2 (Figure 68) the corallite’s bottom half contains golden-colored dolomite crystals, whereas the top half contains clear, larger dolomite crystals.

A possible artifact of sample preparation occurs at the center as non-textured, dark lavender spots (arrow 3). Crystal-shaped moldic porosity is also present within infillings that in other areas stain for calcite.

C. Skeletal Fragments and Other Grains

None noted.
Figure 66. Fabric selective porosity; digital zoom

Figure 67. Thickened corallite walls with orange staining; digital zoom

Figure 68. Two distinct forms of dolomite within a one corallite chamber; digital zoom

Figure 69. Indistinct patch of non-fabric selective dolomite; digital zoom
SPECIMEN 6A

Figure 70. Enlargement of Figure 17; Alizarin Red S and Potassium Ferrocyanide stain
A. Gross Description

Specimen 6A is a colonial tabulate reef coral, cut longitudinal to corallites in the mid to upper portions of the sample and transverse to corallites in the lower portion of the sample (Figure 71). Patches of ferroan staining occur among micritic infillings of the longitudinal sections, and more intensely stained ferroan patches occur within the lower most corallite infillings (Figure 72). Areas of especially micrite are more prominent along the upper most edge from left to right, as well as the left-bottom corner and bottom-right edge (arrow 1). Micritic sections range in color from dark yellow, to light brown and dark brown. Micrite infillings increase in coarseness as their color darkens.

Corallite walls contain a central, dark gray, calcitic line surrounded by yellow-brown-pink non-ferroan microspar fabric (some areas exhibit a more mottled/thickened, gray fabric that is possibly dolomicritic) (Figure 72). Two additional generations of cement are present; purple-black ferroan dolomicrite and a central infilling of non-ferroan to slightly ferroan blocky calcite. High-intensity ferroan staining of calcite occurs in corallites closer to micritic infillings. Intermediate to high-ferroan staining is also present, as well as conspicuous crystal twinning.

Densely opaque accumulations of dark material are present throughout the specimen (arrow 2). This dark material exhibits a thin outline of transparent red under the light microscope and the red intensity increases when viewed through a light microscope with a white paper between the slide and the light source, suggesting a hematite precipitate. However, brassy metallic flecks are visible throughout the specimen when viewing the thin section under indirect light, signifying the presence of pyrite.
The dark material generally occurs along and within corallite walls and tends to cluster in a globular, botryoidal form. The clusters appear to “drip” or “hang” from the corallite walls (“attaching” at the walls nearest the top, as oriented in the enlargement) (Figure 72). These features are also present within pore spaces and among dolomite crystals. Pyrite framboids were able to accumulate as raspberry shaped aggregate; therefore, it is possible a mix of both hematite and pyrite minerals are present.

Circular portions of detached corallite wall material are also present and encased by nodules of the dark precipitates. Less blocky calcite cement occurs within these circular portions than outside.

Corallite bands located at the uppermost right-center of the thin section appear to be crushed, broken, and compacted (arrow 3). These bands occur within an area of HD banding and sediment inclusions, suggesting they are breakage bands as a result of lithification activity following a severe event. Ferroan staining is nearly all located within LD banding areas and the globular mineral precipitates are nearly all located along HD banding areas.

B. Dolomite

Large, zoned, rhomboid dolomite crystals are prominent, with the outer zone more distinguishable than the inner zoning. Most dolomite present is or has undergone dedolomitization (Figure 73). Red to pink material is present as center inclusions within the crystals, and as partial to full outlines of zonation. Dolomite crystals are associated with purple-black (with some hints of iron, hematite, or pyrite precipitate) ferroan
dolomicritic fabric. Ferroan staining surrounds many rhomboids and one large saddle-shaped dolomite crystal is present, also surrounded by ferroan staining. Dolomite crystals typically occur within sediment inclusions and adjacent to HD bands.

C. Skeletal Fragments and Other Grains

A crinoid stem and bryozoan fragments are present, however many traces of probable skeletal grains are occluded or dolomitized.
Figure 71. Transition from polygonal corallites to longitudinal chambers; yellow-brown-olive infillings at bottom are associated with dolomite crystals, and more intense ferroan calcite above; opaque material is clumped along walls at the center of the plate; digital zoom

Figure 72. Corallite walls (thicker, gray towards bottom of plate), “dripping” of dark opaque material from top of corallites; digital zoom

Figure 73. Large rhombohedral dolomite, with dedolomitization, crystal moldic porosity, and associations with densely opaque precipitate; digital zoom
Figure 74. Enlargement of Figure 18; Alizarin Red S stain only

SPECIMEN 6B
A. Gross Description

Specimen 6B is a second sample of the tabulate reef coral, also having both longitudinal (bottom to mid portion of thin section) and transverse (top portion) views. Corallites are tightly packed and polygonal, with densely opaque dark accumulations of precipitate along the walls (see the results of specimen 6A for additional description of these accumulations) (arrow 1). “Dripping” effect does not follow the same pattern as in specimen 6A; the direction is varied in specimen 6B.

Micritic infillings range in color from yellow, to light brown-gray, and dark brown (Figure 76). Infillings are present at mid-bottom and form the top crust of the thin section (arrow 2). These areas occur in a more fine-grained, smooth fabric in lighter and yellow areas. Conversely, the darker brown infillings have a dolomicritic fabric. The accumulations of dark precipitate, as well as dedolomitization, are associated with these micritic corallites. Above the bottom-most filled corallites, chambers are lined with a similar micritic fabric.

Corallite walls contain a central, dark gray, calcitic line surrounded by yellow-brown-pink microspar fabric (some areas exhibit a more mottled/thickened, gray fabric that is possibly dolomicritic). Two additional generations of cement are present; purple-black ferroan dolomicrite and a central infilling of non-ferroan to slightly ferroan blocky calcite. Slightly increased ferroan staining (though still a light stain) of calcite occurs in corallites closer to micritic infillings and from left to right within the middle of the thin section; obvious crystal twinning occurs as well. Evidence of ferroan staining after using only the Alizarin Red S stain is generally associated with dolomite. It is possible the lavender-stained calcite is replacive cement for what was once ferroan dolomite.
Abundant pore space and moldic crystal porosity is present throughout this coral specimen (Figure 75), but confined to areas associated with LD banding. Two prominent areas of HD banding are evident, with some marginal raggedness, but no noticeable growth interruption bands. The sediment inclusions at the lower most portion of the specimen occur in an area likely to have been a third HD banding site, but either absence or breakage of bands has prevented a definitive interpretation. It is a likely indication of a severe event that led to a growth interruption, followed by coral death.

B. Dolomite

Dolomite is associated with brown micritic infillings and is present as large, rounded crystals lacking center inclusions (Figure 76). Dedolomitization is present in most dolomitic areas and is typically associated with crystals of increased zonation and lacking center inclusions (Figure 77).

C. Skeletal Fragments and Other Grains

Probable skeletal fragments are evident as occluded or dolomitized grains.
Figure 75. Crystal moldic porosity; digital image

Figure 76. Variation in color of micritized areas, evidence of dark opaque matter, dedolomitization and dolomite crystals; digital image

Figure 77. Dolomite rounded, without center inclusions; digital image
UNSTAINED SPECIMENS

Unstained thin sections were reserved for any additional staining needed, as well as affirmation of characteristics occurring in an unstained specimen. Mineral precipitates detected in chemically stained specimens were confirmed using physical techniques (as explained below) applied to the unstained slides.

Specimen 6 exhibited an abundance of clustered, opaque material that could not be positively identified with just light microscopy. Therefore, the unstained slide was examined under reflected light, without the manipulation of added color from staining. The red hues of the material were reinforced because of this method, as well as yellow-brown color associations. In addition, metallic flecks were noted throughout the thin section. From the combination of characteristics identified through stained and unstained thin sections, the precipitates were positively identified as hematite and pyrite (in order of greater to lesser accumulations).

Analysis of specimen 5 through stained and unstained thin sections yielded similar characteristics as specimen 6, though to a lesser degree.

Specimen 1 analysis of stained and unstained thin sections yielded results that were similar, but in differing amounts. Pyrite was the dominant of the two precipitates studied, whereas hematite occurred in lesser amounts.
VI. INTERPRETATION OF RESULTS

SPECIMEN 1

This is a laminar stromatoporoid, with folding features characteristic of encrusting forms. The following associations were identified:

• Moderately well preserved latilamina with organic manifestations
• Organic material associated with pyrite precipitation
• Multiple fractures; promoted fluid/mineral influx
• Dolomite located adjacent to and within dolomicrite, organic areas and ferroan areas
• High ferroan availability; as indicated by fracture staining and dedolomitization

The latilamina preservation, occurrence of organic matter, and associated pyrite suggest a reducing, anoxic environment. Dolomite crystals adjacent to organic matter, ferroan fractures, and pyrite precipitates indicate a nucleation of crystals within the reducing environment.
SPECIMEN 2

This is a tabulate reef coral, fully sessile in a shallow marine setting. The following associations were identified:

- Highly ferroan calcite
- Hematite and/or pyrite inclusions within dolomite centers
- Pyrite framboids within sediment inclusions and dolomicritic areas
- Geopetal markers; using geometry of sediment inclusions
- Organic components and pyrite precipitates within corallite bands
- Dedolomitization; indicates increased sulfate concentrations
- Drusy mosaic calcite cementation; indicates marine environment (meteoric)
- Polymodal dolomite crystals
- A pattern of HD banding associated growth interruption bands; indicated by marginal raggedness and sediment inclusions

The association of ferroan precipitate, organic matter, and pyrite framboids and inclusions suggest a reducing, anoxic environment. Dolomite crystals, as well as dedolomitization, occurring within the carbonate rich HD bands and sediment inclusions, indicate nucleation of crystals during periods of reduced oxygen. These periods may be associated with seasonal events as manifested by the regular occurrence of growth interruption bands and increased sedimentation.
SPECIMEN 3

This is a colonial rugose coral marked by a zig-zag structure of the epitheca denoting alteration. The following associations were identified:

- Inclusions of hematite and pyrite within dolomicritic areas and dolomite crystal centers
- Drusy mosaic calcite cementation; indicates marine environment
- Highly ferroan calcite
- Many cubic pyrite crystals within areas of sediment and organic material
- Smaller dolomite crystals within sediment/organic/pyrite areas and larger dolomite crystals toward pore spaces

Combined evidence of ferroan staining, organic rich sediment, and numerous pyrite precipitates suggest a reducing, anoxic environment. The occurrence of smaller dolomite crystals within the organic-rich and pyrite-rich sediment indicates nucleation began within that location and eventually extended to pore spaces. The drusy mosaic cementation pattern additionally suggests a marine setting.
SPECIMEN 4

This specimen is a fossiliferous packstone, mainly composed of crinoidal debris and peloids. The intetinsity of the packstone’s overall redish-brown fabric suggests the abundance of iron and organic matter. The predominant lavender hues of the calcite and bright blue of the cavities are indicative of a very ferruginous material. Evidence for microbial activity is inferred from:

- Micritic halos surrounding the grains
- Microspar infillings of grains
- Clotted, peloidal fabric texture
- Randomly distributed dark matter (of probable organic origin)
- Red deposits throughout the thin section
- Dolomite associations and dolomitization
- Possible borings, subsequent calcitic infills and loss of initial features

These characteristics are suggestive of a predominately oxic environment with intense microbial activity. Some evidence of compaction is present. This is a common occurrence that may have been facilitated by the soft nature of the fecal pellets. However, the overall shape of the grains and pellets is mostly intact, suggesting rapid lithification aided by microbial activity. It is likely these grains were influenced by microbial mediation and served as nucleation sites in a reducing environment.
SPECIMEN 5

This is an unidentified colonial reef coral or boundstone. The following associations were identified:

• Overall iron-rich characterization
• Geopetal indicator; sediment infills and thickening of corallite walls
• Dolomite crystals with cloudy lumens and clear rims
• Drusy mosaic calcite cementation
• Extensive dedolomitization and moldic porosity
• Dolomite crystals occur within dolomicritic areas and micritic infillings
• Banding contains probable organic-rich deposits, with pyrite precipitation
• HD banding associated with pore spaces and dolomite crystals
• Growth interruption bands marked by sediment inclusions and some marginal notching

The iron-rich structure, organic rich deposits, extensive dedolomitization, and pyrite precipitation are suggestive of a reducing, anoxic environment. Dolomite crystals are associated with organically dense HD banding and sediment inclusions, indicating nucleation began within these areas. Hematite and pyrite were less abundant in this specimen than in specimen 2; likewise, dolomite was less abundant in this specimen as well. This could be a result of reduced nucleation sites. The cloudy lumens of the
dolomite and drusy mosaic of the calcite are indicators of a marine environment.

Banding patterns indicate a regular interruptive event that occurred in connection with the anoxic surroundings and dolomite nucleation.
SPECIMEN 6

This is a tabulate reef coral, fully sessile in a shallow marine setting. The following associations were identified:

- Botryoidal aggregates of hematite with evidence of metallic pyrite; possible pyrite oxidation
- Botryoidal hematite along HD bands and within pore spaces adjacent to HD bands
- Probable organic matter within HD bands, although less than other specimens
- Possible geopetal indicator via “dripping” of botryoidal hematite
- Many dolomite crystals with absent cores
- Abundant pore space, moldic porosity, and ferroan staining are all within LD banding areas
- Botryoidal hematite and denser carbonate material are both within HD banding areas
- Breakage bands and absent banding

The presence of organic material, pyrite, and ferroan staining are suggestive of a reducing, anoxic environment. However, unlike other specimens there is clear evidence of a shift in conditions. The pyrite appears to have been oxidized to hematite, the organic matter is in decreased amounts, there is a lack of dolomite crystal cores and the moldic
porosity is within LD banding sites. This specimen indicates a dolomite and carbonate deterioration when conditions shift to a more oxygen-rich environment. There is also indication of an event that severed multiple bands and also led to an absence of banding. Most likely, the oxygenic environment would have encouraged deterioration of the carbonate matter, leaving the less-dense LD banding prone to alteration and/or breakage.
VII. CONCLUSION

The objective of this study was to build on past research concerning the paleoenvironment and diagenetic processes of the Brassfield Formation. The results showed a correlation between dolomitization characteristics and certain precipitates, including ferroan, organic, and pyrite deposits. These correlations may yield further insight into the processes and environments that govern diagenesis.

All thin sections contained evidence of dolomite crystallization and iron precipitates. All thin sections also contained either one or both precipitates of hematite or pyrite. The specimen exhibiting the greatest pyrite precipitation (Specimen 3), in the form of individual cuboid crystals, also exhibited the most extensive occurrences of dolomite. Conversely, the specimen with the greatest amount of hematite (Specimen 6) contained the greatest evidence of dedolomitization and development of porosity.

Xenotypic mosaic dolomite was contained in specimens of abundant micrite and bacterial evidence (Specimens 3 and 4). Intensity of ferroan staining did not correlate with dolomite crystal formation and every slide stained with Potassium Ferrocyanide had some amount of ferrous reaction. However, within some specimens (most noticeably in Specimens 1, 2 and 3) greater ferroan areas were located adjacent to micritic or sediment-laden areas. Most dolomite crystals contained inclusions of hematite or pyrite origin, and some included ferrous staining.
Evidence for anoxic environments and dolomite crystallization mediated by microbial activity are supported with the results provided in the thin sections. Dolomite appears more intact, within larger mosaics and with larger crystal size, in association with anoxic characteristics (pyrite and micritic or microbial associations). Dolomite appears unstable, within patches of dedolomitization, in association with characteristics of oxic environments (increased hematite precipitate and decreased organic carbon).

Growth patterns for all coral specimens have detectable HD and LD banding, most have growth interruption bands, and some have absent or breakage bands. Patterns indicate seasonal events (HD banding) that led to disruption of the coral viability, increased sedimentation, increased carbonate accumulations, and increased precipitates (namely pyrite and dolomite). Some events were marked by sediment infills and breakage bands at the probable point of organism death, suggesting a period of major environmental stress on the coral. Periods inbetween events (LD banding) showed marked cementation, porosity, ferrous precipitation, and dolomite instability.

This research presents a significant correlation between reducing environments and dolomite formation. Additionally, a relationship is probable between increased organic content, pyrite precipitation, and dolomite nucleation. Given that microbial evidence has been detected in past research examining carbonate and/or pyrite deposits, a link between microbial activity and dolomite formation is likely (Schmidt, 2004; Rozanov and Astafleva, 2009; Folk 2005; Schieber, 2002; Berner, 1984, 1985). Continued research into the geologic past may prove that indicators for specific microbial forms are marked by distinct phases of dolomite formation and degradation.
REFERENCES


APPENDIX A

THE ART OF STAINING

It is important to note that carbonate staining is a subjective technique, influenced by a variety of factors. Color presentation and intensity are dependent upon the crystal’s cleavage, its primary reaction with hydrochloric acid (etching), fabric granularity (fine-grained to coarse-grained), and even the presence of other stained precipitates (which may mask or suppress the objective stain) (Adams and MacKenzie, pg.7). Once the stain is created it is then subject to the interpretation of the reader. Thin section analysis may yield differing conclusions based on the experience and technique of the microscopic observer. For this reason, it is best not to base any petrographic analysis on staining alone, but rather in combination with other techniques.

Many stains are also nonspecific, and so may stain more than one precipitate the same color. Conversely, one precipitate might react with more than one stain. Dolomite, for instance, has over 20 stains that yield a range of colors overall. Prior knowledge of the natural dolomite color determines which stain would offer better resolution of the crystals (Friedman 1959).

For this research, the dolomite crystals were not targeted for staining. Alizarin Red S was determined to be an excellent calcite stain, and so was chosen as the primary differentiating tool between calcite and dolomite. The second stain chosen, Potassium
Ferrocyanide, had been routinely used as a reliable iron stain in both petrology and histology disciplines.

Organic stains undergo years of trial and error research. Therefore, favored use of a stain is dependent upon its success following repeated and duplicated staining applications. The two stains selected for this research were chosen because of their routine use and trusted results. The stained thin sections were also supplemented with interpretations from unstained thin sections. These sections were viewed under an indirect light source and with the “white card” method introduced by Folk (1987).
APPENDIX B

DETAILED METHODS

Sanding:

Each rock slab was firmly pressed against the sandpaper, only on the side chosen for slide adhesion, and moved forwards and backwards in circular motions. Before beginning a new, successive paper grade, the rock samples were dipped in water to remove any loose particles. This was done to eliminate possible scratches or pits in the sample. Proper sealing of the sample to the slide could have been hindered if these imperfections were present at time of adhesion.

Cutting:

For cutting, the slide was securely clamped into the machine with the rough end extended outward. A safety hood enclosed the sample and continuous water flow aided the operation of the cutting blade. Excess rock was sliced from the protruding end of each specimen (opposite the slide end).

The MARK II was then used for sanding each specimen as well. A wheel located to the operator’s left was rotated backwards until rotation ceased. Then four quarter turns of the wheel forward were applied to determine the starting position. Before continuing, the safety hood was lowered and water flow was engaged. The specimen was forced
against the sanding apparatus for brief intervals at the operator’s control. Between completed intervals, the wheel was moved a quarter turn forward until the equipment measuring device displayed zero. Alternation of sanding and quarter turns of the wheel continued until two full rotations from zero were executed. The slide was removed and inspected for even cutting, completeness of section, and thickness.