A MULTI-INDICATOR APPROACH TO UNDERSTANDING THE DIAGENESIS OF CARBONATES IN PENNSYLVANIAN MUDROCKS OF THE MIDLAND BASIN

Alex J. Reis

University of Kentucky, alex.reis@uky.edu

Author ORCID Identifier: https://orcid.org/0000-0002-5257-3463

Digital Object Identifier: https://doi.org/10.13023/ETD.2018.183

Recommended Citation

Reis, Alex J., "A MULTI-INDICATOR APPROACH TO UNDERSTANDING THE DIAGENESIS OF CARBONATES IN PENNSYLVANIAN MUDROCKS OF THE MIDLAND BASIN" (2018). Theses and Dissertations--Earth and Environmental Sciences. 56.

https://uknowledge.uky.edu/ees_etds/56

This Master’s Thesis is brought to you for free and open access by the Earth and Environmental Sciences at UKnowledge. It has been accepted for inclusion in Theses and Dissertations--Earth and Environmental Sciences by an authorized administrator of UKnowledge. For more information, please contact UKnowledge@lsv.uky.edu.
STUDENT AGREEMENT:

I represent that my thesis or dissertation and abstract are my original work. Proper attribution has been given to all outside sources. I understand that I am solely responsible for obtaining any needed copyright permissions. I have obtained needed written permission statement(s) from the owner(s) of each third-party copyrighted matter to be included in my work, allowing electronic distribution (if such use is not permitted by the fair use doctrine) which will be submitted to UKnowledge as Additional File.

I hereby grant to The University of Kentucky and its agents the irrevocable, non-exclusive, and royalty-free license to archive and make accessible my work in whole or in part in all forms of media, now or hereafter known. I agree that the document mentioned above may be made available immediately for worldwide access unless an embargo applies.

I retain all other ownership rights to the copyright of my work. I also retain the right to use in future works (such as articles or books) all or part of my work. I understand that I am free to register the copyright to my work.

REVIEW, APPROVAL AND ACCEPTANCE

The document mentioned above has been reviewed and accepted by the student’s advisor, on behalf of the advisory committee, and by the Director of Graduate Studies (DGS), on behalf of the program; we verify that this is the final, approved version of the student’s thesis including all changes required by the advisory committee. The undersigned agree to abide by the statements above.

Alex J. Reis, Student
Dr. Andrea Erhardt, Major Professor
Dr. Ed Woolery, Director of Graduate Studies
Abstract of Thesis

A MULTI-INDICATOR APPROACH TO UNDERSTANDING THE DIAGENESIS OF CARBONATES IN PENNSYLVANIAN MUDROCKS OF THE MIDLAND BASIN

The Late Pennsylvanian was a time of frequent, rapid glacioeustatic sea-level changes. These changes were recorded in the Wolfcamp D Formation of the Midland Basin as a series of cyclothems similar to those studied in the Midcontinent region (e.g., Algeo and Heckel, 2008). This study focuses on identifying the mechanisms and controls on carbonate deposition and diagenesis through the Upper Pennsylvanian Wolfcamp D Formation and evaluating the potential for these layers to be stratigraphically significant. A stepwise progression of diagenetic processes was identified through the use of $\delta^{13}$C$_{\text{carb}}$ and $\delta^{18}$O$_{\text{carb}}$, bulk geochemical and petrographic analysis, and scanning electron microscopy. Carbonate deposition and early-burial diagenesis appears to be strongly influenced by frequent changes in sea-level and benthic redox conditions. The transition to deep-burial diagenesis was controlled by the thermal gradient in the basin and the extent of diagenesis by the amount of clays and organic matter in the surrounding mudrocks. Further diagenesis was induced through interactions with a brine following clay diagenesis. The presence of multiple phases of diagenesis in this system further highlights the need for several lines of inquiry when evaluating the post-depositional evolution of carbonates in a mud-rich setting.

KEYWORDS: Carbonate Diagenesis, Dolomitization, Stable Isotope Analysis, Midland Basin

Alex J. Reis

April 27, 2018
A MULTI-INDICATOR APPROACH TO UNDERSTANDING THE DIAGENESIS OF CARBONATES IN PENNSYLVANIAN MUDROCKS OF THE MIDLAND BASIN

By

Alex Jacob Reis

Dr. Andrea Erhardt
Director of Thesis

Dr. Ed Woolery
Director of Graduate Studies

April 27, 2018
Date
Acknowledgements

This thesis would not have been successful without guidance and input from many people within the department and elsewhere. First and foremost, my advisor Dr. Andrea Erhardt provided excellent feedback and guidance throughout this process, not only enabling me to succeed as in the program at the University of Kentucky, but also rekindling my interest in geoscience research. Next, my committee members, Dr. Michael McGlue and Dr. Frank Ettensohn provided valuable insight and feedback which helped the project grow and succeed. Everyone on my committee helped guide me through this project and helped me grow as a geoscientist.

Beyond my committee, the faculty in the Department of Earth and Environmental Sciences was very welcoming and supportive throughout the project. I would like to thank them for providing the opportunity to succeed in my pursuit of a Master of Science degree. Support from the department allowed me to travel to the Flügel Carbonate Microfacies course in Erlangen, Germany.

In addition to the support I have received from the University of Kentucky, I would also like to thank my family and friends for their support throughout the project. My parents for always pushing me to be the best I can be and Nikita for supporting me no matter what I decide to do next.

Finally, I would like to extend my gratitude to everyone at Pioneer Natural Resources for donating the cores and datasets upon which my research was conducted. In addition to the datasets, I would like to thank them for their financial support which allowed me to focus on my research and travel to the 2017 American Geophysical Union Fall Meeting in New Orleans. I would like to thank Tom Spalding and Lowell Waite for their contributions to the project and Olivia Woodruff, Donny Loughry, and Dan Spaulding for their insight during my time at the University of Kentucky.
Table of Contents

Acknowledgements ........................................................................................................ iii
Table of Contents ........................................................................................................ iv
List of Tables ................................................................................................................ v
List of Figures ............................................................................................................. vi
List of Files ................................................................................................................ vii
Chapter 1: Introduction ...............................................................................................1
Chapter 2: Study Area ................................................................................................ 3
  2.1: Midland Basin ..................................................................................................... 3
  2.2: The Wolfcamp D Formation .............................................................................. 5
  2.3: Core Description ............................................................................................... 8
Chapter 3: Methods ....................................................................................................9
  3.1: Stable Carbon and Oxygen Isotope Analysis ................................................... 9
  3.2: X-ray Fluorescence .......................................................................................... 9
  3.3: Scanning Electron Microscopy .......................................................................10
  3.4: Electron Probe Micro-Analysis .......................................................................11
    3.4.1: Point Analysis ............................................................................................11
    3.4.2: Elemental Abundance Mapping ...............................................................11
  3.5: X-ray Diffraction .............................................................................................12
Chapter 4: Results ....................................................................................................12
  4.1: Bulk Rock Geochemistry ................................................................................12
  4.2: Scanning Electron Microscopy .......................................................................17
  4.3: Electron Probe Micro-Analysis .......................................................................21
  4.4: X-ray Diffraction .............................................................................................23
Chapter 5: Discussion ................................................................................................30
  5.1: Carbonate Deposition in the Midland Basin ....................................................30
  5.2: Carbonate Diagenesis in the Midland Basin ....................................................30
    5.2.1: Meteoric Carbonate Diagenesis .................................................................31
    5.2.2: Microbially Mediated Diagenesis ...............................................................32
    5.2.3: Deep-Burial Processes ...............................................................................33
    5.2.4: Brine-Induced Diagenesis .........................................................................34
    5.2.5: Hydrothermal Dolomitization ..................................................................35
  5.3: Carbonate deposition and diagenesis in the Upton County core .......................36
  5.4: Carbonate deposition and diagenesis in the Midland County core ...................39
  5.5: Diagenetic Sequence in the Midland Basin .....................................................41
  5.6: Changing Carbonate Deposition and Diagenesis over time .........................43
    5.6.1: Lower Wolfcamp D ..................................................................................43
    5.6.2: Middle Wolfcamp D ..................................................................................45
    5.6.3: Upper Wolfcamp D ..................................................................................46
Chapter 6: Conclusions .............................................................................................48
References ..................................................................................................................51
Vita ..............................................................................................................................56
List of Tables

Table 1: Geochemical characteristics of the lithofacies designations……………………8
Table 2: Coefficients of Variation.................................................................13
Table 3: Upton County x-ray diffraction and electron microprobe results…………..26
Table 4: Midland County x-ray diffraction and electron microprobe results………….28
List of Figures

Figure 1: Regional Paleogeography..........................................................4
Figure 2: Late Pennsylvanian—Early Permian Sea-level Curve.....................6
Figure 3: $\delta^{18}O_{\text{carb}}$ vs. $\delta^{13}C_{\text{carb}}$ by facies..............................................................13
Figure 4: Upton County core chemostratigraphic column..............................15
Figure 5: Midland County core chemostratigraphic column..........................16
Figure 6: Deep-burial diagenesis in the Upton County core........................18
Figure 7: Early-burial diagenesis from the Midland County core................19
Figure 8: Deep-burial diagenesis in the Midland County core......................20
Figure 9: Electron probe micro analyzer results for the Upton County core.......22
Figure 10: Electron probe micro analyzer results for the Midland County core...24
Figure 11: X-ray diffraction results from the Upton County core..................25
Figure 12: X-ray diffraction results from the Midland County core..............27
List of Files

Supplemental Table 1: Upton County Stable Isotopes………………………….(PDF 30KB)
Supplemental Table 2: Midland County Stable Isotopes………………………….(PDF 30KB)
Supplemental Table 3: Upton County Electron Microprobe Analysis………..(PDF 229KB)
Supplemental Table 4: Midland County Electron Microprobe Analysis………(PDF 174KB)
Supplemental Table 5: Upton County X-Ray Diffraction Analysis…………….(PDF 19KB)
Supplemental Table 6: Midland County X-Ray Diffraction Analysis………….(PDF 22KB)
1.0 Introduction

Sequence stratigraphic analysis in mud-rich settings can be complicated by the presence of cryptic sequence boundaries (Schieber, 1998). Where carbonates are present it can be tempting to utilize them as key marker beds within parasequences to indicate periods of highstand and for intrabasinal correlations (Handford and Loucks, 1993; Schlager, et al., 1994). Using these carbonates for identifying stratigraphically significant intervals is a potentially powerful tool (Handford and Loucks, 1993). Care must be taken, however, to identify the source of the carbonates, whether they are cement grounds occurring locally or widespread gravity flow deposits, and the potential for diagenesis (Schlager et al., 1994; Taylor et al., 2000). Accurate placement of these carbonates in a stratigraphic framework is contingent on several factors: the timing of deposition is predictable, the carbonates did not undergo significant post-depositional alteration, and carbonate deposition or cementation is widely dispersed over the study area (Irwin and Curtis, 1977; Handford and Loucks, 1993; Schlager et al., 1994; Mazzullo, 2000).

The Wolfcamp D Formation of the Midland Basin is a mud-rich system with intermittent carbonate beds that have been proposed as correlation markers. Carbonate deposition in this area occurred primarily through gravity flows from the various carbonate platforms surrounding the basin (McGlue et al., 2015; Baldwin, 2016; Ryan, 2016) (Figure 1). The current stratigraphic model suggests carbonate deposition is the result of highstand shedding of platform material into the basin (Baldwin, 2016; Ryan, 2016). The presence of dolomite intervals in both cores complicates this interpretation. Dolomitization in the Wolfcamp D Formation is currently thought to occur as replacement and cementation during sediment starvation resulting from periods of rapid sea-level rise (Baldwin 2016;
Periods of sediment starvation increases the residence time of the sediments in the bacterial sulfate reduction (BSR) zone where dolomite and calcite precipitation is induced through microbial activity (Irwin and Curtis, 1977; Mazzullo, 2000). This process, while geologically instantaneous, will be interrupted during periods of moderate to high sedimentation as the sulfate or organic matter source for BSR is cut off (Mazzullo, 2000; Machel, 2004). If any carbonates represent authigenic precipitation during early-burial diagenesis during periods of sediment starvation instead of highstand shedding of carbonate material, it would have an impact on the stratigraphic interpretation.

The interpretation of these carbonate intervals as correlation markers is contingent on the carbonates representing discrete, basinwide events that can be traced through petrographic and geochemical methods between the two cores. As carbonate minerals are highly susceptible to post-depositional alteration, care must be taken when evaluating carbonates as stratigraphic indicators in mudrocks as stratigraphically significant intervals (Berner, 1967; Morse et al., 2007; Swart, 2015). This alteration has the potential to change both the chemistry and fabric of a mineral in a manner that is not always obvious.

To assess the utility of the Wolfcamp D carbonate beds as stratigraphic indicators, a multi-indicator geochemical investigation was undertaken. A combination of several geochemical indicators was utilized to discern whether the diagenesis represented a single basinwide event, was the result of a heterogeneous stepwise progression of changing seawater and porewater chemistry, or a combination of the two. If any of the carbonate beds represented a single basinwide diagenetic event, they could be utilized for correlation to help with stratigraphic reconstructions. Evaluating the diagenesis in the system has been complicated by the heterogenetic distribution of dolomite in the carbonates, with some
intervals entirely dolomitized and others having discrete layers of dolomite within a single carbonate interval. This study will use geochemical indicators to evaluate the diagenetic history of the Wolfcamp D formation, determining the role carbonate beds play in the larger stratigraphic framework.

2.0 Study Area

2.1 The Midland Basin

The Midland Basin was the eastern sub-basin of the Greater Permian Basin (Figure 1a) (Mazzullo and Reid, 1989). It was separated from the Delaware Basin to the west by the fault-bounded uplifted Central Basin Platform (CBP) beginning in Late Mississippian time. It was bounded to the east by the Eastern Shelf, giving it an asymmetric shape. The basin was bounded to the south by the Ozona Arch, a continuation of the CBP uplift, separating it from the Val Verde Basin (Figure 1b) (Galley, 1958; Frenzel et al., 1988; Mazzullo and Reid, 1989; Shumaker, 1992, Hamlin and Baumgardner, 2012). Deposition on the regional uplifts was predominantly carbonate, and the steep slopes of the CBP made it susceptible to gravity flows (Baldwin, 2016; Ryan, 2016).

The Midland Basin was bounded by extensive networks of faults. To the east, it was bounded by the Fort Chadbourne Fault Zone, a north-south trending network of faults (Yang and Dorobek, 1995). To the south, it was bounded by faulting associated with the uplift of the Ozona Arch, the southern expression of the uplift related to the Central Basin Platform (Yang and Dorobek, 1995). Finally, to the west, the Midland Basin was separated from the Delaware Basin by the Central Basin Platform (Yang and Dorobek, 1995). The CBP region was crosscut by multiple fault networks running north-south. In the southern portion of the CBP, extensive east-west faulting extends into the current study area near
the Upton County core (Yang and Dorobek, 1995; Wickard, 2016). These extensive networks of faults around the Midland Basin could influence fluid migration in the subsurface and represent a potential control on carbonate diagenesis in the basin (Eichhubl and Boles, 2000).

Figure 1: A) Paleogeographic reconstruction of the Late Pennsylvanian Midcontinent Sea and Greater Permian Basin Seaway approximately 300 Ma. The upwelling of nutrient-rich, oxygen-poor deep water from the Panthalassic Ocean through the basin generated a pycnocline, leading to anoxic bottom waters in both the Midland Basin and the Late Pennsylvanian Midcontinent Sea. (Modified from Blakey, 2013) B) Map showing the core locations from this study and the physiographic features of the Midland Basin during the Late Pennsylvanian (Modified from Ryan, 2016).

The Greater Permian Basin Seaway (GPBS) was the primary seawater connection between the Eastern Tropical Panthalassic Ocean (ETPO) and the Late Pennsylvanian Midcontinent Sea (LPMS) (Algeo and Heckel, 2008; Algeo et al., 2008a). Circulation between the ETPO and the LPMS through the GPBS during this time is thought to have been super-estuarine (Algeo and Heckel, 2008). Super-estuarine circulation occurs where oxygen-poor deep-water upwells onto the shelf separated from the surface layer by a pycnocline. In a proximal setting, the pycnocline results from differences in salinity created
by freshwater inputs, whereas in a distal setting the pycnocline results from differences in temperature as cold, deep-water is upwelled onto the continental shelf (Algeo et al., 2008b).

Circulation through the GPBS and benthic conditions were strongly impacted by the large (60—150m) glacioeustatic sea-level fluctuations (Algeo and Heckel, 2008). Periodic subaerial exposure of the CBP during sea-level lowstands restricted circulation through the basin (Saller et al., 1999; Baldwin, 2016; Ryan, 2016). The upwelling of nutrient-rich, oxygen-deficient waters from the ETPO resulted in suboxic to anoxic conditions on the seafloor in the Midland Basin (Algeo et al., 2008a). The lack of oxygen allowed the zone of sulfate reduction to expand across the basin as evidenced by trace metal and organic carbon enrichment and the presence of framboidal pyrite (Baldwin, 2016; Ryan, 2016).

During the late Pennsylvanian, the Midland Basin was located at approximately 5°N (Algeo et al., 2008a). Due to its position in the tropics and the Ouachita-Marathon Orogeny in the intertropical convergence zone to the south, it was thought to have experienced a monsoonal climate (Ruddiman, 2001; Algeo and Heckel, 2008; Montañez and Poulsen, 2013). The response of the monsoonal climate to glacial-interglacial cycles is likely the primary driver of runoff and sediment delivery to the Midland Basin (Baldwin, 2016; Ryan, 2016).

2.2 The Wolfcamp D Formation

The Wolfcamp D Formation was deposited during Late Pennsylvanian time beginning in the middle Desmoinesian and continuing through the Virgilian (Waite and Reed, 2014). Global sea-level was in a relatively quiescent low stand during the late Desmoinesian to the early Missourian with minor fluctuations. As the climate began to warm and transition from an icehouse to a greenhouse climate in the middle Missourian,
sea-level rose and began to oscillate more frequently and severely (Figure 2). The primary control on offshore carbonate deposition in the Midland Basin during the Late Pennsylvanian was glacioeustatic sea-level change and resulted in regionally heterogeneous deposition (Baldwin, 2016; Ryan, 2016).

The current stratigraphic model is based upon studying cyclothems in each of three cores from the Midland Basin (Figure 1b). Midland Basin cyclothems record carbonate deposition as debris flows and turbidites resulting from rapid transgression and high stand shedding of platform material with black shale deposition occurring during lowstand (McGlue et al., 2015; Baldwin, 2016; Ryan, 2016). This interpretation is consistent with studies in the Midcontinent region where glacioeustatic sea-level fluctuations are the primary control on deposition (Algeo and Heckel, 2008).

Figure 2: Regional stratigraphy of the Midland Basin through the Pennsylvanian and Permian with an interpreted sea-level curve. This study focused on the basal Wolfcamp and captures the climate variability associated with the beginning of a transition from icehouse to greenhouse conditions. Note the major sea-level lowstand associated with the transition from Lower Absaroka 1.3 to Lower Absaroka 1.4. (Modified from Waite and Reed, 2014).
Sediment deposition was similar in the two cores examined in this study. A typical cyclothem begins with a lowstand black mudrock which transitions to carbonate-cemented gray mudrocks during transgression and ends with carbonate debris flow and turbidite deposits during highstand. Though the Midland Basin was likely dysoxic to anoxic during the deposition of the Wolfcamp D Formation, restriction during sea-level lowstands were thought to enhance benthic anoxia and organic matter preservation (McGlue et al., 2015; Baldwin, 2016; Ryan, 2016). A characteristic of this stratigraphic model is the deposition of carbonates as nearly continuous layers occurring only during highstand (Baldwin, 2016; Ryan, 2016). These gravity flow deposits are thought to be conduits for later fluid migration, suggesting they are laterally continuous (Engle et al. 2016, Saller and Stueber, 2018).

Previous work on these cores suggests benthic redox conditions are one of the major controls on the preservation of organic matter and sedimentation in the basin (McGlue et al., 2015; Baldwin, 2016, Ryan, 2016). The presence of strong benthic anoxia would contribute to an expanded sulfate reduction zone, potentially influencing carbonate diagenesis in the sediments near the sediment-water interface (Irwin and Curtis, 1977; Mazzullo, 2000; Algeo and Maynard, 2004). Conversely, during periods of weak benthic anoxia, the sulfate reduction zone would become limited, in most cases limiting the precipitation of authigenic carbonates (Mazzullo, 2000; Algeo and Maynard 2004). However, during periods of sediment starvation, carbonates can precipitate in the relatively narrow sulfate reduction zone until the sediments are fully cemented provided there is sufficient sulfate delivered to the sulfate reduction zone (Mazzullo, 2000).
2.3 Core Description

Samples analyzed in this study were collected from two cores taken in the Wolfcamp D interval of the Midland Basin by Pioneer Natural Resources. The first core, “Upton County”, was taken proximal to the Central Basin Platform near the deep water opening between the CBP and Ozona Arch and the second, “Midland County”, was taken distal to the Central Basin Platform, near the center of the basin (Figure 1b). Previous work by Baldwin, 2016 and Ryan, 2016 on the Upton and Midland County cores respectively defined nine lithofacies based upon bulk geochemical and core characteristics (Table 1): black mudrock-1 (BMR-1), black mudrock-2 (BMR-2), gray mudrock (GMR), grainstone (GNST), wackestone (WKST), packstone (PKST), mixed facies (MIXED), mudstone (MDST), and dolostone (DOL). This study focused on the carbonate dominated facies as well as some gray mudrocks. Overall, the carbonate facies encompassed 21.3 % of the Upton County core and 6.8 % of the Midland County core.

<table>
<thead>
<tr>
<th>Table 1: Geochemical Constraints on Lithofacies Designations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Facies</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>--------</td>
</tr>
<tr>
<td>BMR-1</td>
</tr>
<tr>
<td>BMR-2</td>
</tr>
<tr>
<td>GMR</td>
</tr>
<tr>
<td>GNST</td>
</tr>
<tr>
<td>WKST</td>
</tr>
<tr>
<td>PKST</td>
</tr>
<tr>
<td>Dol/Ms-L</td>
</tr>
<tr>
<td>MDST</td>
</tr>
<tr>
<td>Mixed</td>
</tr>
</tbody>
</table>

Bulk geochemical constraints on lithofacies designations. Values are in average weight percent. (-) indicates no carbonates of the facies observed in the core.
3.0 Methods

3.1 Stable Carbon and Oxygen Isotopes

Stable isotope analyses were performed on 178 samples from the Midland County core and 186 samples from the Upton County core. The samples were collected at 2-inch intervals through all of the carbonate layers in each core to match the intervals sampled by Baldwin (2016) and Ryan (2016) for bulk geochemistry by x-ray fluorescence. Isotope ratios of inorganic carbon ($^{13}$C/$^{12}$C) and oxygen ($^{18}$O/$^{16}$O) were measured from carbonate samples dissolved in supersaturated H$_3$PO$_4$. The $\delta^{13}$C$_{\text{carb}}$ and $\delta^{18}$O$_{\text{carb}}$ were analyzed in a Thermofinnigan GasBench 2 coupled in continuous flow through a ConFlo III to a ThermoFinnigan Delta Plus IRMS at the University of Kentucky Stable Isotope Lab. The results are reported in delta notation relative to the international Vienna Pee Dee Belemnite (VPDB) standard for both $^{18}$O and $^{13}$C. Analytical reproducibility by repeated analyses of internal and international reference standards of known isotopic composition is shown to be ±0.2‰ for carbon and ±0.2‰ for oxygen in the carbonates.

3.2 X-ray Fluorescence Analysis

X-ray fluorescence analysis was conducted at 2-inch intervals for both major and trace element abundances by Baldwin (2016) for the Upton County core and Ryan (2016) for the Midland County core. The trace metal concentrations from Baldwin (2016) and Ryan (2016) were normalized to aluminum and converted to enrichment factors (EF) using the average crustal composition from Taylor, 1964 (Equation 1).

\[
\text{Equation 1: Enrichment Factor (EF)} = \frac{\left(\frac{\text{Trace Element Concentration}}{\text{Aluminum Concentration}}\right)_{\text{Sample}}}{\left(\frac{\text{Trace Element Concentration}}{\text{Aluminum Concentration}}\right)_{\text{Standard}}} 
\]
An EF greater than 1 indicates authigenic enrichment in the sediment, whereas an EF less than 1 indicates depletion (Little et al., 2015). A coefficient of variation (V) was calculated for each trace metal used and aluminum to validate the use of the enrichment factors (Table 2). If the coefficient of variation for aluminum is significantly higher than that of the trace elements, the variability will impact the validity of the normalization (Van der Weijden, 2002).

3.3 Scanning Electron Microscopy

Scanning electron microscopy was conducted on 17 thin sections from the Midland County core and 22 thin sections from the Upton County core. Imaging techniques included secondary electron (SED), backscatter electron (BSE), and cathodoluminescence (CL). Each technique was conducted to examine different stages of carbonate diagenesis present in the sample. SED and BSE imaging produce grayscale images based upon differences in the average atomic number between molecules in the crystal lattice. The secondary electron detector is located at an angle to the sample enabling it to image topography and/or porosity. The backscatter detector is located above the sample allowing it to measure differences in composition more strongly than the SED. The CL detector utilizes the electron beam from the SEM to image the presence of luminescent components in the carbonate lattice. The output of the CL-detector associated with the SEM is a grayscale image where the iron-poor luminescent minerals are light and the ferroan non-luminescent minerals are black.

Secondary and backscatter electron imaging were utilized to select areas of interest for electron microprobe analysis. A preliminary determination of mineralogy was made
through the use of an electron dispersive spectrometer (EDS). The beam current was set to 15KeV with a probe current of 87 nA at a working distance of 10mm.

Backscatter imaging was utilized to image chemical zoning within the carbonate minerals by measuring the density differences between different zones in the carbonates. In this study, this technique allowed for the identification of ferroan rims surrounding a non-ferroan dolomite core and chemical partitioning in the dolomite cements. These sections were then imaged using a cathodoluminescence detector to differentiate between sharp and gradational zoning.

3.4 Electron Probe Microanalysis

3.4.1 Point Analysis

Initial electron probe microanalysis was conducted on each thin section based upon the areas of interest determined from SEM imaging. A 10µm wide, 10nA raster beam with a beam current of 15 kV was utilized to prevent sample destruction by decarbonation from the electron beam. Each point was analyzed for calcium, magnesium, iron, manganese, strontium, silicon, and aluminum. Silicon and aluminum were included to account for overlapping of small grains or the inclusion of fine cracks in the minerals which could impact the results. The results from the point mode analyses were compared to the bulk rock geochemistry data collected by Baldwin (2016) and Ryan (2016) for the Upton County and Midland County cores respectively to validate the results.

3.4.2 Elemental Abundance Mapping

Elemental abundance mapping was conducted on the electron microprobe analyzer to study the partitioning of magnesium and iron in the carbonates. Mapping each selected area was conducted by sweeping a 30 nA, 15kV beam across a selected area of the sample
at a resolution of 512x512 with a dwell time of 10µs. Each selected area was mapped for magnesium, iron, manganese, and strontium.

3.5 X-ray Diffraction

Samples from each thin section interval were sent to KT-GeoServices, Inc. for x-ray diffraction analysis. Each sample was disaggregated in a mortar and pestle and split for whole rock and clay mineral analysis. The x-ray diffraction analyses were performed using a Siemens D500 automated powder diffractometer using a copper x-ray source (40kV, 30mA) and a scintillation x-ray detector. Whole rock samples were analyzed at five to sixty degrees two theta at a scan rate of one degree per minute. Clay samples were analyzed from two to thirty-six degrees two theta at a scan rate of one degree per minute. The semiquantitative determinations of whole-rock mineralogy was done using Jade Software from Mineral data, Inc. using the Whole Pattern Fitting option coupled with Rietveld refinement.

4.0 Results

4.1 Bulk Rock Geochemistry

Each core exhibited significant variability in both inorganic carbon and oxygen isotope values though a similar overall pattern was observed between the localities (Figure 3 a & b). The majority of samples from both cores had a relatively narrow, approximately 4‰, range in $\delta^{13}$C values and a large range up to 10‰ in $\delta^{18}$O values. The majority of the carbonate layers in both cores had both $\delta^{18}$O and $\delta^{13}$C values that increased towards the center of the layer.
Figure 3: A comparison of oxygen and carbon stable isotopes for the Upton County and Midland County cores highlighting the 4‰ VPDB offset in average carbon isotope values between the cores. 

A) A plot of $\delta^{13}$C$_{carb}$ vs $\delta^{18}$O$_{carb}$ for the Upton County core. The dolomite facies cross both the deep-burial diagenesis and late-stage diagenesis zones. The majority of the carbon isotope values from the Upton County Core were between -2 and 2‰ with several non-dolomite layers retaining an early-burial diagenetic signal. 

B) A plot of $\delta^{13}$C$_{carb}$ vs $\delta^{18}$O$_{carb}$ for the Midland County core. The majority of carbon isotope values for the Midland County core were between -6 and -2‰ VPBD with more carbonates retaining the early-burial diagenetic signal. The dolomite layers in this section were more susceptible to late-stage diagenesis with few layers retaining earlier diagenetic signals.

<table>
<thead>
<tr>
<th>Table 2: Coefficients of Variation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Element</strong></td>
</tr>
<tr>
<td>--------</td>
</tr>
<tr>
<td>Al</td>
</tr>
<tr>
<td>Mo</td>
</tr>
<tr>
<td>Cr</td>
</tr>
<tr>
<td>Mn</td>
</tr>
<tr>
<td>Ti</td>
</tr>
</tbody>
</table>

4.1.1 Upton County

The isotopic composition of the Wolfcamp D carbonates in the Upton County core is shown in Figure 3a. Most $\delta^{13}$C$_{carb}$ measurements were between -3 and 2‰ VPDB, though a few exceptions were seen as low as -12.0‰ VPDB. The $\delta^{18}$O$_{carb}$ value of these carbonates
was more variable, ranging between -6.2 and 2.3‰ VPDB with the most negative isotope values at the base and top of the layer and most positive values in the center.

The carbonate layers coincide with peaks in titanium enrichment factor and manganese enrichment factor. The thin bedded carbonates with exceptionally low $\delta^{13}C_{\text{carb}}$ values precede a spike in redox sensitive trace metals (Figure 4). Whereas the isotopic composition is predominantly independent of lithofacies, the dolomite beds are the most limited in their $\delta^{13}C_{\text{carb}}$ range (between -2 and 1‰). The top of each calcium-enriched interval coincides with a sharp decline in strontium and a sharp increase in redox sensitive trace metals. The trace element cyclicity is the most pronounced in the Middle Wolfcamp D where the frequency of cycles increases up section.

4.1.2 Midland County

The isotopic composition of the Wolfcamp D carbonates in the Midland County core are shown in Figure 3b. Most of the $\delta^{13}C_{\text{carb}}$ measurements were between -4.5 and -2.5‰ VPDB, with some values as low as -15.8‰ VPDB. The $\delta^{18}O_{\text{carb}}$ measurements for this core were similar to the Upton County core, ranging from –6.5 to 2.5‰ VPDB. As in the Upton County core, most of the carbonates in the Midland County core have isotope value minima at the cap and base of the layer, with the maxima near the core.

The carbonate beds in the Midland County core are generally thinner than those in the Upton County core and are more enriched in magnesium (Figure 5). As in the Upton County core, the Middle Wolfcamp D in the Midland County core showed the most cyclicity in the trace metal enrichment factors. These cycles in the Midland County core are bounded by calcium-enriched layers with magnesium enrichment at the core of many cycles.
Figure 4: Upton County Geochemical Indicators with important carbonate intervals highlighted in blue. A) $\delta^{18}O_{\text{carb}}$ (‰, VPDB), B) $\delta^{13}C_{\text{carb}}$ (‰, VPDB), C) Calcium (weight %), D) Magnesium (weight %), E) Iron (weight %), F) Sulfur (weight %), G) Strontium (weight %), H) Barium (weight %), I) Aluminum (weight %), J) Silicon (weight %), K) Molybdenum (enrichment factor), L) Chromium (enrichment factor) M) Manganese (enrichment factor), N)Titanium (enrichment factor), O) Porosity (%), P) Permeability (mD).

Periodic enrichment in molybdenum and chromium increase in frequency moving up section. These enrichments follow carbonate deposition and manganese enrichment. Oxygen and carbon stable isotope values show core to edge decreases consistent with deep-burial diagenetic processes impacting the edges more than the core.
Figure 5: Midland County Geochemical Indicators with important carbonate intervals highlighted in blue. A) $\delta^{18}O_{\text{carb}}$ (‰, VPDB), B) $\delta^{13}C_{\text{carb}}$ (‰, VPDB), C) Calcium (weight %), D) Magnesium (weight %), E) Iron (weight %), F) Sulfur (weight %), G) Strontium (weight %), H) Barium (weight %), I) Aluminum (weight %), J) Silicon (weight %), K) Molybdenum (enrichment factor), L) Chromium (enrichment factor) M) Manganese (enrichment factor), N) Titanium (enrichment factor), O) Porosity (%), P) Permeability (mD). Peri-odic enrichment and the subsequent gradual decline in redox sensitive trace metals follows carbonate deposition. Evidence for period-ie oxygenation of the bottom waters is shown by concurrent increases in manganese enrichment factor, Ti/Al values, calcium, and a decline in redox sensitive trace metals. Most carbonate intervals show core-to-edge decreases in oxygen and carbon isotope values consistent with deep-burial diagenetic effects. A single interval in the Lower Wolfcamp D is nearly uniform throughout, showing the impact of late-stage diagenesis.
4.2 Scanning Electron Microscopy

4.2.1 Upton County

Backscatter electron (BSE) imaging revealed significant compositional sector zoning in the subhedral to euhedral dolomite grains in the matrix of the Upton County core carbonates. The proportion of sector zoned dolomites observed in the Upton County samples corresponds to the amount of intergranular pore space available. The coarse-grained carbonates from the Upper Wolfcamp D interval show more sector zoned dolomite than the fine grained dolomites from the Lower Wolfcamp D interval (Figure 6). The carbonates with early calcite or quartz cementation show dolomite growth with less pronounced zonation. Dolomite grain size ranged from less than 4 to 100 microns with the grain size limited primarily by the available space for crystal growth.

Framboidal and replacement pyrite was frequently observed in the carbonate layers, increasing in abundance concurrent with the presence of non-ferroan dolomite. Individual pyrite framboids were limited to less than 10 microns, though clusters of pyrite framboids were up as large as 500 microns. Occasionally framboidal pyrite was observed occurring within and surrounding barite and sphalerite. Several detrital minerals such as apatite and zircon were noted in the fine-grained carbonate layers as well. The EDS on the SEM identified chemical compositional differences in the dolomite zones as alternating ferroan and non-ferroan bands.

4.2.2 Midland County

BSE imaging of the Midland County core samples identified the presence of a ferroan calcite (Figure 7) and two dolomite facies: non-ferroan dolomite and non-ferroan dolomites with ferroan rims (Figure 8). The ferroan-rimmed dolomites occur with abundant
Figure 6: Carbonate sample from the Upton County core showing the dolomite cements with compositional sector zoning. A) Photomicrograph of the sample showing the intercrystalline porosity in the dolomite cement. B) Backscatter SEM image showing the compositional sector zoning in the dolomite cements as well as the extent of diagenesis in the larger allochems. C) Electron Microprobe compositional map showing the distribution of magnesium in the dolomite cements. D) Electron microprobe compositional map showing the distribution of iron in the dolomite cements. The boundaries between the ferroan and non-ferroan layers are not sharp contacts, suggesting a more gradual transition from iron-rich to iron-poor conditions during the precipitation of the dolomites.
Figure 7: Carbonate sample from the Midland County core showing early burial cementation. A) Photomicrograph showing the preservation of calcitic fossil fragments and ferroan calcite cement. B) Backscatter SEM image showing replacement pyrite in the non-ferroan calcite cement. C) Electron microprobe compositional map showing the enrichment of magnesium in the calcite cement. D) Electron microprobe compositional map showing the enrichment of iron in the calcitic fossil fragments.
Figure 8: Carbonate sample from the Midland County core showing a ferroan dolomite rim on a non-ferroan dolomite core and void filling strontium-rich barite. A) Photomicrograph of the sample showing the barite and dolomite microspar with frambooidal pyrite. B) Backscatter SEM image showing the zoning of the dolomite and the interaction between the dolomite and barite. C) Electron microprobe compositional map showing the distribution of magnesium in the dolomites. D) Electron microprobe compositional map showing the distribution of iron in the dolomites. This sample is representative of the majority of dolomite intervals in the Midland County core and those in the Lower Wolfcamp D interval in the Upton County core.
framboidal pyrite and have a wide distribution in grain size from less than 5 to 100 microns. The size of the rim and core are also variable, with the rim size inversely proportionate to the abundance of pyrite nearby. The pyrite framboids in the Midland County core are less than 10 microns in diameter, though as in the Upton County core, the framboid clusters are as large as 500 microns.

As in the Upton County core, there are occurrences of barite and celestine filling the void space in fossils and pore space. Where the sulfate precipitation occurred within the void space in a fossil there was no occurrence of pyrite or sphalerite with the sulfate minerals. The pore filling sulfates were commonly partially replaced by sulfide minerals.

4.3 Electron Probe Microanalysis

4.3.1 Upton County

The analysis of 844 points from the Upton County core thin sections on the electron probe micro-analyzer resulted in a bimodal distribution between calcite and dolomite samples (Figure 9). Samples were designated calcite or dolomite based upon if their magnesium concentration was greater or less than 6 wt % magnesium. The calcites had calcium concentrations between 33 and 43 wt %, and magnesium and iron concentrations between 0 and 3 wt %. The dolomite samples had calcium concentrations between 21 and 27 wt %, magnesium concentrations between 6 and 13 wt % and iron concentrations between 0 and 10 wt %. Both the calcite and dolomite samples had manganese concentrations between 0 and 0.6 wt %. The majority of the dolomite samples were below 0.2 wt % strontium, with a few strontium enriched samples analyzed near barite or celestine ranging from 0.2 to 1 wt %.
Figure 9: Microprobe data from the Upton County core. A) calcium vs. magnesium. Most samples fit into either the dolomite or calcite groups with the exception of five points which have high iron concentrations but are still below the 6 weight percent magnesium designation for dolomite. B) magnesium vs. iron. The wide range in iron related to magnesium is likely tied to the influence of clay diagenesis. C) iron + manganese vs. strontium. The samples from the Upton County core follow the expected L-shaped distribution associated with progressive diagenesis, however, the strontium concentrations in the dolomite is much higher than anticipated. The elevated strontium is likely tied to an aragonite precursor and diagenesis following the migration brine fluids through the system. D) manganese vs. strontium to calcium. The samples from the Upton County core show the expected inverse relationship between manganese and strontium to calcium ratio. This results from the replacement of strontium with manganese in the carbonate lattice during diagenesis.
4.3.2 Midland County

The analysis of 656 points from the Midland County core thin sections on the electron probe micro-analyzer resulted in a similar bimodal distribution between calcite and dolomite, though one thin section collected at 90.5 ft. fits the mixing line between iron-poor calcites and iron-rich dolomites (Figure 10). The calcites in the Midland County core have calcium concentrations between 35 and 43 wt % and magnesium and iron concentrations between 0 and 3 wt %. As in the Upton County core, both the calcite and dolomite samples have similar manganese concentrations, ranging between 0 and 0.5 wt %. The strontium concentrations in the Midland County core range from 0 to 0.9 wt % in both the calcite and dolomite samples, though most samples had concentrations below 0.3 wt % (Figure 10).

4.3.3 Elemental Abundance Mapping

The samples from the Upton County core showed iron enrichment in the calcite cements and ferroan/non-ferroan banding in the dolomite grains. The samples from the Midland County core further highlighted the ferroan rims surrounding non-ferroan dolomite cores without the compositional sector zoning seen in the Upton County dolomites.

4.4 X-ray Diffraction

4.4.1 Upton County

X-ray diffraction (XRD) analysis of the major carbonate facies from the Upton County core show variations in the predominant carbonate mineral between the layers. The dolomites in this core are primarily ferroan, ranging from 2.4 % at 157 feet below top of core (ft btc) to 82.47 at 267.3 ft btc. Non-ferroan dolomite occurs in two layers, 208.87 and
Figure 10: Microprobe data from the Midland County core: A) calcium vs. magnesium. Most samples plot in either the dolomite or calcite groups as defined in the text. A sample from 90.5 ft bfc represents an approximate mixing line between the two groups. B) magnesium vs. iron. There is a large range in iron concentrations within the dolomite group thought to be associated with the influence of clay diagenesis on dolomitization. C) iron + manganese versus strontium. This sample set deviates from the expected L-shaped distribution related to the loss of strontium during diagenesis. This likely results from having an aragonite precursor and the influence of the brine fluid on diagenesis. D) manganese vs. strontium to calcium. This plot also does not follow the expected inverse relationship from progressing carbonate diagenesis. It is thought to be the result of an aragonite precursor and the influence of the brine fluid on diagenesis.
Figure 11: X-ray diffraction results from the Upton County core compared to the stable isotope results. The predominant carbonate mineral changes in each interval of the Wolfcamp D Formation beginning with ferroan dolomite in the Lower Wolfcamp D then transitioning to ferroan calcite in the Middle Wolfcamp D, finally ending with calcite in the Upper Wolfcamp D. The intervals with more dolomite coincide with more positive oxygen and carbon isotopes, suggesting brine fluid interactions were responsible for the final stage of dolomitization. The samples with higher percentages of ferroan calcite, particularly in the Middle Wolfcamp D, coincide with the low $\delta^{13}$C$_{\text{carb}}$ values associated with early burial diagenesis in the BSR zone.
<table>
<thead>
<tr>
<th>Depth</th>
<th>Calcite</th>
<th>Ferroan</th>
<th>Dolomite</th>
<th>Ferroan</th>
<th>Dolomite</th>
<th>Quartz</th>
<th>Pyrite</th>
<th>MnO(_{eq})</th>
<th>TiO(_{eq})</th>
<th>Calcium</th>
<th>Magnesium</th>
<th>Manganese</th>
<th>Iron</th>
<th>Strontium</th>
</tr>
</thead>
<tbody>
<tr>
<td>119.83</td>
<td>6.00</td>
<td>0.00</td>
<td>0.00</td>
<td>2.50</td>
<td>16.60</td>
<td>3.70</td>
<td>13.46</td>
<td>0.35</td>
<td>0.62</td>
<td>39.42</td>
<td>0.34</td>
<td>0.04</td>
<td>0.04</td>
<td>0.50</td>
</tr>
<tr>
<td>121.67</td>
<td>39.30</td>
<td>0.00</td>
<td>0.00</td>
<td>30.70</td>
<td>19.80</td>
<td>0.70</td>
<td>0.00</td>
<td>1.83</td>
<td>1.24</td>
<td>39.14</td>
<td>23.87</td>
<td>0.44</td>
<td>9.70</td>
<td>0.04</td>
</tr>
<tr>
<td>128.67</td>
<td>50.20</td>
<td>0.00</td>
<td>0.00</td>
<td>2.30</td>
<td>29.40</td>
<td>1.50</td>
<td>5.96</td>
<td>0.29</td>
<td>0.67</td>
<td>39.45</td>
<td>0.47</td>
<td>0.05</td>
<td>0.50</td>
<td>0.61</td>
</tr>
<tr>
<td>141.17</td>
<td>49.00</td>
<td>0.00</td>
<td>0.00</td>
<td>4.40</td>
<td>32.40</td>
<td>1.60</td>
<td>0.00</td>
<td>29.11</td>
<td>5.75</td>
<td>-</td>
<td>22.46</td>
<td>-</td>
<td>7.49</td>
<td>-</td>
</tr>
<tr>
<td>157.00</td>
<td>80.10</td>
<td>0.00</td>
<td>0.00</td>
<td>2.40</td>
<td>11.10</td>
<td>1.10</td>
<td>0.00</td>
<td>7.83</td>
<td>4.05</td>
<td>-</td>
<td>24.54</td>
<td>-</td>
<td>11.63</td>
<td>-</td>
</tr>
<tr>
<td>162.17</td>
<td>22.50</td>
<td>0.00</td>
<td>0.00</td>
<td>50.40</td>
<td>14.20</td>
<td>0.80</td>
<td>0.00</td>
<td>1.26</td>
<td>0.93</td>
<td>-</td>
<td>24.39</td>
<td>-</td>
<td>9.99</td>
<td>-</td>
</tr>
<tr>
<td>167.00</td>
<td>28.30</td>
<td>0.00</td>
<td>0.00</td>
<td>54.00</td>
<td>11.20</td>
<td>0.50</td>
<td>5.13</td>
<td>1.86</td>
<td>2.11</td>
<td>38.06</td>
<td>24.92</td>
<td>1.24</td>
<td>9.16</td>
<td>0.05</td>
</tr>
<tr>
<td>168.50</td>
<td>27.90</td>
<td>0.00</td>
<td>0.00</td>
<td>57.50</td>
<td>8.40</td>
<td>0.60</td>
<td>0.00</td>
<td>1.54</td>
<td>1.65</td>
<td>39.51</td>
<td>24.46</td>
<td>0.28</td>
<td>9.71</td>
<td>0.04</td>
</tr>
<tr>
<td>176.84</td>
<td>0.00</td>
<td>28.00</td>
<td>0.00</td>
<td>5.00</td>
<td>32.00</td>
<td>1.20</td>
<td>0.00</td>
<td>1.03</td>
<td>1.15</td>
<td>39.55</td>
<td>0.60</td>
<td>-</td>
<td>0.04</td>
<td>-</td>
</tr>
<tr>
<td>187.50</td>
<td>0.00</td>
<td>83.00</td>
<td>0.00</td>
<td>7.60</td>
<td>3.90</td>
<td>1.00</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>38.72</td>
<td>24.59</td>
<td>0.44</td>
<td>9.53</td>
<td>0.11</td>
</tr>
<tr>
<td>188.67</td>
<td>0.00</td>
<td>25.50</td>
<td>0.00</td>
<td>46.80</td>
<td>14.40</td>
<td>2.40</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>38.57</td>
<td>23.67</td>
<td>0.66</td>
<td>10.70</td>
<td>0.09</td>
</tr>
<tr>
<td>194.84</td>
<td>0.00</td>
<td>64.30</td>
<td>0.00</td>
<td>21.90</td>
<td>8.60</td>
<td>0.60</td>
<td>0.00</td>
<td>5.06</td>
<td>1.70</td>
<td>37.44</td>
<td>23.81</td>
<td>0.72</td>
<td>9.59</td>
<td>0.12</td>
</tr>
<tr>
<td>208.84</td>
<td>0.00</td>
<td>92.20</td>
<td>1.10</td>
<td>0.00</td>
<td>5.20</td>
<td>0.40</td>
<td>0.00</td>
<td>1.78</td>
<td>1.91</td>
<td>38.44</td>
<td>-</td>
<td>1.25</td>
<td>-</td>
<td>0.10</td>
</tr>
<tr>
<td>211.83</td>
<td>0.00</td>
<td>59.20</td>
<td>1.70</td>
<td>0.00</td>
<td>30.50</td>
<td>3.80</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>39.11</td>
<td>-</td>
<td>0.94</td>
<td>-</td>
<td>0.12</td>
</tr>
<tr>
<td>262.00</td>
<td>4.50</td>
<td>0.00</td>
<td>0.00</td>
<td>60.70</td>
<td>17.30</td>
<td>0.70</td>
<td>0.00</td>
<td>1.49</td>
<td>0.59</td>
<td>39.57</td>
<td>24.17</td>
<td>0.30</td>
<td>9.51</td>
<td>0.05</td>
</tr>
<tr>
<td>265.00</td>
<td>43.10</td>
<td>0.00</td>
<td>0.00</td>
<td>11.70</td>
<td>33.70</td>
<td>2.10</td>
<td>0.00</td>
<td>2.87</td>
<td>2.15</td>
<td>38.75</td>
<td>23.97</td>
<td>0.37</td>
<td>9.63</td>
<td>0.08</td>
</tr>
<tr>
<td>267.34</td>
<td>4.50</td>
<td>0.00</td>
<td>0.00</td>
<td>82.70</td>
<td>6.80</td>
<td>0.50</td>
<td>0.00</td>
<td>23.06</td>
<td>4.05</td>
<td>4.05</td>
<td>1.39</td>
<td>-</td>
<td>23.97</td>
<td>-</td>
</tr>
<tr>
<td>309.84</td>
<td>12.00</td>
<td>0.00</td>
<td>0.00</td>
<td>71.40</td>
<td>10.30</td>
<td>0.50</td>
<td>0.00</td>
<td>2.35</td>
<td>1.30</td>
<td>39.63</td>
<td>24.69</td>
<td>0.25</td>
<td>10.61</td>
<td>0.05</td>
</tr>
<tr>
<td>322.17</td>
<td>47.20</td>
<td>0.00</td>
<td>0.00</td>
<td>5.50</td>
<td>37.50</td>
<td>1.10</td>
<td>0.00</td>
<td>8.14</td>
<td>4.69</td>
<td>38.30</td>
<td>23.36</td>
<td>0.35</td>
<td>8.36</td>
<td>0.04</td>
</tr>
<tr>
<td>342.34</td>
<td>35.90</td>
<td>0.00</td>
<td>0.00</td>
<td>30.50</td>
<td>26.50</td>
<td>0.90</td>
<td>0.00</td>
<td>8.38</td>
<td>1.50</td>
<td>1.38</td>
<td>39.02</td>
<td>23.18</td>
<td>0.34</td>
<td>9.45</td>
</tr>
</tbody>
</table>

* No Data

* No Al in sample for enrichment factor calculation
Figure 12: X-ray diffraction results from the Midland County core compared to the stable isotope results. The predominant carbonate mineral in a majority of the carbonate layers in the Midland County core was ferroan dolomite. This likely resulted from the influence of clay diagenesis on deep burial diagenesis. As in the Upton County core, the dolomites coincide with intervals of higher carbon and oxygen values. Ferroan calcite coincides with intervals of negative carbon isotope values associated with formation in the BSR zone.
### Table 4: Midland County X-Ray Diffraction and Electron Microprobe Data

<table>
<thead>
<tr>
<th>Depth</th>
<th>Calcite</th>
<th>Ferroan</th>
<th>Dolomite</th>
<th>Ferroan</th>
<th>Dolomite</th>
<th>Quartz</th>
<th>Pyrite</th>
<th>Mo&lt;sub&gt;tr&lt;/sub&gt;</th>
<th>Mn&lt;sub&gt;tr&lt;/sub&gt;</th>
<th>Ti&lt;sub&gt;tr&lt;/sub&gt;</th>
<th>Calcium</th>
<th>Magnesium</th>
<th>Manganese</th>
<th>Iron</th>
<th>Strontium</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>61.665</td>
<td>7.6</td>
<td>0</td>
<td>0</td>
<td>44</td>
<td>16.1</td>
<td>1.9</td>
<td>0.00</td>
<td>1.72</td>
<td>0.84</td>
<td>-</td>
<td>10.6725</td>
<td>-</td>
<td>23.87951</td>
<td>-</td>
<td>0.15308</td>
</tr>
<tr>
<td>62.165</td>
<td>2.9</td>
<td>0</td>
<td>0</td>
<td>85.2</td>
<td>3.3</td>
<td>0.6</td>
<td>0.00</td>
<td>2.71</td>
<td>0.51</td>
<td>-</td>
<td>8.1589</td>
<td>-</td>
<td>23.8462</td>
<td>-</td>
<td>0.137781</td>
</tr>
<tr>
<td>63.465</td>
<td>3.2</td>
<td>0</td>
<td>0</td>
<td>82.4</td>
<td>3.2</td>
<td>0.7</td>
<td>0.00</td>
<td>5.75</td>
<td>0.28</td>
<td>-</td>
<td>10.7394</td>
<td>-</td>
<td>23.8862</td>
<td>-</td>
<td>0.137781</td>
</tr>
<tr>
<td>90.499</td>
<td>3.7</td>
<td>0</td>
<td>0</td>
<td>50.6</td>
<td>3.1</td>
<td>0.9</td>
<td>9.40</td>
<td>0.39</td>
<td>0.67</td>
<td>36.67802</td>
<td>4.819567</td>
<td>1.605993</td>
<td>27.2933</td>
<td>0.146589</td>
<td></td>
</tr>
<tr>
<td>101</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>6.9</td>
<td>27.8</td>
<td>2.3</td>
<td>0.00</td>
<td>3.56</td>
<td>1.73</td>
<td>38.05541</td>
<td>0.736369</td>
<td>-</td>
<td>0.092332</td>
<td>-</td>
<td>0.734936</td>
</tr>
<tr>
<td>118.332</td>
<td>4.9</td>
<td>0</td>
<td>0</td>
<td>63.3</td>
<td>13.2</td>
<td>1</td>
<td>0.00</td>
<td>2.29</td>
<td>0.62</td>
<td>-</td>
<td>23.8795</td>
<td>-</td>
<td>23.8895</td>
<td>-</td>
<td>0.203056</td>
</tr>
<tr>
<td>118.833</td>
<td>3.5</td>
<td>0</td>
<td>0</td>
<td>77.9</td>
<td>6.4</td>
<td>0.7</td>
<td>0.00</td>
<td>6.29</td>
<td>1.16</td>
<td>40.5022</td>
<td>9.24073</td>
<td>0.00725</td>
<td>0.22183</td>
<td>0.0777</td>
<td></td>
</tr>
<tr>
<td>119.165</td>
<td>4.2</td>
<td>0</td>
<td>0</td>
<td>80.9</td>
<td>6.2</td>
<td>0.5</td>
<td>0.00</td>
<td>6.74</td>
<td>1.10</td>
<td>-</td>
<td>23.8895</td>
<td>-</td>
<td>23.8795</td>
<td>-</td>
<td>0.138203</td>
</tr>
<tr>
<td>131.332</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>74.8</td>
<td>4.6</td>
<td>0.9</td>
<td>0.00</td>
<td>3.13</td>
<td>1.30</td>
<td>37.1342</td>
<td>0.965645</td>
<td>-</td>
<td>0.07299</td>
<td>-</td>
<td>1.15204</td>
</tr>
<tr>
<td>138</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>7</td>
<td>15.7</td>
<td>1.5</td>
<td>0.00</td>
<td>22.54</td>
<td>2.22</td>
<td>38.25764</td>
<td>-</td>
<td>0.78281</td>
<td>-</td>
<td>0.23299</td>
<td></td>
</tr>
<tr>
<td>147</td>
<td>4.7</td>
<td>0</td>
<td>0</td>
<td>65.3</td>
<td>16.6</td>
<td>0.8</td>
<td>0.00</td>
<td>2.61</td>
<td>0.94</td>
<td>39.3575</td>
<td>10.05716</td>
<td>0.6448</td>
<td>24.8316</td>
<td>0.2005</td>
<td></td>
</tr>
<tr>
<td>165</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>4.6</td>
<td>35.8</td>
<td>0.6</td>
<td>0.00</td>
<td>6.25</td>
<td>1.98</td>
<td>39.54751</td>
<td>-</td>
<td>0.699414</td>
<td>-</td>
<td>0.11086</td>
<td></td>
</tr>
<tr>
<td>166.666</td>
<td>3.8</td>
<td>0</td>
<td>0</td>
<td>81.8</td>
<td>8.8</td>
<td>0.5</td>
<td>0.28</td>
<td>0.21</td>
<td>0.93</td>
<td>-</td>
<td>10.2265</td>
<td>-</td>
<td>23.1638</td>
<td>-</td>
<td>0.07299</td>
</tr>
<tr>
<td>168.165</td>
<td>4.6</td>
<td>0</td>
<td>0</td>
<td>80</td>
<td>8</td>
<td>0.6</td>
<td>82.01</td>
<td>2.17</td>
<td>5.65</td>
<td>9.444758</td>
<td>-</td>
<td>23.6417</td>
<td>-</td>
<td>0.1382</td>
<td></td>
</tr>
<tr>
<td>184.165</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>60.1</td>
<td>9.9</td>
<td>16.8</td>
<td>1.2</td>
<td>0.00</td>
<td>1.55</td>
<td>0.73</td>
<td>38.7342</td>
<td>-</td>
<td>0.06435</td>
<td>-</td>
<td>0.504374</td>
</tr>
<tr>
<td>222.666</td>
<td>5.5</td>
<td>0</td>
<td>0</td>
<td>50.5</td>
<td>15.2</td>
<td>1.4</td>
<td>1.75</td>
<td>1.28</td>
<td>0.73</td>
<td>33.56005</td>
<td>9.548407</td>
<td>2.6324</td>
<td>23.81657</td>
<td>0.06555</td>
<td></td>
</tr>
<tr>
<td>224.499</td>
<td>6.4</td>
<td>0</td>
<td>0</td>
<td>34.5</td>
<td>20.4</td>
<td>1.6</td>
<td>4.35</td>
<td>0.77</td>
<td>0.74</td>
<td>35.8561</td>
<td>9.588752</td>
<td>2.0488</td>
<td>23.3594</td>
<td>0.045</td>
<td></td>
</tr>
<tr>
<td>246.332</td>
<td>8.9</td>
<td>0</td>
<td>0</td>
<td>74.7</td>
<td>8</td>
<td>0.8</td>
<td>0.00</td>
<td>4.35</td>
<td>1.23</td>
<td>37.9257</td>
<td>10.05347</td>
<td>0.7793</td>
<td>24.3574</td>
<td>0.044578</td>
<td></td>
</tr>
<tr>
<td>262.165</td>
<td>94.4</td>
<td>0</td>
<td>0</td>
<td>2.4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>38.84231</td>
<td>10.62373</td>
<td>1.192477</td>
<td>24.2746</td>
<td>0.02561</td>
<td></td>
</tr>
<tr>
<td>264.065</td>
<td>14.8</td>
<td>0</td>
<td>0</td>
<td>77.3</td>
<td>4.6</td>
<td>0.4</td>
<td>0.00</td>
<td>19.63</td>
<td>6.20</td>
<td>35.6655</td>
<td>10.8983</td>
<td>3.9395</td>
<td>25.64335</td>
<td>0.04735</td>
<td></td>
</tr>
</tbody>
</table>

* No Al in sample for enrichment factor calculation
211.87 ft btc, though it is a minor component at 1.1 and 1.7 % respectively. The majority of the calcite in the Upton County core is non-ferroan, observed in 16 out of 19 samples through the Wolfcamp D ranging in bulk composition from 4.5 to 80.1 wt %. Ferroan calcite was restricted to a series of six samples collected through the upper Middle Wolfcamp D into the first carbonate layer in the Upper Wolfcamp D with bulk compositions ranging from 92.2 wt %. Pyrite was observed in all 19 samples from the Upton County core from the Wolfcamp D ranging from 0.4 to 3.8 %. K-feldspar and plagioclase were observed in a majority of the carbonate layers as well, with bulk compositions ranging from 0 to 1.8 % and 0.6 to 7.9 % respectively.

4.4.2 Midland County

XRD analysis of the carbonate facies from the Midland County core show less variation in carbonate mineralogy than the Upton County core. Ferroan dolomite or ferroan calcite represent the predominant carbonate mineral in every carbonate layer except one. Ferroan dolomite was present in all 18 Wolfcamp D samples, with ferroan dolomite bulk composition ranging from 4.6 to 85.2 % in each sample studied. Ferroan calcite was present in 6 out of the 18 Wolfcamp D samples ranging from 49.7 to 74.8 % of the bulk composition of each studied sample. The ferroan calcite in the Midland County core is limited to the Middle Wolfcamp D and the first carbonate layer in the Upper Wolfcamp D. Pyrite is present in the Wolfcamp D carbonates from the Midland County core ranging from 0.4 to 2.3 % of the bulk sample composition. K-feldspar was observed in 18 out of 19 carbonate samples, with a bulk sample composition ranging from 0.4 to 1.8 %. Plagioclase was observed in 18 out of 19 carbonate samples, representing 0.6 to 7.9 % of the bulk sample composition.
5.0 Discussion

5.1 Carbonate Deposition in the Midland Basin

Offshore carbonate deposition in the Midland Basin occurred primarily through debris flows and turbidity currents during rapid sea-level transgressions and as a result of high stand shedding of carbonate platform materials (McGlue et al., 2015; Baldwin, 2016; Ryan, 2016). The presence of calcitic fossils such as brachiopods and ostracods in the fine-grained dolomite matrix suggests that the original carbonate mud in the system was predominantly aragonite. Concurrent increases in detrital influx (titanium enrichment factor) and benthic oxygen (manganese enrichment factor) indicators provide evidence for these flows providing stochastic pulses of oxygen to the benthic environment (Figures 4 and 5) (Sageman et al., 2003; Little et al., 2015). These pulses are followed by increases in redox sensitive trace metals as the oxygen in the system is consumed and there is a rapid return to benthic anoxia.

The pairing of the initial benthic oxygenation, followed by increased anoxia resulting from carbonate deposition in the Midland Basin, suggests the system was sensitive to sea-level driven perturbations (Figures 4 and 5). Preservation of the initial cementation signal in both cores appears to be tied to a combination of a limited BSR zone, low sedimentation rate, and a thin carbonate interval. These conditions are likely tied to basinwide events occurring primarily in the Middle Wolfcamp D interval during relatively short periods of sea-level rise.

5.2 Carbonate Diagenetic Processes

Building upon previous work in the Midland Basin, this study identified six possible mechanisms for carbonate diagenesis and dolomitization: meteoric (Saller et al.,
1999), microbi ally mediated, dolomitization associated with clay diagenesis and thermocatalytic decarboxylation, brine interactions (Engle et al., 2016; Saller and Stueber, 2018), diagenesis associated with thermochemical sulfate reduction, and hydrothermal alteration.

5.2.1 Meteoric Carbonate Diagenesis

Meteoric carbonate diagenesis occurs when the carbonates are exposed to precipitation. Exposure to precipitation can generate porosity through meteoric waters interacting with the carbonates dissolving and reprecipitating carbonate. This process progressively lowers the $\delta^{18}O_{\text{carb}}$ and $\delta^{13}C_{\text{carb}}$ values following an inverted J pattern (Swart, 2015). The inverted J isotopic pattern associated with meteoric diagenesis begins with a decline in $\delta^{18}O_{\text{carb}}$ values as the carbonates dissolve and precipitate in equilibrium with meteoric waters with more negative $\delta^{18}O_{\text{carb}}$ values (Swart, 2015). The downward trend in $\delta^{18}O_{\text{carb}}$ is followed by a negative trend in $\delta^{13}C_{\text{carb}}$ values as the oxidation of organic matter releases isotopically light carbon into the system (Swart, 2015). As the carbonates are exposed to meteoric water, their $\delta^{18}O_{\text{carb}}$ values trend towards an equilibrium value with the local groundwater.

Meteoric alteration has been observed on the Central Basin Platform in the Midland Basin. There, carbonates demonstrate increasing porosity and the characteristic inverted J isotopic pattern, consistent with prolonged periods of subaerial exposure and meteoric diagenesis (Saller et al., 1999). These isotopic trends are absent in the carbonates deposited offshore at the Upton County and Midland County core locations considered in this study. Samples from the Midland and Upton County cores record decreasing $\delta^{18}O_{\text{carb}}$ values with increasing $\delta^{13}C_{\text{carb}}$ values (Figure 3), the opposite of expected results in a
meteoric diagenesis influenced system. In addition to a lack of geochemical evidence, there was no evidence from petrographic analysis for meteoric diagenesis such as pendent or meniscus cements.

5.2.2 Microbially Mediated Diagenesis

Transitioning from subaerial exposure to the marine setting, early burial diagenesis occurs through the influence of microbes and changing redox chemistry. Microbially mediated carbonate diagenesis occurs when bacteria in the sediment consume organic matter in their metabolic processes. This occurs in two settings, namely the sulfate reduction zone and the methanogenic zone (Irwin and Curtis, 1977). The presence of several intervals in each core with isotopically light carbon values, as low as -15.8‰ VPDB (Figure 3) suggests the initial conversion of fine-grain carbonate material to calcite spar likely occurred in the sulfate reduction zone (Mazzullo, 2000). The presence of well-preserved originally low-Mg calcitic fossils and fossil fragments indicates the surrounding carbonate muds were originally aragonite (Sibley, 1982). This initial cementation would have likely limited the effect of deep-burial diagenetic processes by closing pores and reducing permeability, particularly in the case of early burial dolomites (Murray, 1960; Irwin, 1980). Many of these layers were deposited and subsequently cemented during periods of sediment starvation under dysoxic conditions. These intervals are typically restricted to a single bed within a carbonate unit or a very thin interval no more than four inches thick (Figures 4 and 5). These thin-bedded carbonates coincide with moderate molybdenum enrichment and minor peaks in manganese, demonstrating a shift from anoxic to suboxic conditions associated with oxygenation from the gravity flow deposits (Sageman et al., 2003; Algeo and Maynard, 2004).
The transition from cementation and diagenesis in the BSR zone to diagenesis in the methanogenic zone is thought to begin once at least 90% of the dissolved sulfate in the porewater has been consumed (Mazzullo, 2000). The CO$_2$ released during methanogenesis is isotopically heavy, resulting in the formation of isotopically heavy carbonates with $\delta^{13}$C$_{carb}$ values up to 15‰ VPDB. Carbonates in the Upton County core likely underwent limited methanogenesis, evidenced by $\delta^{13}$C$_{carb}$ values between 0 and 2‰. The carbonates in the Midland County core likely did not experience diagenesis associated with methanogenesis as the highest $\delta^{13}$C$_{carb}$ value was around -1‰ VPDB.

5.2.3 Deep-Burial Processes

The transition from microbially mediated diagenesis to abiotic processes begins once the sediments reach a burial depth where the temperature reaches 50 to 60°C, about 2km in the Midland Basin (Ruppel et al., 2005). The abiotic processes influencing carbonate diagenesis in the Wolfcamp D Formation are the conversion of smectite to illite and the thermal breakdown of organic matter. As the conversion of smectite to illite releases magnesium and iron into the porewater, it is expected that the carbonates formed as a result of this process would be magnesium and iron rich. Coinciding with the release of cations from clay diagenesis, the thermal breakdown of organic matter releases CO$_2$ into the porewater resulting in the increase in bicarbonate in the system. This bicarbonate is isotopically light as it is derived from organic matter, though the $\delta^{13}$C$_{carb}$ values are not as low as carbonates formed through microbial mediation, with values between -5 and -10‰ VPDB. Carbonates in both the Upton and Midland County cores indicate the influence of both clay diagenesis and the thermal breakdown of organic matter. The majority of carbonates in the Upton County core have negative $\delta^{13}$C$_{carb}$ values between 0 and -3‰.
VPDB (Figure 3a) and exhibit zonation related to differences in iron and magnesium content (Figure 6b). The carbonates in the Midland County core demonstrate stronger influence of these abiotic processes than the Upton County core, with approximately a -4‰ offset between the average $\delta^{13}C_{\text{carb}}$ values for each core (Figure 3). The dolomites in the Midland County core also have two layers instead of the several zones present in the Upton County core. These layers are separated into a non-ferroan core, typical of microbial mediation in the BSR zone, and a ferroan rim resulting from the influx of iron following clay diagenesis separated by a sharp contact (Figure 8).

5.2.4 Brine-Induced Dolomitization

Following these abiotic processes, Late Permian age brines migrated into the carbonates in the Wolfcamp D Formation and remain there today (Engle et al., 2016; Saller and Stueber, 2018). These fluids typically have elevated $\delta^{18}O_{\text{carb}}$ values relative to Late Pennsylvanian seawater associated with the preferential evaporation of $^{16}O$ in an evaporitic basin resulting in carbonates with elevated $\delta^{18}O_{\text{carb}}$ values (Swart, 2015). The majority of dolomite samples in both cores have $\delta^{18}O_{\text{carb}}$ values which range from 0 to 2.5‰ VPDB. These values suggest enrichment in $^{18}O$ resulting from evaporation as the accepted seawater $\delta^{18}O_{\text{carb}}$ value for the Late Pennsylvanian is near -2‰ VPDB (Jaffrès et al., 2007). Additionally, these fluids are not potassium depleted as would be expected following clay diagenesis (Engle et al., 2016; Saller and Stueber, 2018). Formation waters collected from wells in the Wolfcamp D interval by Saller and Stueber (2018) are deficient in Mg, indicating Mg loss to dolomitization by carbonate-rich brines. Brine migration is likely a widespread mechanism for carbonate diagenesis in the Midland Basin in evidence.
from the presence of celestine and barite (Figure 8) as well as elevated $\delta^{18}O_{\text{carb}}$ values in center of the carbonate intervals (Figures 4 and 5).

Once the sulfate-rich brine migrated into the system, TSR likely began as the dissolved sulfate in the system reacted with organic matter. As TSR is limited by the availability of reactive sulfate in the system and direct contact between sulfate and organic matter, it likely occurred only in limited capacity in the carbonates of the Midland Basin (Machel, 2001). This process was limited to near the void-filling barites and celestine as it slowly dissolved. This is seen in the precipitation of pyrite and high-Sr dolomites within and surrounding the barite and celestine (Figure 8). Dissolution of these sulfate minerals was likely slow, as barite and celestine are typically resistant to dissolution (Paytan et al., 1993; Dove and Cank, 1995). The slow dissolution of the sulfates likely limited the influence of TSR associated diagenesis to those carbonate minerals close to the sulfates. This is observed as the dolomites near the sulfates are enriched in strontium relative to dolomites in the same interval that did not occur near the sulfates (Figure 9).

### 5.2.5 Hydrothermal Dolomitization

The final mechanism for carbonate diagenesis considered in this study is hydrothermal diagenesis. This process occurs when a hydrothermal fluid is channeled through a conduit, precipitating dolomite in the process (Machel, 2004). Dolomitization through this process is limited to regions adjacent to the conduit and is rarely regionally extensive (Al-Awadi et al., 2009). Hydrothermal dolomitization can be more widespread if the fluids are forced through the system as a result of nearby tectonics. An example of this is found in the Appalachian Basin (Montañez, 1994). In the Appalachian Basin, dolomitizing fluids are thought to have traveled nearly 50 km through extensive fault
networks generated by the Alleghenian Orogeny (Montañez, 1994). While the fault maps of the Midland Basin are incomplete, the cores utilized for this study are well within 50 km of the major fault networks bounding the CBP (Yang and Dorobek, 1995; Baldwin 2016; Ryan, 2016). As a result, we cannot exclude this mechanism based on regional structure alone.

Hydrothermal carbonates are characterized by the presence of saddle dolomite and negative $\delta^{18}\text{O}_{\text{carb}}$ values, as low as -15‰ VPDB associated with fluids at temperatures higher than the geothermal gradient (Montañez, 1994; Davies and Smith, 2006; Al-Awadi et al., 2009). The presence of faults near both the Upton County and Midland County cores make this a possibility (Baldwin, 2016; Ryan, 2016), though the positive $\delta^{18}\text{O}_{\text{carb}}$ values for the majority of dolomite samples suggest other mechanisms are more likely. Additionally, no saddle dolomites were observed in thin section or SEM analysis.

5.3 Carbonate Deposition and Diagenesis in the Upton County Core

Primary carbonate deposition proximal to the CBP occurred through gravity-flow deposits as both turbidity currents and debris flows. Baldwin (2016) identified the presence of scour surfaces in the gray mudrock and at the basal contact of many carbonate layers, though they were rare in the wackestone and packstone facies. The differences in evidence for erosion was attributed to the difference between turbulent flow depositing turbidites and laminar flow depositing debrites with poorly sorted, matrix supported grains. The disparity in grain sizes between turbidites and debrites resulted in differences in the degree of diagenesis, particularly the extent of dolomitization, in the region proximal to the CBP.

Isotopic and bulk-geochemical evidence from the carbonate layers in the Upton County core suggest organogenic diagenesis associated with BSR and methanogenesis was
likely the initial driver of carbonate cementation. Thin-bedded carbonates preserved the strongest signal of the initial BSR zone cementation: $\delta^{13}\text{C}_\text{carb}$ values as low as -12‰ VPDB with $\delta^{18}\text{O}_\text{carb}$ values around -3 to -1‰ VPDB, consistent with estimates of Late Pennsylvanian seawater oxygen isotope values (Jaffrés et al., 2007). These thin bedded carbonates are tied to brief periods of benthic oxygenation within otherwise anoxic conditions.

An example organogenic diagenesis is at approximately 233 ft btc, where manganese enrichment factor values increase to over 400 then decrease to near 1 within the span of 1.2 ft while maintaining molybdenum enrichment factors between 20 and 40. Other thin bedded carbonates occur during prolonged periods of low sedimentation rates in dysoxic environments. One example at approximately 208 ft btc where manganese enrichment factor range from 0.5 to 1.8 and molybdenum enrichment factor range from 0 to 8 over a 4 inch interval. The slight increase in titanium enrichment factor from 0.7 to 1.9 over the same carbonate layer near 208 ft btc suggests the oxygenation resulted from a gravity flow during a time of very low sedimentation. The low sedimentation rates would allow more complete cementation in the relatively thin carbonate intervals making them more resistant to later diagenetic processes. The thick carbonate layers are typically more coarse-grained and exhibit more positive $\delta^{13}\text{C}_\text{carb}$ and more negative $\delta^{18}\text{O}_\text{carb}$ values consistent with deep-burial processes.

Frequent pulses of oxygenation from gravity flow deposits into the region proximal to the CBP would have limited the benthic anoxia and the extent of the BSR zone. Once the sediments were buried below the thermal limit for BSR (approximately 80°C Machel, 2001) or the existing sulfate in the pore waters was consumed, methanogenesis surpassed
BSR as the dominant organogenic process (Irwin and Curtis, 1977; Mazzullo, 2000; Machel, 2004). Maximum $\delta^{13}C_{\text{carb}}$ values approaching 2‰ for the thick carbonate intervals suggest a weak to moderate influence of methanogenesis in the carbonate diagenesis in the proximal setting. Decreasing $\delta^{18}O_{\text{carb}}$ values associated with the elevated $\delta^{13}C_{\text{carb}}$ values indicate diagenesis associated with increasing depth. These values tend to occur near the center of each carbonate interval, suggesting later diagenetic overprinting was inhibited by the transport of fluids through the carbonate intervals.

Deep-burial processes in the Upton county core resulted in little dolomitization. Instead, they altered the existing carbonates to ferroan calcites. The extent to which the carbonates were altered was likely controlled by the ability of deep-burial fluids to migrate or diffuse from the mudrocks where they formed to the carbonates. This resulted in gradational isotope values across the bed, with a maximum at the center of the bed, for most carbonate layers greater than 6 inches thick. Where present, the dolomites exhibit compositional sector zoning associated with changing porewater chemistry during the development of a dolomite cement (Figure 6). The dolomites in the Upton County core are typically limited to the middle of each carbonate bedset. These intervals exhibited high (-1 to 2‰ VPDB) $\delta^{18}O_{\text{carb}}$ values consistent with carbonates precipitated from an evaporitic brine rather than a deep-burial process at elevated temperatures.

Following the initial deep-burial processes, evaporated Permian age seawater migrated through the carbonates in the Midland Basin (Engle et al., 2016; Saller and Stueber, 2018). The brines flowing through the carbonates deposited strontium-rich barite and celestine in pore spaces and as void fill in fossils such as brachiopods and foraminifera (Figure 6). The brines flowing through the system were supersaturated with respect to
carbonate and precipitated calcite and dolomite with elevated $\delta^{18}O_{\text{carb}}$ values relative to deep-burial carbonates between -2 and 2.5‰ VPDB (Figure 3a). Once the brines migrated through the system, the barite and celestine slowly dissolved, providing dissolved sulfate for TSR. The chemical stability of barite and celestine likely limited the effect of TSR on diagenesis in the Upton County core carbonates by limiting the amount of dissolved sulfate in the system, though carbonates surrounding the late-stage sulfate minerals show enrichment in strontium up to 9800ppm (Figure 9).

### 5.4 Carbonate Deposition and Diagenesis in the Midland County Core

Carbonate deposition distal to the CBP was primarily fine-grained carbonates transported to the Midland County core locality through turbidity currents. The predominant carbonate-rich facies, gray mudrock and grainstone, both have pronounced erosional features such as scours along the basal contact and normal grading as well as fragmented body fossils (Ryan, 2016). Whereas the carbonates in the Upton County core had a wide range of grain sizes, the transport distance into the center of the basin restricted carbonate deposition to fine-grain material. The Midland County core is located on a local bedrock high (Ryan, 2016), which may have also prevented larger grained material from reaching the core site. The central location of the Midland County core likely enabled input from more sediment sources than the Upton County site, evidenced by the increased number of carbonate layers in the Midland County core, particularly in the Middle Wolfcamp D interval.

Evidence from higher redox-sensitive trace-metal enrichment factors and $\delta^{13}C_{\text{carb}}$ values as low as -15.8‰ suggest more pronounced periods of benthic anoxia in the Midland County core than at the Upton County site, leading to stronger BSR-mediated carbonate
diagenesis. As in the Upton County site, the majority of the significantly negative values occur in the thin-bedded carbonates with $\delta^{18}O_{\text{carb}}$ values consistent with estimates for Late Pennsylvanian seawater (Jaffrés et al., 2007). These carbonates likely formed during periods of sediment starvation with in a limited zone of sulfate reduction, suggested by evidence of low detrital input, the presence of pyritized and micrite-filled burrows, and elevated benthic oxygenation. Framboidal or replacement pyrite was observed in every carbonate layer, constituting up to 2% of the bulk composition (Figure 12). These pyrites were nearly all larger than 10mm, indicating formation in dysoxic to anoxic, but not euxinic, conditions (Wilkin et al., 1996). The BSR mediated carbonates provided the nucleation point for deep-burial and late-stage diagenetic dolomites (Figure 8). Maximum $\delta^{13}C_{\text{carb}}$ values near 0‰ VPDB for the Wolfcamp D carbonates in the Midland county core indicate a limited role of methanogenic bacteria mediated carbonate diagenesis.

The higher mudrock:carbonate ratio in the Midland County core led to a stronger influence of deep-burial diagenetic processes than observed in the Upton County core. The thinner beds decreased the amount of diagenetic fluid diffusion necessary for complete dolomitization. The magnesium, iron, and bicarbonate enriched pore waters precipitated the ferroan dolomite rims observed through BSE imaging. These ferroan dolomites were the predominant carbonate mineral throughout most of the Midland County core, indicating the prevalence of this mechanism during diagenesis. The growth of deep-burial diagenesis appears to hinge on the precursor BSR mediated non-ferroan dolomites as every ferroan dolomite was formed in a concentric rim around a non-ferroan core (Figure 8). The ferroan dolomites precipitated during this process have the nearly 1:1 ratio of magnesium to iron.
expected from pore waters altered through clay diagenesis (Boles and Franks, 1979) (Figure 12).

Further diagenesis of the Midland County core carbonates was similar to that observed in the Upton County core. The migration of brines from evaporated Permian seawater deposited void filling barite and celestine in several layers of the core. As in the Upton County core, the highest $\delta^{18}$O$_{\text{carb}}$ values in the center of the bed indicates preferential flow through the higher porosity, higher permeability carbonates.

5.5 Diagenetic Sequence in the Midland Basin

The mechanisms and extent of diagenesis in the Midland Basin appears to be tied to the frequency of gravity flows into the basin. Where carbonate deposition is limited, resulting in beds less than 6 inches thick, the carbonates appear to preserve the early burial diagenetic signal. This is identified with $\delta^{18}$O$_{\text{carb}}$ values approximately equal to the assumed seawater between -3 and -1‰ VPDB. Additionally, $\delta^{13}$C$_{\text{carb}}$ values are below -8‰ VPDB, suggesting cementation in the BSR zone. Thicker carbonate intervals in both the Upton County and Midland County cores appear to be more susceptible to local diagenetic overprinting of the initial BSR signal by carbonate diagenesis in the methanogenic zone, deep-burial, and late-stage diagenetic events (Figures 4 and 5).

Nearly all of the carbonates in the basin greater than 6 inches thick exhibit an increase in $\delta^{18}$O$_{\text{carb}}$ and $\delta^{13}$C$_{\text{carb}}$ values towards the center of the bed, coinciding with the majority of dolomites in both cores. Large increases in manganese enrichment factors associated with thick carbonate beds suggest periodic benthic oxygenation associated with carbonate deposition (Figures 4 and 5). The oxygenation of the bottom waters would have
reduced the impact of sulfate reduction in the basin, inhibiting BSR induced carbonate cementation (Machel, 2001, 2004; Algeo and Maynard, 2004).

Deep-burial processes begin with clay diagenesis and thermocatalytic decarboxylation in the mudrocks surrounding the carbonate layers (Irwin and Curtis, 1977; McHargue and Price, 1982). The effectiveness of these processes is controlled by the communication of diagenetic fluids through the carbonate layers (McHargue and Price, 1982; Mazzullo, 2000). As a result, most carbonates that underwent deep-burial diagenesis show the most evidence near the contact between the mudrocks and carbonates. The influence of clay diagenesis and thermocatalytic decarboxylation appears to decrease towards the center of the carbonate intervals, seen by the increase in $\delta^{18}O_{\text{carb}}$ and $\delta^{13}C_{\text{carb}}$ values towards the center of the layer.

Through the use of boron concentrations and stable isotopes in the formation water from the Wolfcamp D Formation, Engle (2016) proposed that brine migration through the carbonates occurred after clay diagenesis. This was suggested by a lack of potassium or boron loss in the formation waters. Potassium loss would be expected had the current formation waters been present during clay diagenesis as potassium from the porewater is used in the smectite to illite conversion (Boles and Franks, 1979). Recovered formation waters from the Wolfcamp D interval also have low concentrations of Mg$^{2+}$, suggesting the precipitation of dolomite resulting from the brine migration (Saller and Stueber, 2018). Whereas they show similar trends, the extent of dolomitization and differences in geochemistry between the two localities inhibits any characterization of the deep-burial diagenesis as occurring during discrete, basinwide events.
5.6 Changing Carbonate Deposition and Diagenesis over time

The deposition and evolution of carbonates in the Midland Basin was strongly tied to glacioeustatic sea-level changes throughout the Late Pennsylvanian. By controlling circulation and carbonate deposition, these sea-level changes also played a role in benthic redox conditions and carbonate diagenesis both proximal and distal to the Central Basin platform. The carbonates in the Upton County core generally coarsen up section, resulting in differences in the predominant carbonate mineral. By comparison, the Midland County core is generally fine-grained carbonate throughout the Wolfcamp D Formation resulting in ferroan dolomite being the predominant carbonate mineral in most of the layers. Carbonate diagenesis likely evolved through several processes initiated by early-burial organogenesis in the BSR zone, followed by deep-burial processes related to clay diagenesis and the breakdown of organic matter, and ended following dolomitization induced by interactions with a Late Permian aged brine which flowed through following deep-burial.

5.6.1 Lower Wolfcamp D

Carbonate deposition in the Lower Wolfcamp D led to conditions favorable for dolomitization, recording the most dolomite intervals in both the Upton County and Midland County cores. The carbonates in both cores were fine-grained with frambooidal pyrite. The deposition of carbonates in the basin in both cores is associated with decreases in the enrichment factors for molybdenum and chromium and increases in the enrichment factors of titanium and manganese indicating the oxygenation of the benthic environment. These oxygenation events are followed by a steady rise in molybdenum and chromium enrichment factors associated with a return to benthic anoxia (Figures 4 and 5). Extended periods of limited to no carbonate deposition were observed in both cores and are thought
to be tied to periods of relatively little sea-level change during late Desmoinesian time (Waite and Reed, 2014) (Figure 2).

The dolomites in the Upton County exhibit compositional-sector zoning associated with fluctuations in porewater chemistry during precipitation (Figure 6). These dolomites typically exhibit increases in both $\delta^{18}O_{\text{carb}}$ and $\delta^{13}C_{\text{carb}}$ values toward the center of the layer. A pause in carbonate sedimentation is seen through most of the middle of the Lower Wolfcamp D, recorded by prolonged periods of black-mudrock deposition. The lowermost and uppermost carbonate intervals in the Lower Wolfcamp D interval have a larger grain size than those of the other layers, and as such were more resistant to dolomitization. These layers have calcite allochems surrounded by dolomite cement. The dolomites in the Midland County Core are all fine-grained dolomite cements with frambooidal and replacement pyrite. These dolomites have non-ferroan dolomite cores surrounded by a ferroan-dolomite rim associated with initial precipitation in the BSR zone followed by later overgrowths of dolomite during deep-burial diagenesis. The thickest dolomite interval in the Midland County core (220.5 to 224.3 ft b.c.) recorded nearly constant $\delta^{18}O_{\text{carb}}$ and $\delta^{13}C_{\text{carb}}$ values throughout the section, with a sharp negative $\delta^{18}O_{\text{carb}}$ excursion at the cap. The isotope values ranging from -1.6 to -1.1‰ VPDB for $\delta^{18}O_{\text{carb}}$ and -3.7 to -2.3‰ VPDB for $\delta^{13}C_{\text{carb}}$ are consistent with values expected from diagenesis during brine migration. The remaining dolomite layers exhibit increases in $\delta^{18}O_{\text{carb}}$ and $\delta^{13}C_{\text{carb}}$ values towards the center of the layer expected from diagenetic carbonates in this system. These dolomites are associated with periodic benthic oxygenation seen by decreases in molybdenum and chromium enrichment factors and increases in manganese and titanium enrichment factors.
Carbonate deposition ceases in the Midland County core near the middle of the Lower Wolfcamp D as gray and black mudrock becomes dominant.

5.6.2 Middle Wolfcamp D

A divergence in carbonate deposition and diagenesis is present in the Middle Wolfcamp D interval between the two cores. The Upton County core maintained the number of carbonate deposition events, with an overall decline in carbonate volume (Figure 4). The Midland County core recorded an increase in the frequency of carbonate deposition, with 12 separate carbonate beds and an overall increase in carbonate volume (Figure 5). Petrographic, mineralogical, and isotopic similarities between the thin-bedded carbonates in this interval indicate basinwide sediment starvation and there is a potential to use them as a regional correlation marker, though more work is needed to confirm the trends recorded in the carbonate intervals and identify similar trends in the mudrocks.

Carbonate deposition was absent throughout much of the Middle Wolfcamp D interval in the Upton County core locality. The majority of carbonates were deposited in the uppermost section of the Middle Wolfcamp D, though a few relatively thin, less-than-a-foot thick, layers were deposited midway through the interval. These carbonates were nearly all ferroan calcite and dolomite spar with some subhedral to euhedral and framboidal pyrite. These layers coincided with increases in benthic oxygenation and detrital indicators. Increases in barium and strontium in the carbonate intervals suggest brine-induced diagenesis occurring in the section; however, very few dolomite grains with the compositional sector zoning associated with late-stage cement growth observed in the samples from this interval.
Carbonate deposition in the Midland County core increased significantly in the Middle Wolfcamp D with a mix of ferroan-calcite and dolomite-dominated layers. Each of these layers was associated with an increase in benthic oxygenation, recorded as a decrease in molybdenum enrichment factor and an increase in manganese and titanium enrichment factors (Figure 5). The ferroan-calcite layers were typically thin (less than 6 inches thick) and exhibited a basal scour. These calcites typically have very negative $\delta^{13}C_{\text{carb}}$ values and $\delta^{18}O_{\text{carb}}$ values near -2‰ VPDB, similar to values near Late Pennsylvanian sea water (Jaffrés et al., 2007) indicating early burial diagenesis in the BSR zone. Through early cementation, they were able to retain the early-burial diagenesis signal as later diagenetic fluids were unable to pass through and alter the layers. The beds larger than six inches were nearly all dolomitized and exhibited the typical basal and top to center increase in $\delta^{18}O_{\text{carb}}$ and $\delta^{13}C_{\text{carb}}$ values seen in carbonate layers undergoing multiple rounds of diagenesis. The top and basal contacts of these layers recorded diagenesis related to deep-burial processes, with negative $\delta^{18}O_{\text{carb}}$ and $\delta^{13}C_{\text{carb}}$ values, whereas the center of each layer recorded late-stage diagenesis with more positive $\delta^{18}O_{\text{carb}}$ and $\delta^{13}C_{\text{carb}}$ values associated with brine migration.

5.6.3 Upper Wolfcamp D

The Upper Wolfcamp D saw an increase in carbonate deposition in the Upton County core and a slight decline in the Midland County core. Similar to the Lower and Middle Wolfcamp D intervals, the beds larger than 6 inches thick showed an increase in both $\delta^{18}O_{\text{carb}}$ and $\delta^{13}C_{\text{carb}}$ values towards the center of the layer indicating late-stage dolomitization. The extent of late-stage diagenesis was likely controlled by the amount of intergranular porosity resulting from poor sorting of debris flow deposits. As in the
previous intervals, dolomitization was more complete in the Midland County core than in the Upton County core and was more prevalent in beds greater than six inches thick.

The carbonates deposited in the Upton County core were highly variable, consisting of debrites and fine-grained turbidites. The two main carbonate intervals consisted of a series of thinner, approximately four to five ft thick carbonates separated by mudrocks before a thicker, 10- to 20-ft thick carbonate section was deposited. These intervals were separated by a thick package of black mudrock with a single thin-bedded carbonate at approximately 145 ft btc. These bedsets exhibit the expected increase in $\delta^{18}$O$_{\text{carb}}$ and $\delta^{13}$C$_{\text{carb}}$ values towards the center of the layer associated with multiple phases of diagenesis. Dolomitization in the Upper Wolfcamp D was limited to the center of the first carbonate bedset from 165 to 170 ft btc. This interval recorded sharp, intense fluctuations in benthic anoxia, with molybdenum-enrichment factors ranging from 0 to 250 and manganese-enrichment factors between 0.8 and 1.5. The dolomites in this section coincide with manganese-enrichment factors below 1, indicating periods of benthic anoxia.

The carbonates in the Midland County core were similar to those deposited in the Middle Wolfcamp D, the majority were less than a foot thick and nearly all of the thin-bedded non-dolomitized intervals recorded $\delta^{18}$O$_{\text{carb}}$ and $\delta^{13}$C$_{\text{carb}}$ values consistent with diagenesis and cementation in the sulfate reduction zone. The thick-bedded dolomite in this interval from 60.5 to 64.1 ft btc recorded an increase in $\delta^{18}$O$_{\text{carb}}$ and $\delta^{13}$C$_{\text{carb}}$ values towards the center of each layer associated with deep-burial diagenesis and late-stage brine migration.
6 Conclusion

The results of this study suggest caution is needed when attempting to assign stratigraphic significance to dolomite layers in the Wolfcamp D Formation. The geochemical and petrographic data suggest the carbonates do not always record the original or, in most cases, early-burial geochemical indicators of discrete, syndepositional, basinwide events. Instead, they record a stepwise progression of diagenetic processes. Diagenesis typically begins with organogenesis in the BSR zone, followed by clay diagenesis and the thermal breakdown of organic matter, and finally dolomitization through interactions with an evaporitic brine.

The impact of these processes is controlled by the proximity of the study section to the carbonate source and the benthic redox conditions of the basin. The proximity to the carbonate source controls the thickness and average grain-size of the carbonate intervals, with thicker, coarser-grained carbonates deposited more proximal to the source. Benthic redox conditions controls the influence of early-burial diagenesis on the carbonates and the preservation of the early-burial signal. Many of the thin bedded carbonate intervals in both the Upton and Midland County cores suggest the preservation of an early-burial diagenesis signal. The carbon isotopic measurements are consistent with calcite precipitation in a narrow BSR zone during periods of sediment starvation in a dysoxic setting. These thin beds are completely cemented through this process, preventing further diagenesis. Thicker carbonates likely spent insufficient time in the BSR zone too cement completely, leaving them susceptible to later diagenesis. Deep-burial diagenesis is controlled by the transmission of diagenetic fluids from the surrounding mudrocks into the carbonates. As a result, the isotopic evidence for deep-burial processes such as clay diagenesis was recorded
near the top and bottom of each bed where the carbonates are more likely to interact with these fluids. This is evidenced by increasing carbon and oxygen isotope values towards the center of each carbonate bed as the influence of deep-burial fluids declines following cementation eliminating pathways for fluid flow.

Early-burial and deep-burial processes predominantly precipitated calcite or ferroan calcite cements, whereas the predominant dolomitization mechanism in the Wolfcamp D Formation was likely the interaction with a Late Permian—Early Triassic brine. These carbonates have elevated $\delta^{18}O_{\text{carb}}$ values relative to seawater (Figure 3), are enriched in strontium and barium (Figures 4 and 5), and have high-strontium barite void fills (Figure 8). These brines migrated through the carbonates following deep-burial processes within the carbonate intervals.

The complexity of this system highlights the need for a complete characterization of diagenesis when evaluating carbonate depositional systems, particularly in mud-rich settings. Within the Wolfcamp D, future work is needed to isolate the geochemical signature of multiple diagenetic phases. High-precision tools, such as laser ablation or micromill sampling, can target specific grains or cements to geochemically differentiate multiple phases of diagenesis. This enhanced resolution can isolate which diagenetic processes predominate within each bed, allowing for basin-wide diagenetic predictions.

Overall, the integration of geochemical and petrographic indicators, using the data generated from this study as a guide, provide a framework for understanding carbonate diagenesis in muddy depositional environments. Stable inorganic carbon and oxygen isotopes can be utilized to identify the timing and relative influence of chemical processes such as bacterial sulfate reduction or clay diagenesis. Supplementing the isotope data with
SEM imaging, bulk geochemistry, and high resolution electron probe micro-analysis provides multiple lines of evidence for identifying the processes and their relative impact on carbonate diagenesis. Utilizing these datasets across multiple locations within a basin helps evaluate the spatial differences in diagenetic processes and how the carbonates fit into a stratigraphic framework.

Further work on these cores is required to fully integrate the stable isotope geochemistry and carbonate diagenesis model into the stratigraphic model. The use of sulfur isotopes in pyrite and carbonate associated sulfur could verify the presence or absence of sulfate reduction in the carbonate intervals with anomalously negative $\delta^{13}C_{\text{carb}}$ values. In addition to sulfur isotopes, high resolution sampling of the thin sections using a micromill to sample the dolomite cement and calcite grains would help differentiate the various diagenetic processes influencing the carbonates in the system. Finally, expanding the inorganic carbon and oxygen isotope analyses to the surrounding mudrocks will help place the results of this study in a stratigraphic context.
References


Vita

Alex Jacob Reis

Education
B.S. Geology with Honors (2015)
University of Cincinnati

Experience
Graduate Research Assistant
Stable Isotope Lab
Department of Earth and Environmental Sciences
University of Kentucky, 40506

Graduate Teaching Assistant
Department of Earth and Environmental Sciences
University of Kentucky, 40506

Hydrogeologist I
AECOM Technical Services, INC
Cincinnati, OH 45202

Laboratory Manager
Fisk Laboratory of Sedimentology
University of Cincinnati, 45221