

ISOTOPE CHEMOSTRATIGRAPHY OF THE LOWER
MISSISSIPPIAN ST. JOE GROUP IN SOUTHWESTERN
MISSOURI AND NORTHWESTERN ARKANSAS

By

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Submitted to the Faculty of the
Graduate College of the
Oklahoma State University
in partial fulfillment of
the requirements for
the Degree of
MASTER OF SCIENCE
July 2021

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ACKNOWLEDGEMENTS

I first must acknowledge Dr. Jim Puckette for his guidance and patience as my advisor. His encouragement to take the next step, wherever it leads, has been a necessary and driving force in both my undergraduate and graduate journeys. I am proud to have worked with him and consider myself fortunate to call him my friend.

My other committee members, Dr. Michael Grammer and Dr. Mary Hileman, for their time and contributions in getting my thesis to final form. Additional thanks to Dr. Natascha Riedinger, Dr. Mohamed Abdel-Salam, and Dr. Anna Cruse for their assistance.

The late Dr. Darwin Boardman, always had a laugh and a great story to tell, and his professional and personal mentorship ended far too soon.

I would like to acknowledge all the friends I made at Oklahoma State, but two in particular stand out. I met Joey Dineen when he was an undergraduate student sent to help me collect rock samples at Roaring River; his assistance, and enthusiasm to hit rocks with a sledgehammer, were greatly appreciated. Chase Watkins encouraged me more than he knows, his friendly conversations that always seemed to start with “so how’s your thesis going?” kept me focused.

Lastly, there is no way I would be where I am without the love and support of my family. My parents, Dr. Douglas and Mrs. Cynthia Stevenson, from vacations as a child with my dad pointing out all the geology he knew, to helping with my outcrop work, they pushed me to succeed and be the best scientist I can be and most importantly they provided the solid foundation for my life. My sister, Jan, is someone I can always count on when the chips are down. I hope I have made them proud.

Name: BETH ELOISE STEVENSON

Date of Degree: JULY 2021

Title of Study: ISOTOPE CHEMOSTRATIGRAPHY OF THE LOWER MISSISSIPPIAN ST. JOE GROUP IN SOUTHWESTERN MISSOURI AND NORTHWESTERN ARKANSAS

Major Field: GEOLOGY

Abstract: The petrography and isotope geochemistry of the St. Joe Group in southwestern Missouri and northwestern Arkansas were analyzed to determine (1) if the positive excursion in the global isotopic curve for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ during the Tournaisian (Kinderhookian) is evident in the St. Joe Group, and (2) if isotopic evidence can be used to interpret the completeness of the section and the nature of contacts within the group. The results indicate that the robust positive excursion for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in the Tournaisian is not evident in profiles of the examined sections. A weak positive excursion is evident in $\delta^{13}\text{C}$ profiles for the thicker sections and $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ are not covariant. In addition, there is no evidence to support significant intervals of missing section. The St. Joe Group is determined to be conformable in the study area and there is no evidence that diagenetic changes induced by subaerial exposure overprinted the original isotope values. $\delta^{18}\text{O}$ values were likely modified by meteoric water and diagenetic fluids. The weak to absent positive excursion in $\delta^{13}\text{C}$ values in Tournaisian (Kinderhookian) samples is problematic but could be the result of meteoric processes and/or isolation of the area from the Tournaisian sea. Integrated geochemistry, lithology and existing conodont biostratigraphy support the contention that the respective contacts between the Compton Limestone, Northview Formation and Pierson Formation are relatively conformable in the outcrops in this study area and these formations have isotopic profiles that at best, weakly correlate to regional and global Kinderhookian isotope profiles.

TABLE OF CONTENTS

Chapter	Page
I. INTRODUCTION.....	1
Introduction	1
Stable Isotope Geochemistry Overview	6
Objectives.....	10
II. GEOLOGIC SETTING.....	11
Research Area.....	11
Stratigraphy	14
Bachelor Sandstone.....	15
Compton Limestone.....	16
Northview Formation.....	17
Pierson Limestone	18
Reeds Spring Formation.....	19
Biostratigraphy	20
III. METHODOLOGY	21
Outcrop Sample Collection	21
Acetate Peel Thin Section Preparation	22
Stable Isotope Sample Preparation	22
IV. RESULTS	24
General Observations.....	24
Petrography	24
Geochemical Results.....	25

Chapter	Page
V. DISCUSSION	34
Depositional Environment	34
Chronostratigraphic Correlation	35
VI. CONCLUSION and FUTURE WORK	41
REFERENCES	43
APPENDIX	50

LIST OF FIGURES

Figure	Page
1. Figure 1 Stratigraphic nomenclature of the western Ozark outcrop section including the St. Joe Group,).	3
2. Mississippian outcrop pattern showing outcrop sections examined and sampled in this study.	4
3. Paleogeographic map showing Burlington shelf margin in early Mississippian time.	5
4. An early Mississippian paleogeographical map of southern Laurentia	6
5. Coastal onlap curve for the Mississippian Subperiod.....	9
6. Thickness of the St. Joe Group.	12
7. The Bachelor Sandstone at the Roaring River State Park section.....	16
8. The base of the Compton Limestone at Roaring River	17
9. The Northview and base of the Pierson formations at Roaring River.	18
10. The Pierson formation at Roaring River	19
11. The upper Pierson and basal Reeds Spring formations	20
12. Select thin section photographs from the formations of the St. Joe Group at Roaring River.	255
13. A cross-plot of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ from all formations and outcrops.....	27
14. Stratigraphic column for Roaring River with conodont zonation.	28
15. Stratigraphic column for Omaha East outcrop with isotope data.	29
16. Stratigraphic column for AR-74 outcrop with isotope data.	30
17. Stratigraphic column for Harriet East outcrop with isotope data.	311
18. Stratigraphic column for Walls Ferry South outcrop with isotope data.	32
19. Stratigraphic column for Glenn Creek outcrop with isotope data.	33
20. Current study data plotted with select environments and diagenetic changes that affect isotopic signatures	39
21. Correlation of the St. Joe Group compared to previous studies.	40

CHAPTER I

INTRODUCTION

The Mississippian (Tournaisian/Kinderhookian) St. Joe Group (Figure 1) is comprised of mostly limestone, with lesser amounts of cherty limestone and thin argillaceous siliciclastic units where it outcrops in southwestern Missouri, northeastern Oklahoma and northwestern Arkansas (Figure 2). In northeastern Oklahoma, the three formations that make up the group, Compton, Northview and Pierson, have distinct weathering characteristics and generate a recognizable weathering profile. The Compton Limestone forms ledges, whereas the overlying Northview Formation is more argillaceous and weathers to form recesses. The Pierson Formation is a relatively cleaner crinoidal limestone that forms prominent ledges. These compositional characteristics are retained, but are less prominent in Arkansas and Missouri and can be recognized in the shallow subsurface in Oklahoma (Godwin, 2017). Attempts to correlate the outcrop section to the subsurface Mississippian section in the major oil and gas plays in central Oklahoma is tenuous at best due to the lack of biostratigraphic control (Stukey, 2020). Because of its economic importance as an oil- and gas-producing reservoir in the subsurface of Oklahoma, a source of aggregate stone and as an aquifer, the Mississippian section has been studied for more than 100 years including (Girty, 1915; Anglin, 1966; Lane and DeKeyser, 1980; Shelby, 1986; Mazzullo et al., 2013; Morris et al., 2013; and others). Most of these earlier studies were descriptive with only minor attention to depositional setting and processes. Within the last few decades, research emerged describing depositional settings and environments (Kammer and Matchen, 2008; Dineen 2015, and others), biostratigraphy (Thompson, 1967; Thompson and Fellows, 1970; Boardman et al., 2013; Godwin 2017), sequence stratigraphy (Childress and

Grammer, 2015); and chemostratigraphy (Koch et al., 2014; Dupont, 2019; Sessions et al., 2019). This study focuses on the isotopic profiles of the Mississippian St. Joe Group in six outcrops: one in southwestern Missouri and five in northwestern Arkansas (Figure 2) with thorough biostratigraphic control (Thompson, 1967; Thompson and Fellows, 1970). This data will be compared to the published Mississippian (secular) isotopic curve (Saltzman, 2002; Batt et al., 2007), and regional curves (Frank and Lohmann, 1995; Sessions et al., 2019). Biostratigraphic control is essential to interpreting stratigraphy as the Mississippian carbonates, including the St. Joe Group, were deposited in a shelf to slope setting including the Burlington Shelf (Lane and DeKeyser, 1980) (Figure 3), whose southern margin is interpreted as a shallow carbonate ramp (Boardman and Thompson, 2010). Consequently, as a result of facies changes along the slope of the ramp, the system is laterally complex, a property that resulted in the generation of multiple interpretations of its depositional setting. More recent studies of the Mississippian by Childress (2015); Miller (2015); Jaeckel (2016); and Hunt (2017) have refined the Lane and DeKeyser (1980) carbonate shelf to propose that Mississippian carbonate deposition occurred on a distally steepened ramp in a shallow epeiric sea that covered the Midcontinent during the Early Mississippian (Figure 4).

The position of the six studied outcrops in a shelf margin/ramp setting should favor section preservation and their suitability for retaining the geochemical changes in the Mississippian sea with minimal overprint by carbon cycling processes associated with subaerial exposure and high rates of evaporation (Huck et al., 2017). However, the impact of sea level fluctuations in a shallow epeiric sea cannot be ignored. Localized thinning of the Compton

Formation in Oklahoma near the community of Tahlequah (Thompson and Fellows, 1970) can be attributed to erosion following a drop in base level associated with the Northview Formation, and could be subaerial or subaqueous. Childress and Grammer (2015) proposed that

the Northview Formation near Jane, Missouri represents a marine lowstand and contains evidence of subaerial exposure.

System	Subsystem	Global Stages	N. American Stages	Group	Formation	
Carboniferous	Mississippian	Visean	Osagean	Boone Group	Reeds Spring	
				St. Joe Group	Pierson	
		Northview				
		Compton				
		Tournaisian	Kinderhookian			Bachelor
						Woodford (Chattanooga) Shale
		Dev.		Fam.		

Figure 1. Stratigraphic nomenclature of the western Ozark outcrop section of the Mississippian Kinderhookian and Osagean series including the St. Joe Group, northeastern Oklahoma and parts of southwestern Missouri modified from Mazzullo et al. (2013).

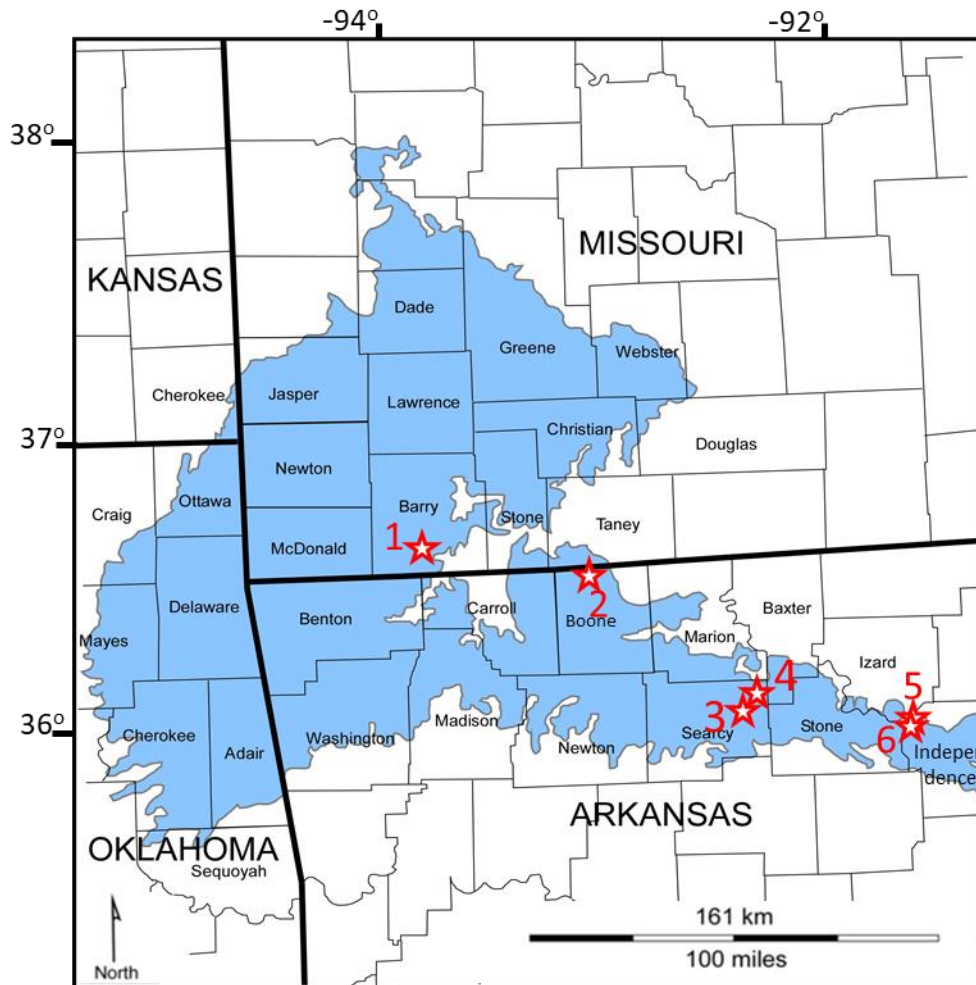


Figure 2. Mississippian outcrop pattern (blue) from Miller (2015) showing outcrop sections examined and sampled in this study. Location 1 is Roaring River State Park in Barry County, Missouri. Location 2 is the Omaha East location in Boone County, Arkansas. Locations 3 and 4 are the Highway 74 locations and Harriet East locations, respectively, in Searcy County, Arkansas. Locations 5 and 6 are Walls Ferry South and Glenn Creek, respectively in Independence County, Arkansas. Complete descriptions of outcrops 2, 3, 4, 5 and 6 are found in Dineen (2015).

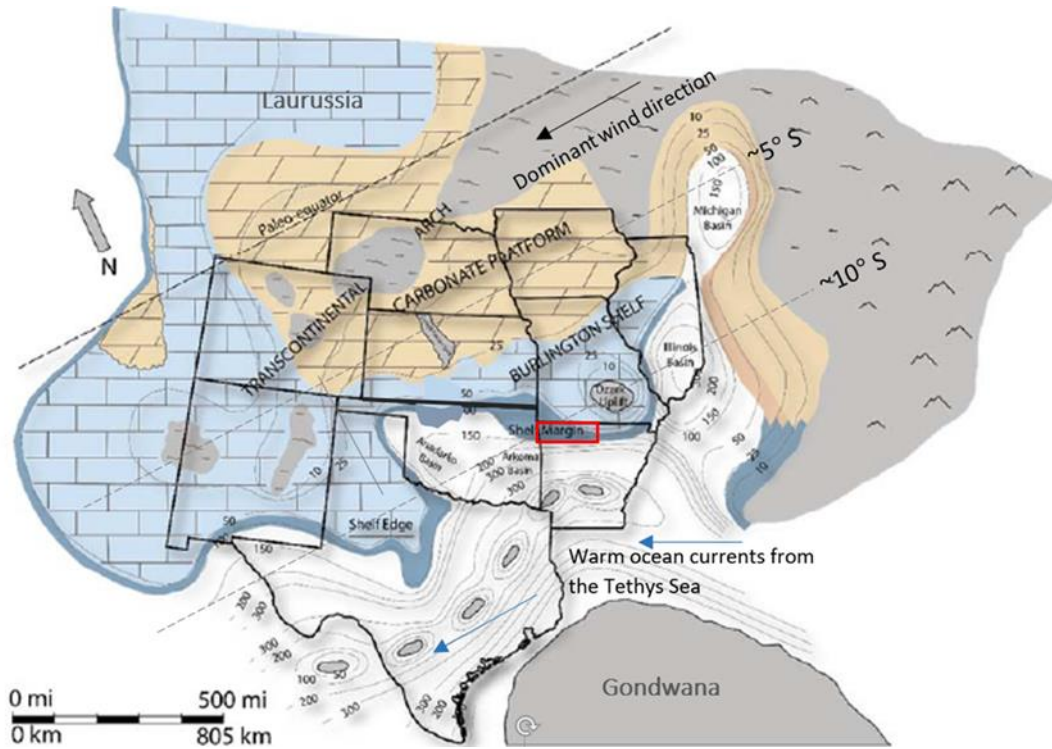


Figure 3. Paleogeographic map, with state borders for reference, showing the approximate location of the study area outlined in red on the Burlington shelf margin in early Mississippian time. Areas of uplift (dark gray) are flanked by dolomite (tan), limestone (blue), fine-grained mixed facies (dark blue) and basin facies (white). Water depth contours vary, but are mostly 50 meters. Ocean current direction is from Ross and Ross (1987) and Mii et al. (1999), whereas wind direction data from Witzke (1990) and Golonka et al. (1994), all reported in Hunt (2017). Original figure after Gutschick and Sandberg (1983) and Lane and DeKeyser, 1980).



Figure 4. An early Mississippian paleogeographical map of southern Laurentia approximately 345 Mya, with the approximate study area highlighted in red approximately 15° south of the paleo-equator (modified from Blakey, 2013).

Stable Isotope Geochemistry Overview

Isotopes of a given element have slightly different masses and chemical properties because while each isotope has the same number of protons, each has a different number of neutrons. Sometimes these isotopes are unstable, as in the case of ^{14}C , and the radioactive decay can be useful for purposes such as absolute dating. In this study, stable, non-radioactive isotopes of carbon and oxygen are used. Stable isotopes, which do not decay over time, allow us to examine conditions as they were at the time of deposition. Variations in isotopic composition are called isotopic fractionation (Morse and McKenzie, 1990). The relative variations are expressed

as a ratio of heavy isotopes to light isotopes. These ratios are measured against a standard; in this study the Vienna Pee Dee Belemnite (VPDB) standard is used for comparison. These ratios are expressed in delta notation in parts per thousand (‰) according to the equation:

$$\delta^{13}\text{C} = \frac{R_x - R_{STD}}{R_{STD}} \text{ where } R_x = {}^{13}\text{C} / {}^{12}\text{C} \text{ in sample; and } R_{STD} = {}^{13}\text{C} / {}^{12}\text{C} \text{ in standard}$$

A similar equation, substituting oxygen isotopes for carbon isotopes, is used for the stable isotopes of oxygen, ^{18}O and ^{16}O . These values are a standardized unit of measurement to understand short- and long-term variations and can be cross-plotted to understand these variations (Allan and Matthews, 1982).

The diagenetic history of carbonate rocks must be integrated to find the cause of any isotopic variation (Swart, 2015). Stable isotope abundance varies over time in response to a variety of factors. The precipitation of carbonate rocks from seawater produces only low levels of isotopic fractionation of carbon compared to dissolved inorganic carbon in seawater (Lynch-Stieglitz, 2003), meaning carbonate rocks contain a record of paleoceanographic conditions and resulting changes in elemental cycling. Long term changes in $\delta^{13}\text{C}$ are a result of variation in the ratio of organic carbon to carbon dioxide, bicarbonate, and carbonate minerals (Berner, 1990). Short term variation results from organic carbon burial rates and organic productivity (Tucker and Wright, 1990).

While carbon isotopes in carbonate rocks tend to be stable, oxygen isotopes are more subject to fractionation due to post-depositional factors, resetting the values due to intrusion of isotopically light meteoric water or very light basinal brines (Lohmann, 1988). While a detailed analysis of water-rock interactions is beyond the scope of this paper, precipitation of carbonates from marine and mixed marine/meteoric waters plot very similarly to seawater values. Precipitation from meteoric water results in more depleted $\delta^{18}\text{O}$ values, while burial results in highly depleted $\delta^{18}\text{O}$ values that can be covariant with $\delta^{13}\text{C}$ (Dupont, 2019).

The Mississippian is recognized as a time of shifting climate as the Earth transitioned from an essentially ice-free (greenhouse) to ice-covered (icehouse) conditions (Figure 5) (Mii et al., 1999). As a result, the Early Mississippian isotope curve has been studied in locations throughout the world and can be used to correlate new datasets (Bruckschen et al., 1999; Mii et al., 1999; Satlzman, 2003; Buggisch et al., 2008; Koch et al., 2014, Sessions et al., 2019). Regionally across the midcontinent the Mississippian is highly time-transgressive and cyclical response to base level changes (LeBlanc, 2014; Price, 2014; Childress and Grammer, 2015; Jaeckel, 2016; Vanden Berg, 2016). As base level changed through these cycles, vertical stacked facies belts developed that are difficult to delineate based on lithology alone, and geochemical data may be useful to understand this complex system. Stable isotope analysis for the St. Joe Group has been published for a limited number of outcrops (Sessions et al., 2019) and cores (Dupont, 2019; Koch et al., 2014; Mii et al., 1999) and this study seeks to expand on that work through collection and analysis of stable isotope data. Because secular changes in seawater composition are tied to subdivisions in geologic time and, as a result, stratigraphy, an unaltered stable isotope curve can be used for chronostratigraphic interpretation. Similarity of a given profile to the secular curve or wiggle similarity (Huck et al., 2017) can be examined to make inferences regarding the conformability of a section. This study uses bulk samples to construct $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ profiles from six outcrops in the southwestern Missouri and northwestern Arkansas. These profiles are integrated with biostratigraphic data to evaluate the conformability of strata and determine if excursions in the secular curves are apparent in the Early Mississippian section on the southern and western flanks of the Ozark Uplift.

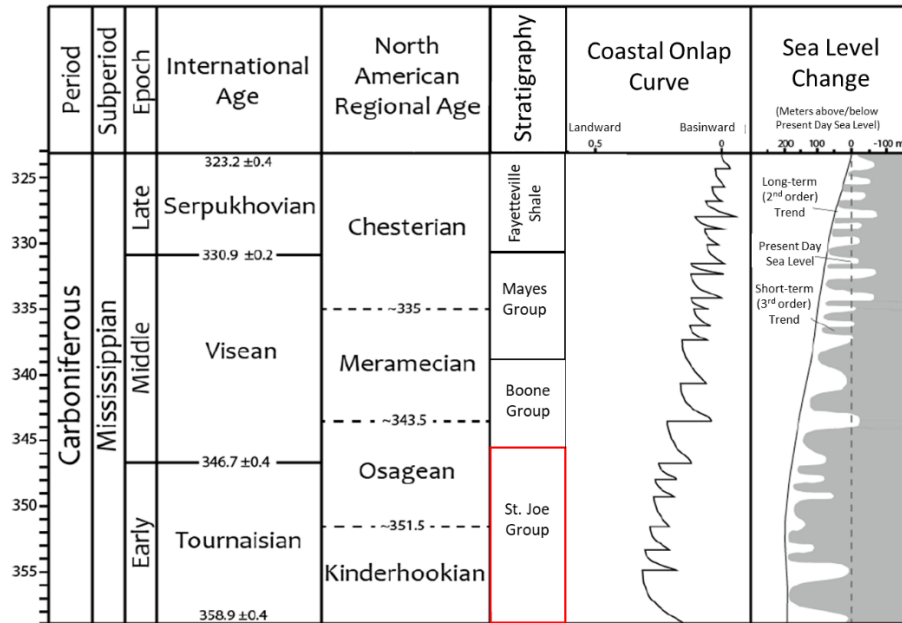


Figure 5. Coastal onlap curve for the Mississippian Subperiod modified from Hunt (2017) after Gradstein et al. (2012) and Haq and Schutter (2008). Transition to higher frequency cycles in the Meramecian and Chesterian and basinward shift of the coastal onlap curve reflect shift from greenhouse to icehouse conditions during the Mississippian.

Brachiopods can be analyzed using stable isotopes and have been used to determine isotopic signatures for specific time periods (Saltzman, 2002). Brachiopods that precipitate low magnesium calcite are useful for stable isotope analysis because their shell mineralogy remains relatively constant during burial and subsequent diagenesis (Al-Aasm and Veizer, 1982). Stable isotope data from brachiopod shells represent isotopic equilibrium at the time of deposition in normal saline conditions, however they can be isotopically fractionated and must be analyzed for diagenetic alteration (Grossman et al., 2008). Brachiopods were common throughout the Paleozoic, globally widespread and abundant from the tropics to polar regions and in a wide range of seawater depths, making them important for seawater temperature reconstructions based on relative oxygen isotope shell composition (Bajnai, et al., 2018). Brachiopod shells adequately large to sample can be difficult to find, so the technique of bulk sampling the carbonate is used instead. Bulk samples provide similar data to brachiopod shell studies and have similar data trends in stable isotope data (Saltzman, 2002; Saltzman et al., 2004; Fouke, 2005; Allègre, 2008).

This study will present new data from bulk samples for six outcrops of St. Joe Group rocks in the study area. The St. Joe Group has previously been analyzed biostratigraphically but there has been only limited chemostratigraphic analysis (Boardman et al., 2013; Session et al., 2019). This study combines existing biostratigraphic data with bulk isotopic data to provide new insights into the depositional setting of the study area and address the two principal hypotheses: (1) the global positive isotopic excursion in the Kinderhookian should be present in the Ozark sections, and (2) the contacts between the formations that make up the St. Joe Group are conformable at the formational level.

Objectives

To test the hypotheses that (1) the global positive isotopic excursion in the Kinderhookian should be present in the Ozark sections, and (2) the contacts between the formations that make up the St. Joe Group are conformable, the following objectives are proposed.

1. Establish an isotopic record across the St. Joe Group to determine through “wiggle similarity” (Huck et al., 2017) if the Kinderhookian positive excursion is evident,
2. Compare the isotopic record to conodont biostratigraphy of the St. Joe Group,
3. Use chemostratigraphy to determine if the sedimentary section is complete as the St. Joe Group thins basinward, and
4. Determine through integration of biostratigraphy and chemostratigraphy if the contacts between the formations that make up the St. Joe Group are conformable.

These objectives will be met by comparing the lithostratigraphy, conodont biostratigraphy and isotopic chemostratigraphy for the outcrops in this study. The results from the Ozark Uplift will be compared to isotope curves in the literature to make inferences about the impact of paleoclimatic conditions in the Early Mississippian sea in the study area.

CHAPTER II

GEOLOGIC SETTING

Research Area

The St. Joe Group outcrops selected for this study are in southwestern Missouri and northwestern Arkansas. These outcrops were chosen because the St. Joe Group thins to the south and east (Figure 6) and one of the objectives of this study is to determine if the thinner sections contain the three formations, or if undetected erosion or nondeposition has resulted in missing formations. The Mississippian section in the study area dips westward into the subsurface in eastern Oklahoma. Many of the westernmost outcrops and shallow subsurface sections in cores are described in Godwin (2017). St. Joe Group sediments were deposited on the margin of the Burlington Shelf in the early Mississippian (Lane and DeKeyser, 1980) in a foreland ramp setting on the southwestern Ozark Uplift (Boardman and Thompson, 2010).

Lane (1978) published a paleoecological model of the Mississippian carbonates based on selected marker fossils that were interpreted to make inferences regarding water depth during deposition and establish the age of the stratigraphic units. Lane and De Keyser (1980) expanded on the Lane (1978) work to generate a regional paleogeographic map (Figure 3) and compare the carbonate shelf system to a previously-existing model of same-age rocks in Europe.

Early Mississippian carbonates on the southern margin of the Burlington shelf represent a transgressive system tract (Shelby, 1986). The Bachelor Formation marks the beginning of sea level rise at the Woodford Shale-Mississippian contact. The overlying formations of the St. Joe Group represent cyclic carbonate and shale deposition during continued marine transgressions and regressions (Shelby, 1986; Mazzullo et al., 2011; Mazzullo et al., 2013).

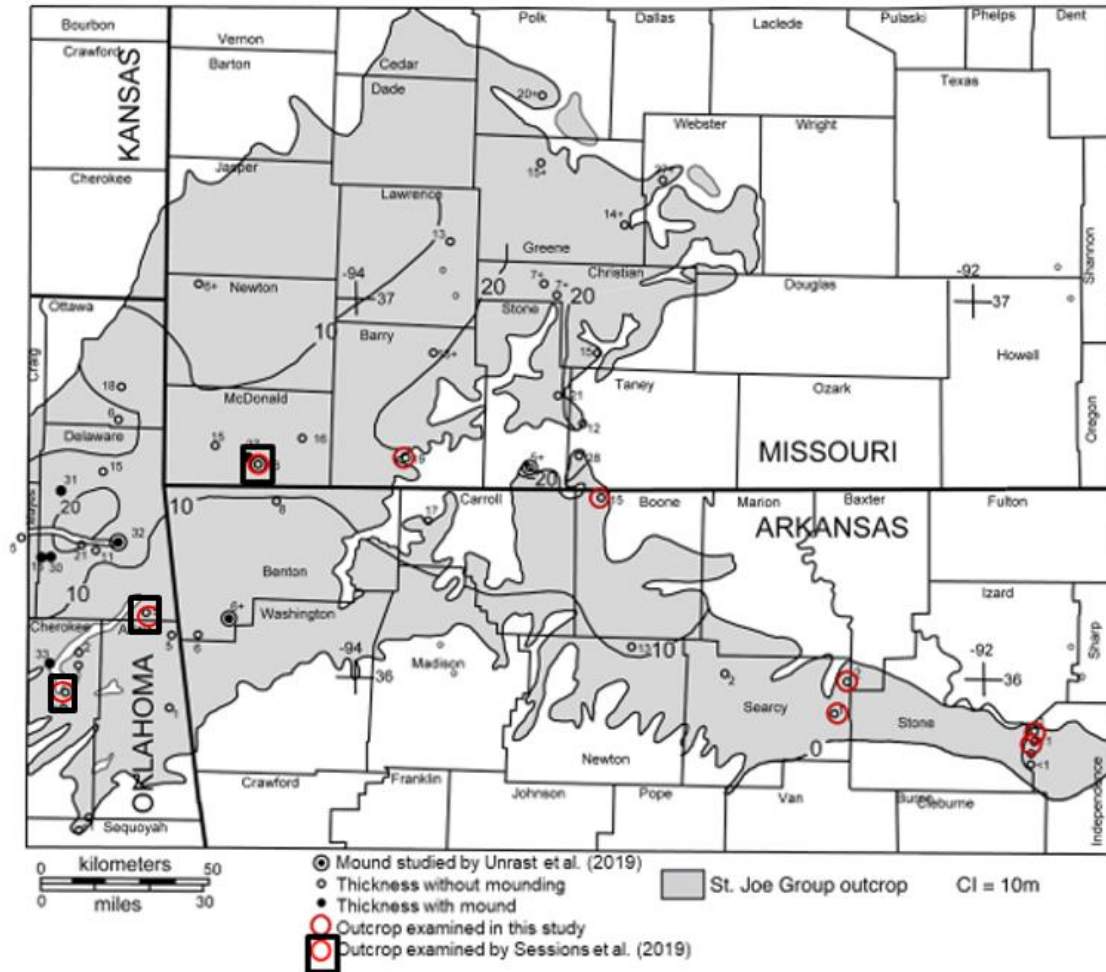


Figure 6. Thickness of the St. Joe Group from Unrast et al. (2019). Gray area is the generalized outcrop pattern in the Ozark region and contours represent the combined thickness of the Compton, Northview, and Pierson formations. Isolated thicker sections exceeding 20 m (66 ft) are Compton or Pierson mounds (shown as filled circles). Map is after Thompson and Fellows (1970) and locations of mounds and thickness values are from Laudon (1939), Harbaugh (1957), Thompson and Fellows (1970), Lopez (2012), Shoeia (2012) and McNabb (2014).

The six outcrops under investigation in this study are representative of the Tournaisian-Viséan stages and consist of St. Joe Group overlain by the Reeds Spring Formation of the Boone Group. Each of the six outcrops included has conodont biostratigraphy, lithostratigraphy and chemostratigraphy, with the more complete datasets from the thicker sections. The locations and summaries of the stratigraphy for each section follow.

- 1) Roaring River (RR): 36°34'43.40"N, 93°50'12.74"W, Roaring River State Park, Missouri. Thompson (1967) established the stratigraphy of this outcrop using conodont biostratigraphy. Additional conodont biostratigraphy established that contacts within the St. Joe Group were conformable (Thompson and Fellows, 1970). At the base of the section is the Bachelor Shale, which is included in the stratigraphic descriptions but was not sampled in this study. In ascending order, the Compton, Northview, and Pierson Formations are included and sampled. These units are overlain by the Reeds Spring Formation, for which a brief description is given but it was not a focus of this study. The current study uses the unit designations of Thompson (1967) and further subdivides each section by bedding planes, labeling individual beds alphabetically in ascending order from the base of the formation.
- 2) Omaha East (OE): 36°28'12.21"N, 93° 6'55.81"W, Boone County, Arkansas. This is the type reference section for the St. Joe Group in Boone County. Present here are the Compton, Northview, and Pierson formations. Dineen (2015) studied the stratigraphy and petrography of this outcrop at high resolution. Samples collected by Dineen (2015) at all the outcrops in Arkansas were used in the current stable isotope analysis.
- 3) AR-74: 35°56'37.44"N, 92°31'30.54"W, Searcy County, Arkansas. This outcrop is situated on the south side of AR-74. The St. Joe Group here includes the Compton and Pierson formations. The Northview Formation is not recognized at this location, however

a shale bed less than 1 cm thick separates the underlying Compton Formation from the overlying Pierson Formation (Dineen, 2015).

- 4) Harriet East (HE): 35°58'44.48"N, 92°27'37.38"W, Searcy County, Arkansas. This outcrop is a road cut on the north side of AR-14. As with the outcrop at AR-74, the Northview Formation is not recognized, but there is a thin (>1 cm) shale break between the Compton and Pierson formations (Dineen, 2015).
- 5) Walls Ferry South (WFS): 35°50'50.71"N, 91°50'49.23"W, Independence County, Arkansas. This outcrop is a railroad cut of the Missouri Pacific Railroad. The Northview Formation is absent at this location and the contact between the Compton and Pierson is not obvious in outcrop (Dineen, 2015). Dineen did not differentiate between the two formations, collectively referring to them in his stratigraphic study as St. Joe Group. The contact was identified with conodont biostratigraphy by Thompson and Fellows (1970), however for the current study these units are referred to collectively because the contact could not positively be identified in the samples collected by Dineen (2015).
- 6) Glenn Creek (GC): 35°49'21.89"N, 91°51'22.90"W, Independence County, Arkansas. This is the southernmost and thinnest St. Joe Group section included in this study. The St. Joe Group is only 0.8 m thick at this location, which is located along a railroad cut for the Missouri Pacific Railroad. As with the Walls Ferry South location, the Northview Formation is absent (Dineen, 2015) and the Compton and Pierson formations are referred to collectively as the St. Joe Group.

Stratigraphy

The Early Mississippian is marked by marine transgression, flooding the southwestern margin of Laurentia and beginning deposition of the Bachelor Formation and St. Joe Group (Hopkins, 1893). Cline (1934) defined the St. Joe Group as the chert-free basal member of the

Mississippian limestone. The St. Joe Group in Oklahoma does not include the Bachelor, neither does the St. Joe Group in Missouri (Miller, 2015). In Arkansas, the Bachelor Sandstone is included in the St. Joe Member of the Boone Formation or the St. Joe Formation of the Boone Group. In all three interpretations, the Pearson Formation or Member (Arkansas) is succeeded by the Reeds Spring Formation or Lower Boone Formation (Arkansas) (Miller, 2015; Mazzullo et al. (2013). For this study, the proposed stratigraphic nomenclature proposed by Mazzullo et al. (2013) will be used. This stratigraphy follows that in widespread use by the Oklahoma Geological Survey and Missouri Geological Survey and states that the St. Joe Group consists of the Compton Formation, Northview Formation and Pierson Formation.

Bachelor Sandstone

The basal unit in the Mississippian Subsystem is the Bachelor Formation, which was described by Mehl (1960). The Bachelor Formation is approximately one-foot-thick and has two members. The lower member is a buff, medium grained, poorly sorted quartz arenite sandstone. The sandstone has no clear depositional or sedimentary structure and is not continuous. The upper member is a well-cemented gray shale. The contact between the Bachelor Formation and underlying Woodford (Chattanooga) Shale is sharp, and the Bachelor thins to the east as it approaches the Ozark Dome (Thomson and Fellows, 1970). The Bachelor Formation is not continuous over much of the western part of the shelf, however it is present in the study area and the well-indurated example of the Bachelor Sandstone at the base of the section at Roaring River State Park is shown in Figure 7.



Figure 7. The Bachelor Sandstone at the Roaring River State Park section, marked with red lines at the top and base. An Estwing® rock hammer (12-inch length) is shown for scale.

Compton Limestone

The Compton Limestone (Compton Formation) (Figure 8), like the overlying Northview Formation, was named and described by Swallow (1855). The Compton Formation is a crinoid-rich fine-grained limestone that is dominantly wackestone-packstone (Dineen, 2015). This formation is green to gray and interbedded with dark green clay (Thompson and Fellows, 1970). This is thinly bedded finely crystalline limestone is laterally extensive across the entire shelf margin (Lane 1978). The Compton Limestone is up to 30 feet thick near the Roaring River study location and thins to the southeast and southwest, where it pinches out (Thompson and Fellows, 1970). Carbonate mounds are prevalent in the Compton Limestone (Mazzullo et al., 2019; Unrast et al., 2019; Childress and Grammer, 2015), but were not observed in the studied outcrops.



Figure 8. The base of the Compton Limestone at Roaring River is marked in orange, with an Estwing® rock hammer for scale.

Northview Formation

The Northview was first named by Swallow (1855) and approaches 80 feet thick at maximum but thickness is variable (Lane 1978). It is easily distinguished from the Compton below it and the Pierson above due to the distinct red and green color of the rocks. The upper and lower contacts are both conformable at the outcrop under study, however it has previously been identified in other areas as unconformable (Kammer and Matchen, 2008). The lithology is

generally a green to reddish-brown limestone grading upward to shale (Figure 9). The Northview pinches out southward in the study area.

Pierson Limestone

The Pierson Limestone (Figures 9 and 10) conformably overlies the Northview formation, and unconformably underlies the Reeds Spring (Mazzullo et al., 2010). It was first named and described by Weller (1901). It is a thin bedded, gray- to buff-colored, crystalline limestone with significant echinoderm and bryozoan fossil content. Toward the southern end of its extent, the Pierson becomes difficult to distinguish from the Compton Limestone in areas where the Northview is absent (Mazzullo et al., 2010). The Pierson is approximately 140 feet thick at its maximum, hosts carbonate mounds that extenuate its thickness and that of the St. Joe Group (Figure 6) (Unrast et al., 2019) and thins to the southeast (Mazzullo et al., 2010).



Figure 9. The Northview and base of the Pierson formations at Roaring River, with boundaries marked in orange. An Estwing® rock hammer provides scale. The numbers on the beds are the same as Thompson (1967), whereas the letter denotes further subdivision used in this investigation.

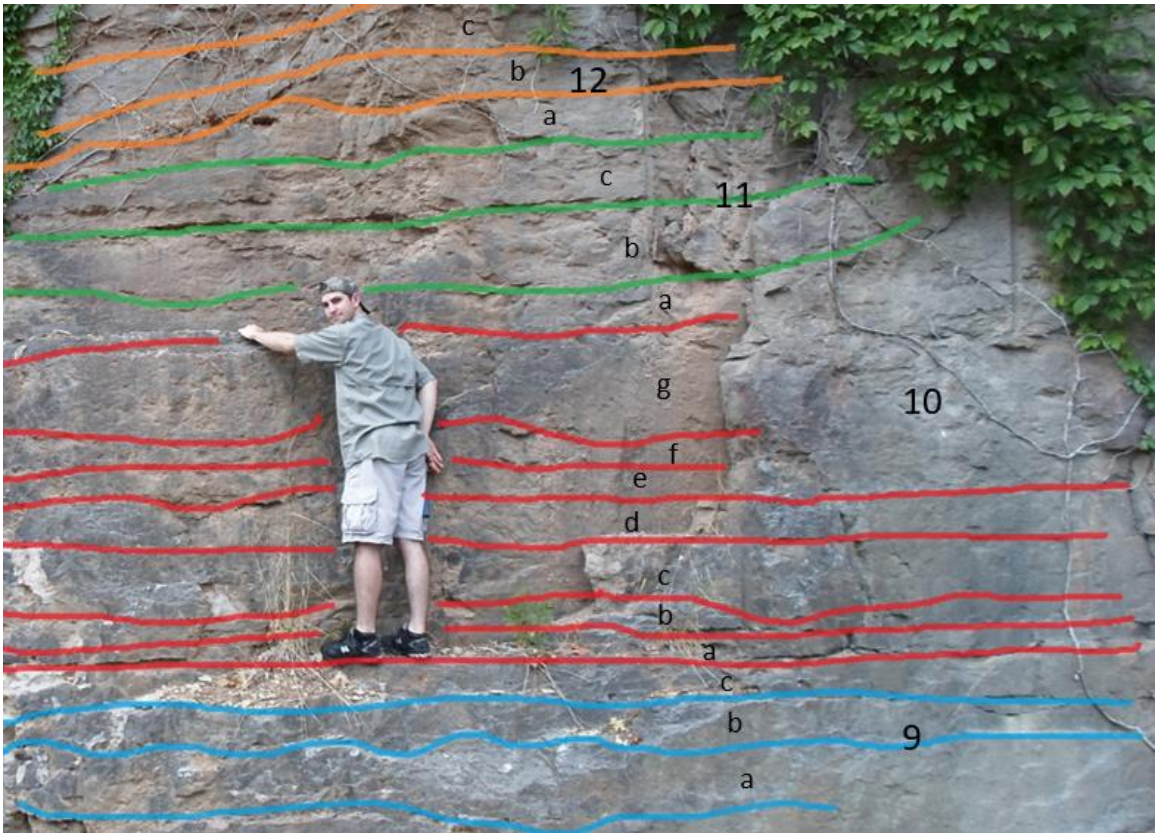


Figure 10. The Pierson formation at Roaring River, with Thompson's (1967) bed set numbers noted, and letters denoting further subdivision for this investigation. Joseph Dineen (1.8 m; 5.8 ft) for scale.

Reeds Spring Formation

The Reeds Spring Formation (Figure 11) was first named and described as a member of the Boone Formation by Moore (1928). The Reeds Spring is approximately 200-225 feet thick at its maximum (Moore, 1928; and Mazzullo et al., 2010). It is predominately gray, cherty limestone, finely crystalline with scarce macrofossils (Thompson and Fellows, 1970). The formation is exposed throughout the region and is continuous in the subsurface into southeastern Kansas (Mazzullo et al., 2010).

The Reeds Spring is laterally more extensive than the underlying strata, stretching from northwestern Stone County, Missouri (Thompson and Fellows, 1970) to southern Sequoyah County, Oklahoma and east to Independence County, Arkansas (Mazzullo et al., 2010).

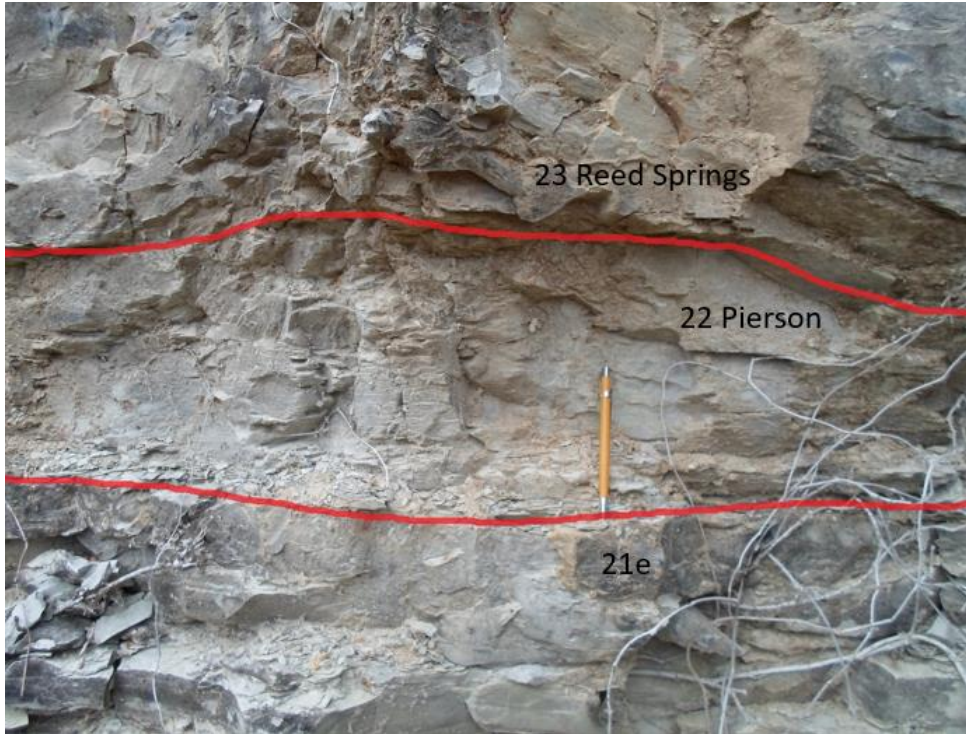


Figure 11. The upper Pierson and basal Reeds Spring formations, demarcated in red. A standard ink pen is used to show scale.

Biostratigraphy

The St. Joe Group is replete with fossils. These are well-documented to include crinoids, bryozoans, brachiopods, ostracods, and corals; crinoids and bryozoans are the more prominent fossil species (Hopkins, 1893; Huffman, 1959; Anglin, 1966; and many others). Though macrofossils are abundant, the current biostratigraphy for these units is based predominately on conodonts and reported in Thompson and Fellows (1970), Boardman and Thompson (2010), Thompson (2015) and Boardman et al. (2013).

CHAPTER III

METHODOLOGY

Outcrop sample collection

One hundred and seventy-nine samples were collected from the beds at the six outcrops in the study area. Locations for sampling were selected and the orientation of each prospective sample was marked with a permanent marker prior to collection. Samples were then broken off the face of the outcrop using a 10-pound sledgehammer with a 36-inch handle, or 5-pound sledgehammer with a 12-inch handle, or 13-ounce Estwing® rock hammer with a 12-inch handle, or 25-inch paleo pick, or a 3-inch chisel where needed. These samples were a minimum of 4 inches on each side. When beds were thinner than 4 inches the full bed thickness was used. The location name and bed number were written on each sample with a permanent marker and each sample was placed in an individual one-gallon zip-top freezer bag, labeled with the location name and bed number. Additionally, a minimum of 2 kg of rock from each bed were bagged in one-gallon zip-top freezer bags for conodont extraction. Bagged samples were collected in 5-gallon buckets for transportation to the laboratory. In some instances, samples could not be obtained due to safety hazards, unexposed rock faces, or by request of a Missouri State Parks Ranger to discontinue sample collection. Personal protective equipment worn during sample collection consisted of boots, work gloves, and safety glasses. A 25-foot measuring tape was used to measure bed thicknesses on each outcrop.

Acetate peel thin section preparation

Acetate peels were prepared for 92 samples from the Roaring River location. This process required use of a rock saw, 200 and 800 grit silicon carbide polishing powder, 10% dilute hydrochloric acid, acetone, acetate sheets, and a sink.

Each sample was cut into a block approximately 3-inches by 3-inches, as the size of the sample permitted, with two cut surfaces on opposing sides. One of those surfaces was polished first using 200 grit silicon carbide polishing powder to remove saw marks, then the same surface was polished with 800 grit silicon carbide polishing powder on a glass plate. The polished surface was etched with hydrochloric acid for 10 seconds and excess hydrochloric acid was removed by rinsing the sample in tap water. Immediately the polished surface was coated in acetone and covered with a precut acetate sheet. After approximately 15 minutes wait time, the acetate sheet was carefully peeled away from the sample, and with it a thin layer of rock. The peel was then trimmed and mounted between two 2-inch x 3-inch glass slides. The two slides were taped together and labeled.

Each sample was described and analyzed for texture, constituent grains, and diagenesis using the Leica DM EP polarizing microscope, the Dunham (1962) carbonate classification, and the Color Guide to the Petrography of Carbonate Rocks (Scholle and Ulmer-Scholle, 2006). The samples were then photographed using an Olympus BX51 microscope with camera.

Stable isotope sample preparation

Using the blocks cut for acetate peel thin sections, a Dremel rotary tool with a cutting bur bit was used to powder approximately 1 gram of rock from a face of the sample that had not been used for acetate peel preparation. Each sample was collected on clean paper and transferred to a sample vial. The drill was cleaned with isopropyl alcohol and a fresh piece of paper was used to cover the sample collection area before each sample was powdered. These samples were then sent

to the University of Miami Rosenstiel School of Marine and Atmospheric Science Stable Isotope Laboratory in Miami, Florida for stable isotope analysis using a common acid bath interfaced to a Finnigan-MAT 251 Mass spectrometer. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ data are reported per mill (‰) relative to the Vienna Pee Dee Belemnite (VPDB) isotopic standard.

CHAPTER IV

RESULTS

General Observations

The six outcrops in this study area document thinning from northwest to southeast. Macrofossils observed in outcrop and samples are similar to those described in previous studies and include in order of estimated abundance: crinoids, brachiopods, bryozoans, ostracods, and corals. Sampling locations were selected to avoid northeast-southwest fractures that are visible in most outcrops.

The St. Joe Group outcrops at an elevation of approximately 1250 ft (~380 m) at the Roaring River location, and elevation decreases steadily across the study area to 230 ft (~70 m) at the Glenn Creek location. Present structural attitude of beds was affected by the uplift of the Ozark Dome and the evolution of the Arkoma basin. As a result, strata dip gently westward and continue into the subsurface in Oklahoma.

Petrography

The petrography of the outcrops under investigation in Arkansas has previously been described (Dineen, 2015), and while petrography was not the main focus of this investigation, the Roaring River outcrop was examined and found similar to the Jane, Missouri outcrop described in other work (Sessions et al., 2019). The Compton Limestone represents an overall coarsening upward. It is wackestone-packstone containing numerous crinoids and brachiopods. Sponge spicules were observed in acetate

peels of samples from the Roaring River outcrop. The Northview Formation is a wackestone-grainstone with a significant amount of interbedded shale. Fossils observed in thin section at the Roaring River location were brachiopods, crinoids, and ostracods. Bed set 5 in the Northview at Roaring River is predominately shale. The Pierson is a wackestone-packstone with crinoids, brachiopods, ostracods, and occasional trilobites (Figure 12).

All outcrops and formations in this study had whole and fragmented fossils. Fractures and calcite dissolution account for the majority of microporosity. Pyrite is common in the St. Joe group and in the Northview formation iron staining is present. As a result of compaction there is minimal porosity and dolomite concentrated in fractures. Dolomite and pyrite are interpreted to have formed during burial diagenesis.

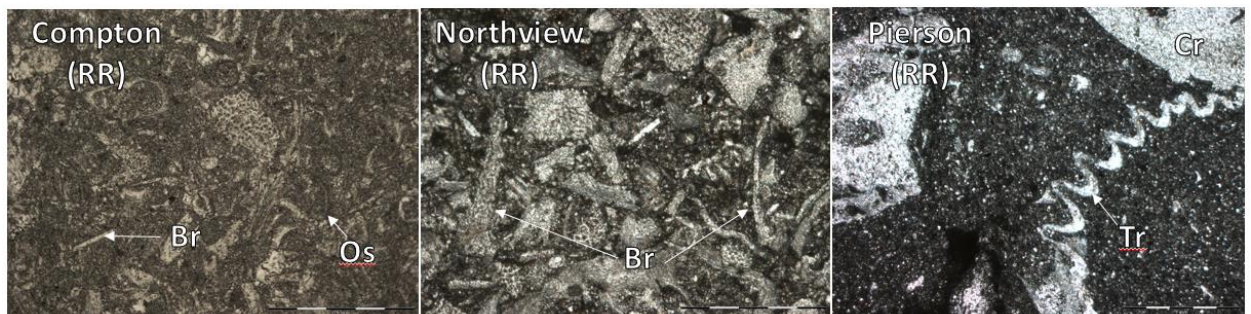


Figure 12. Select thin section photomicrographs from the formations of the St. Joe Group at Roaring River. Pictured fossils include brachiopods (Br), ostracods (Os), crinoids (Cr), and trilobites (Tr). The scale of the photos is 0.5mm per black or white scale segment.

Geochemical Results

The effects of carbonate diagenesis on carbon and oxygen isotopes can be analyzed with the variation among values of cross-plotted isotope data (Allan and Matthews, 1982; Figure 13). The Lower Mississippian marine calcite initial isotope values are -1 to -0.25‰ $\delta^{18}\text{O}$ and 3.5 to 4‰ $\delta^{13}\text{C}$ and are represented by the orange box (Frank and Lohmann, 1995; Figure 13). A subsurface study of the Anadarko Shelf in

western Oklahoma determined the bulk sample range for the Mississippian: -6 to -1.5‰ $\delta^{18}\text{O}$ and 0 to 3‰ $\delta^{13}\text{C}$ (Koch et al., 2014), represented by the green box (Figure 13). The data spread for the current study is -6.96 to 0.02‰ $\delta^{18}\text{O}$ and 0.29 to 4.91‰ $\delta^{13}\text{C}$.

However, the Roaring River outcrop in particular has a relatively flat $\delta^{13}\text{C}$ curve in the lower Kinderhookian, lacking the robust rightward shift well-documented in literature (Mii et al., 1999; Saltzman, 2002; Koch et al., 2014; Dupont and Grammer 2019).

The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ curves were correlated to the stratigraphic columns for each outcrop under study (Figures 14-19). Additionally, the Roaring River stratigraphic column is correlated with conodont biostratigraphy from Boardman et al. (2013). Most outcrops have a negative deflection at the top of the Pierson and a similar general trend. Additionally, the smaller outcrops have fewer data points, providing less definition within data profiles. Bulk sample data often has a higher or lower overall value compared to targeted site sampling but because the results have similar characteristics and trends they can still provide a confident correlation. The $\delta^{18}\text{O}$ values are relatively uniform across all outcrops in this study.

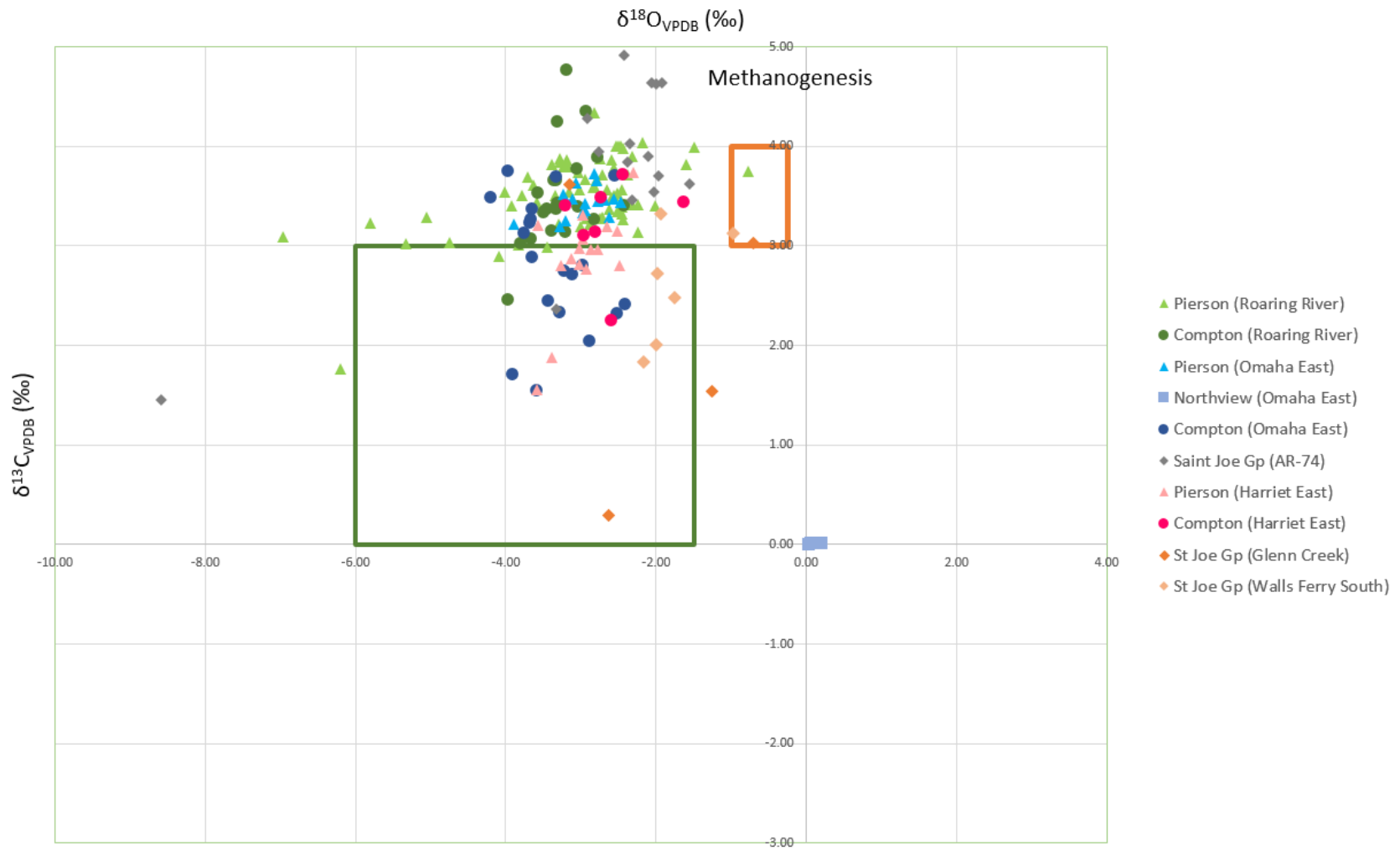


Figure 13. A cross-plot of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ from all formations and outcrops. Orange box (Frank and Lohmann, 1995) represents estimated initial Lower Mississippian marine calcite values and green box (Koch et al., 2014) represents the bulk sample range for the Mississippian of the Anadarko Shelf in western Oklahoma.

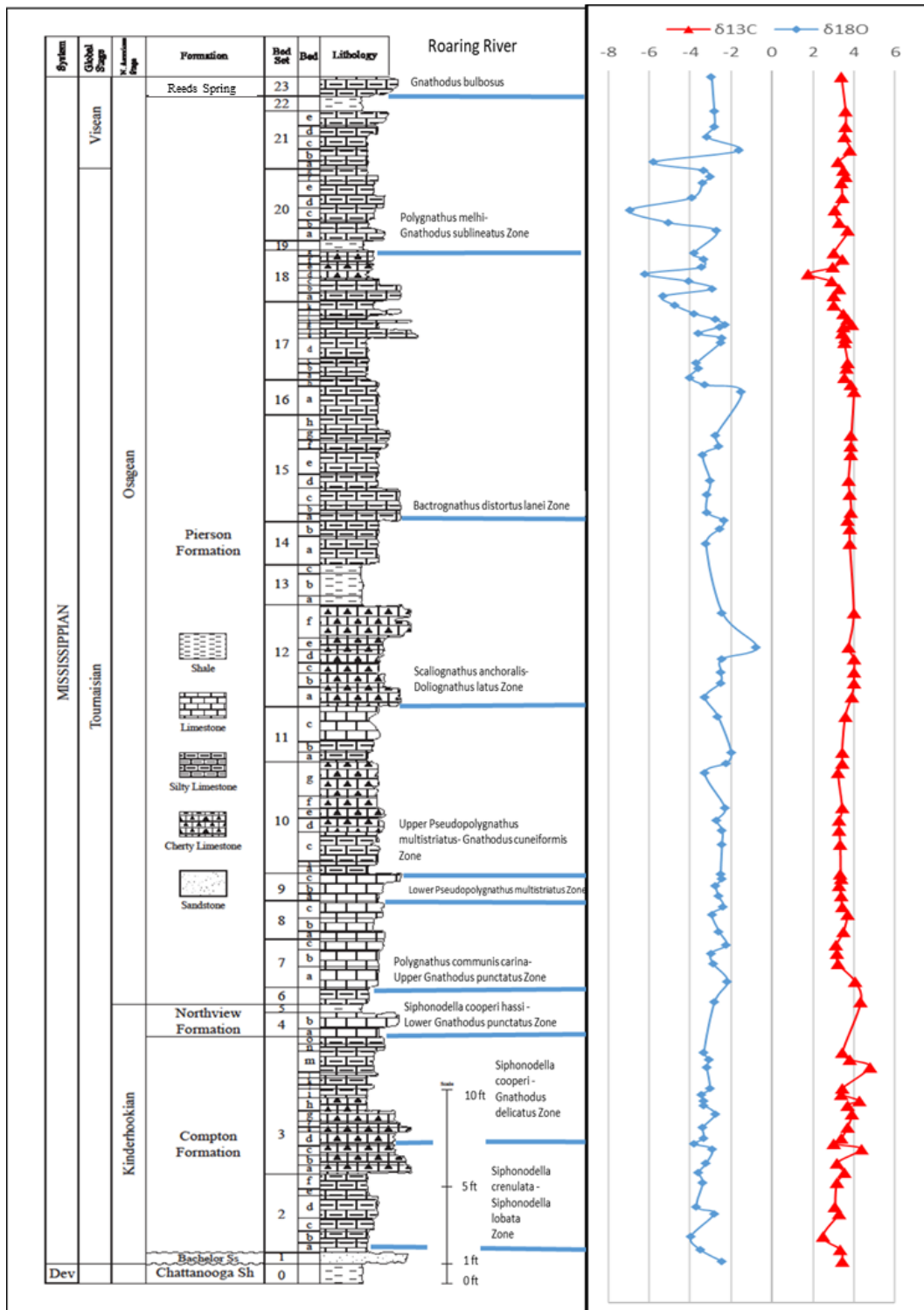


Figure 14. Stratigraphic column for Roaring River with conodont zonation (Boardman et al., 2013) plotted with isotope geochemistry data.

Omaha East

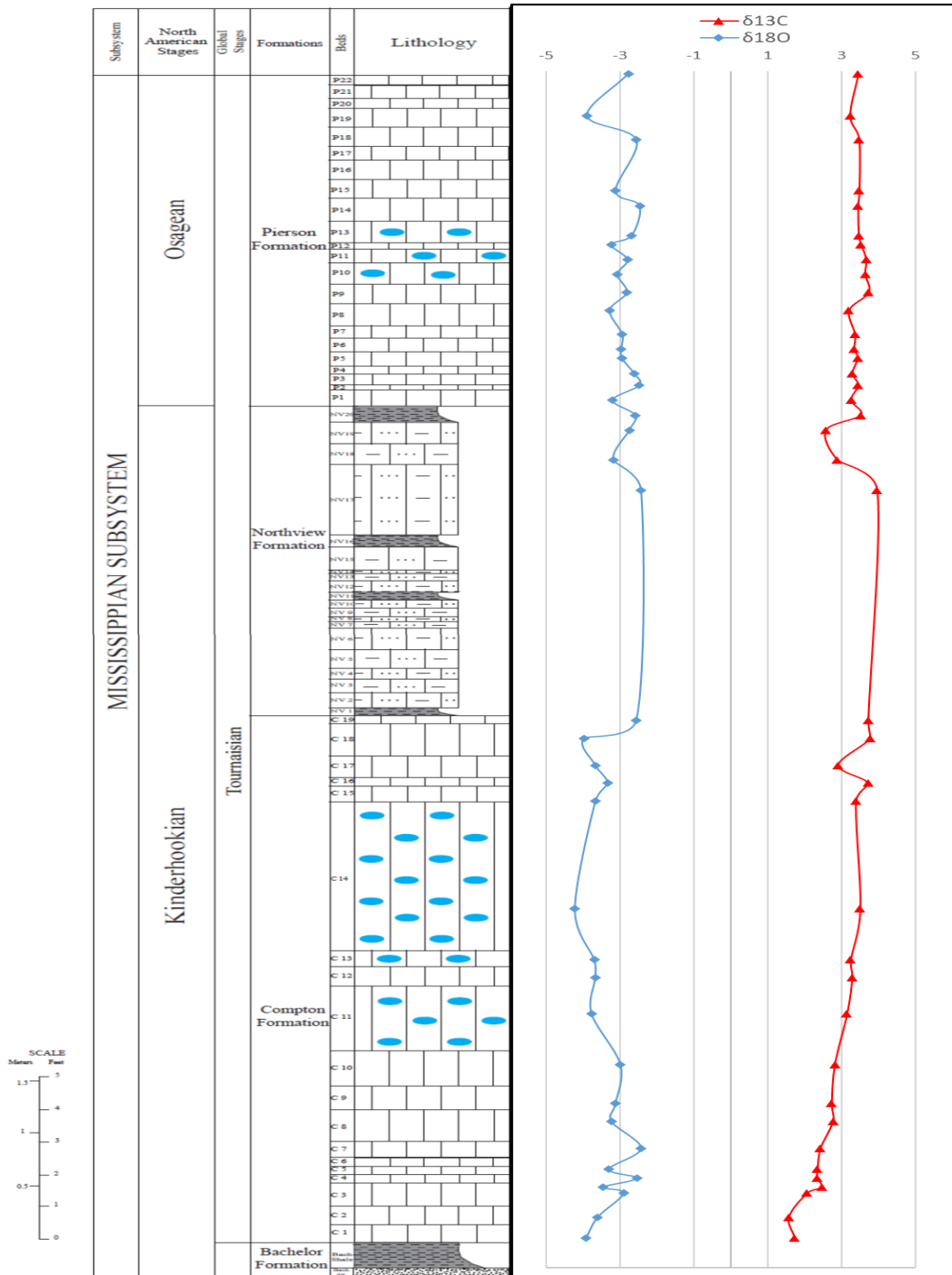


Figure 15. Stratigraphic column for Omaha East outcrop with isotope data (modified from Dineen, 2015).

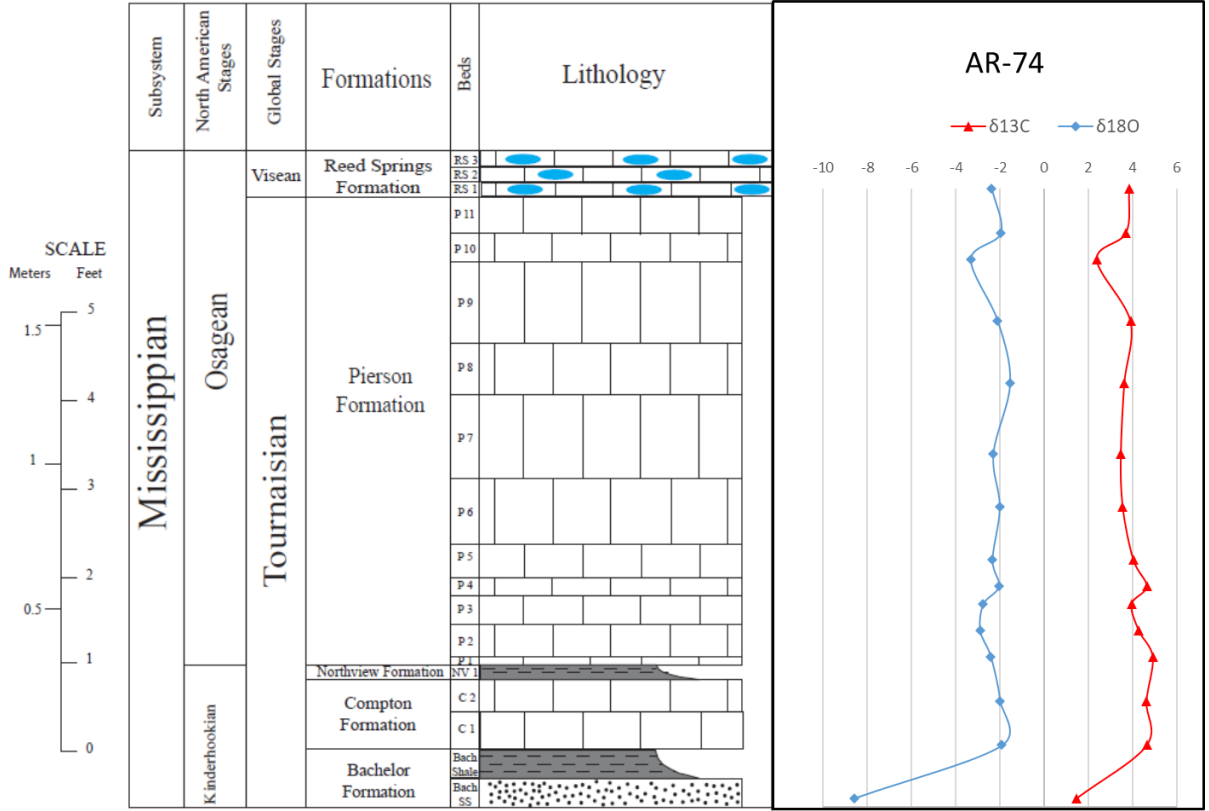


Figure 16. Stratigraphic column for AR-74 outcrop with isotope data (modified from Dineen, 2015).

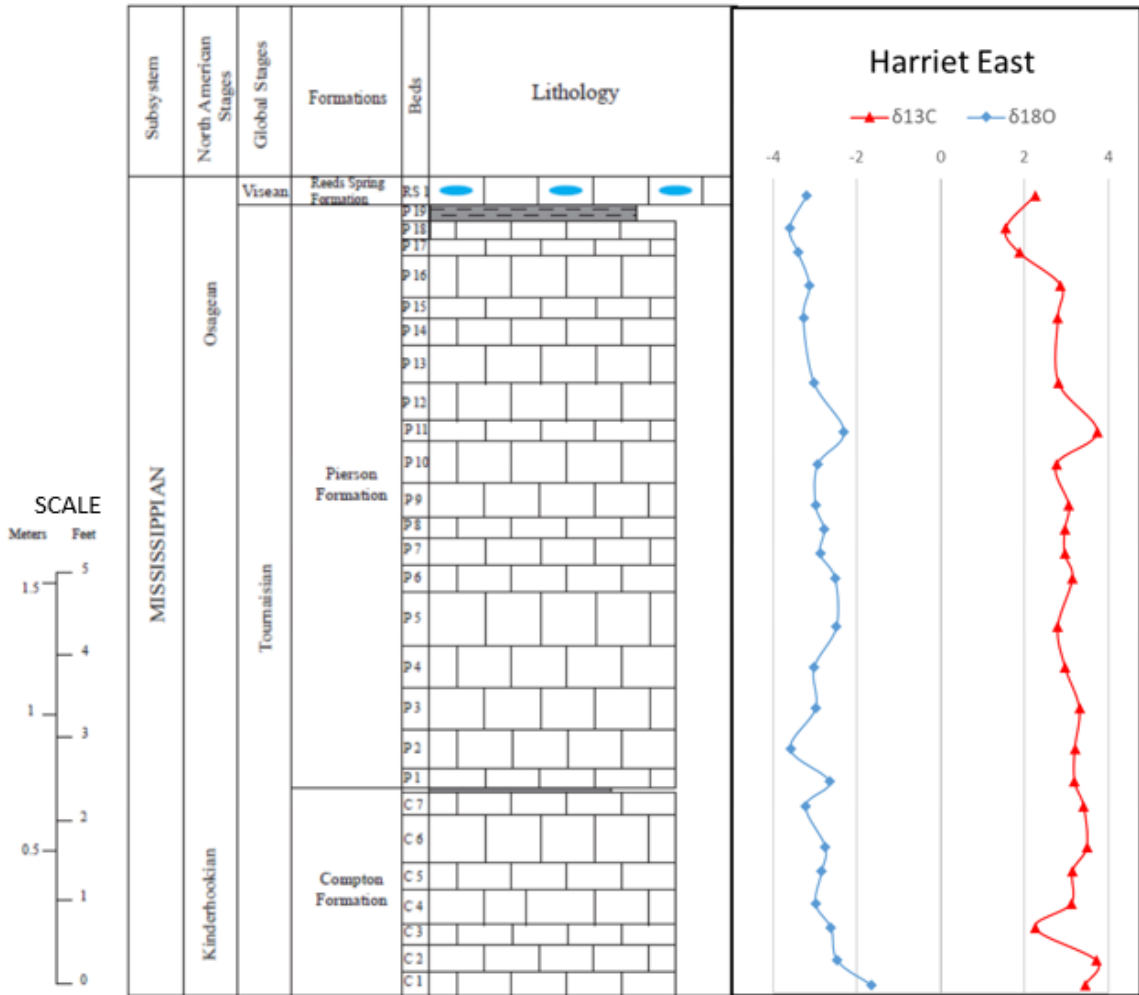


Figure 17. Stratigraphic column for Harriet East outcrop with isotope data (modified from Dineen, 2015).

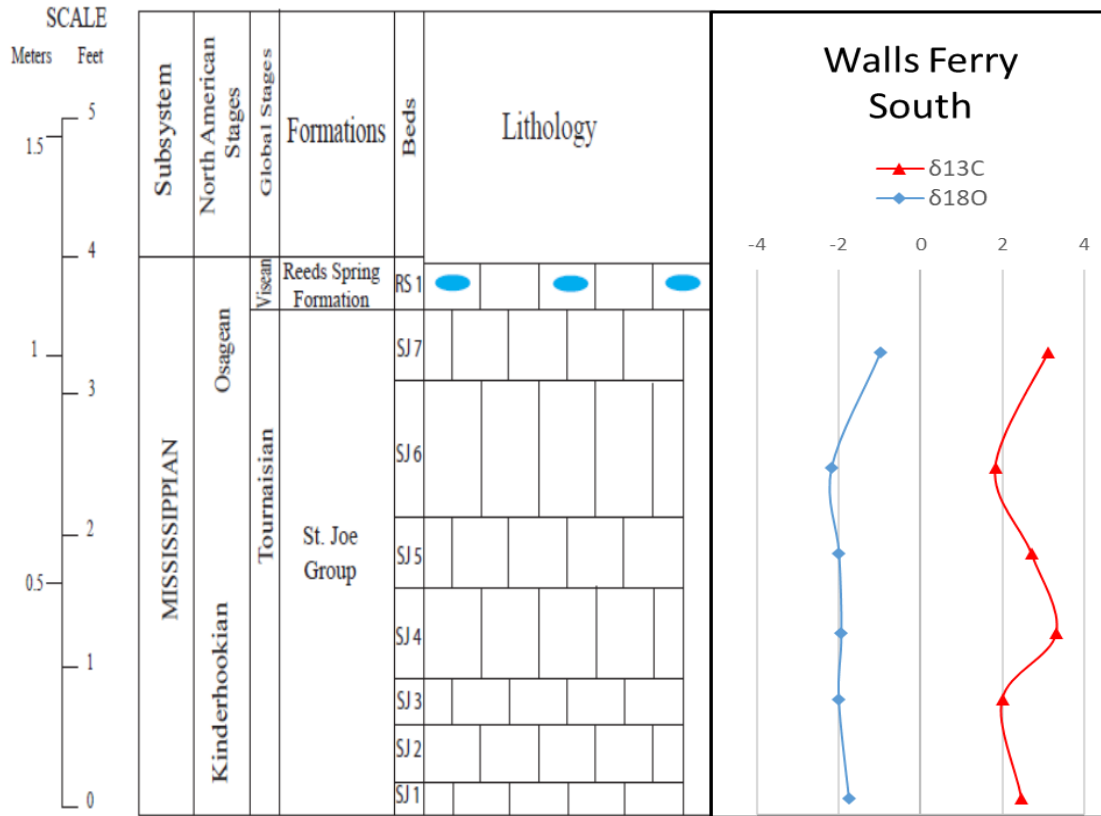


Figure 18. Stratigraphic column for Walls Ferry South outcrop with isotope data (modified from Dineen, 2015).

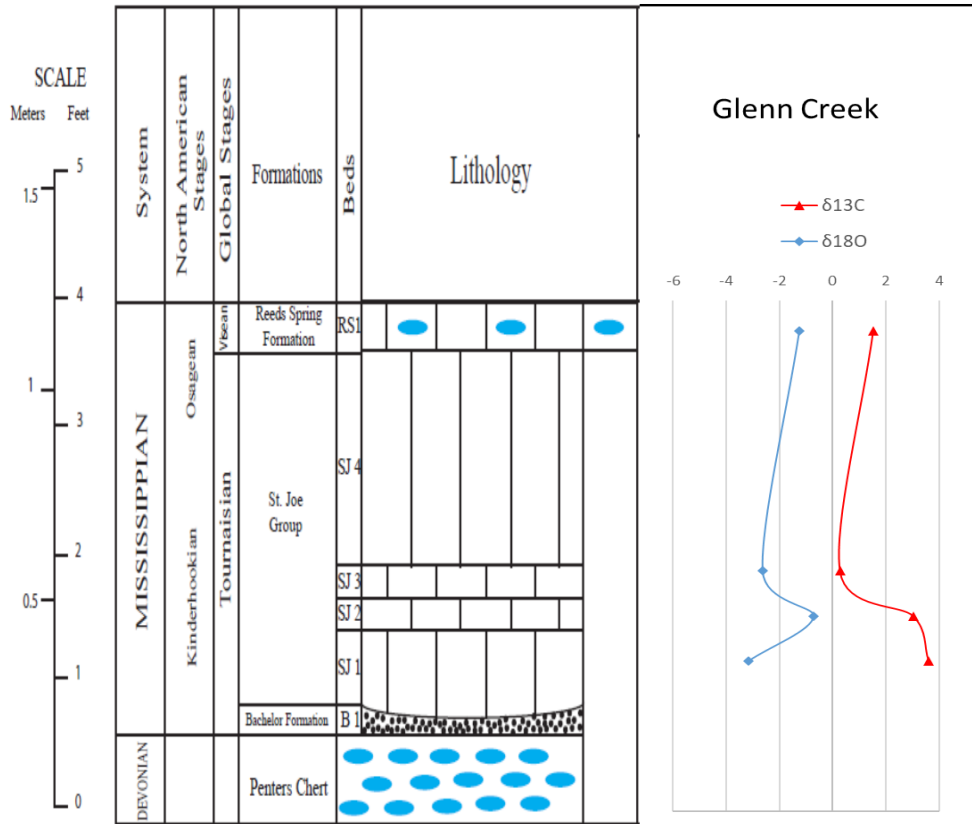


Figure 19. Stratigraphic column for Glenn Creek outcrop with isotope data (modified from Dineen, 2015).

CHAPTER V

DISCUSSION

Depositional Environment

The interpretation of the depositional environment of the Tournaisian has been evolved over time as the number of studies increased. Lane and DeKeyser (1980) proposed a mid-ramp environment. Later work refined this interpretation to a distally steepened mid- to outer-ramp (Boardman et al., 2013; Mazzullo et al., 2013). The petrographic and isotopic data contained herein are interpreted to agree with these findings, consistent with Sessions et al. (2019). The fossil assemblages present in thin section and Dunham (1962) classification of predominately wackestone-packstone indicate a shallow marine environment between fair weather and storm wavebase.

The St. Joe Group in the study area represents an overall shallowing upward sequence with smaller scale transgressive-regressive cycles. At the Roaring River outcrop the base of the Compton is a mudstone-wackestone that shallows upward to a wackestone-packstone at the top of the formation, with minor fluctuations in water depth across the interval represented by higher frequency changes in texture and bioclast content. Toward the south, deepening water is proposed as lithofacies transition to increased mudstone, darker color, and fewer fossils (Dineen, 2015). These changes are interpreted as representing a more distal, deeper water environment toward the south.

The Northview Formation at Roaring River is a packstone-grainstone with interbedded shale that becomes entirely shale near the top of the formation. This is interpreted as indicating increasing water depth. The Northview Formation thins to the southeast and becomes entirely shale before being absent in

the more easterly outcrops. This is consistent with the overall thickness of the St. Joe Group that also thins to the south and east. A lack of evidence of erosion and subaerial exposure and the presence of fossil assemblages support the distally steepened mid- to outer-ramp in a low energy system. This differs with some previous work (Mazzullo et al., 2013; Childress and Grammer, 2015), but importantly in those outcrops, west of the current study area, the Northview is siltier than it is in the Roaring River section and represents a shallower setting. Additionally, Thompson (1986) recognized the Northview as carbonate-rich to the south, and more siliciclastic-rich north of the current study area, with “brick-red” limestone in Stone and Barry counties, Missouri. However, it should be mentioned that differences in interpretation of water depth at given outcrops may reflect localized conditions and/or high-frequency fluctuations in sea level and should not be interpreted as generalized trends and applied across the region.

The basal Pierson limestone represents a sharp change from clay-rich carbonate to limestone, and a return to a higher-energy system. There is no evidence of scouring or reworking, but the contact is sharp at all six outcrops in the study. The lithofacies in the Pierson are consistent with increased energy of shallower water during marine regression.

Chronostratigraphic correlation

Conodont biostratigraphy (Boardman et al., 2013) correlates the Roaring River section to the upper Tournaisian Stage. Although the $\delta^{13}\text{C}$ curve records only a weak positive $\delta^{13}\text{C}$ excursion at the base of the Kinderhookian seen in other global $\delta^{13}\text{C}$ curves (Mii et al., 1999; Saltzman, 2002; Koch et al., 2014; Sessions et al., 2019; Figure 21) the curves fit the overall data through the upper Tournaisian Stage. Despite the differences in the isotope data, the general fit of these data, the lithofacies and conodont biostratigraphy provide enough evidence to positively correlate the Roaring River section to other Mississippian $\delta^{13}\text{C}$ curves.

The late Kinderhookian positive $\delta^{13}\text{C}$ excursion of $\sim 5\text{‰}$ is a global phenomenon, identified in cores and outcrops from multiple geological provinces including U.S. basin and range (Nevada), the mid-

continent region including Iowa, Illinois, Kansas, Missouri, Nebraska, Texas, and Oklahoma, as well as Belgium and Russia (Saltzman et al., 2004; Mii et al., 1999; Koch et al., 2014, Sessions et al., 2019). This excursion is interpreted to be a result of eustatic sea level fall resulting from the glaciation of Gondwana in the early Mississippian (Kammer and Matchen, 2008). This excursion is often paired with a positive $\delta^{18}\text{O}$ deflection of $\sim 6\text{‰}$. This deflection is interpreted as a result of global cooling or lighter oxygen isotopes being preferentially sequestered in glaciers (Marshall, 1992).

These deflections, though present in St. Joe Group rocks west of the study area, are absent or only weakly expressed in the outcrops in this study. There is no evidence of long-term subaerial exposure and erosion that removed formations and conodont biostratigraphy confirms the correlation to other St. Joe Group outcrops. However, diagenetic alteration can be examined as a potential explanation for the weak expression of the Kinderhookian positive excursion. The ratio of dissolved inorganic carbon is unchanged by the precipitation of carbonates, making the isotopic profile of carbonate rocks a good indicator of paleoceanographic conditions (Saltzman and Thomas, 2012). Long-term changes in $\delta^{13}\text{C}$ can be a result of variations in the ratio of organic carbon to carbon dioxide, bicarbonate and carbonate minerals (Saltzman and Thomas, 2012). The $\delta^{13}\text{C}$ profile, because of the carbonate's resilience, is preferred to the $\delta^{18}\text{O}$ for interpreting paleoceanographic conditions as marine, meteoric, or burial conditions can overwrite the $\delta^{18}\text{O}$ signature (Oehlert and Swart, 2014). When carbonate is precipitated from marine or mixed marine/meteoric waters, isotope data plot similarly to seawater; meteoric deposition results in slightly depleted $\delta^{18}\text{O}$ values, and burial results in highly depleted values and are often covariant with $\delta^{13}\text{C}$ (Knauth and Kennedy, 2009; Cochran et al., 2010). Data for the current study are plotted (Figure 20) with boxes denoting expected data distribution for different depositional environments and diagenetic effects from Dupont (2019), and with previous studies. Most data points are slightly depleted relative to carbonates deposited in marine environments, suggesting diagenetic alteration by meteoric water. This is consistent with previous studies that have found minor diagenetic alteration in the nearby Jane, Missouri outcrop (Steinman, 2017; Sessions et al., 2019). Oxidation of organic matter may also cause a negative

shift in $\delta^{13}\text{C}$ values (Oehlert and Swart, 2014). Additionally, due to bulk sampling and the presence of crinoids and other fossils, the isotope signature may have been affected as isotopic variability in crinoids may be as high as $\sim 2.8\%$ for $\delta^{13}\text{C}$ and $\sim 1.2\%$ for $\delta^{18}\text{O}$ (Gorzalak, et al., 2011). Bryozoans have been found to excrete carbonate in equilibrium with seawater, but there is variation among species that could also cause fractionation in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ (Smith et al., 2003). Additionally, the presence of aragonite fossils may produce fractionation of $\delta^{13}\text{C}$ values (Romanek et al., 1992), but have a minor or negligible impact on $\delta^{18}\text{O}$ values (Dettman et al., 1999).

Thompson (1967) identified the outcrop at Roaring River as a conformable section, and Boardman et al. (2013) provided biostratigraphic evidence of conformability. The absence of a major leftward (negative) deflection at the Compton-Northview and Northview-Pierson contact is further evidence of its conformability.

Examination of isotope profiles for the St. Joe Group and the same age intervals from the Arrow Canyon, Nevada section (Saltzman, 2002; Batt et al., 2007) and the Anadarko basin (Koch et al., 2014); Midcontinent (Mii et al., 1999) clearly demonstrate that the outcrops in Missouri and northwestern Arkansas lack the more robust positive excursion in values across the Kinderhookian. Figure 21 shows the detailed correlation of the outcrops from Sessions et al. (2019) with Roaring River, Omaha East, Saltzman (2002), and Koch et al. (2014). The Ozark profiles of this study and Sessions et al. (2019) indicate the signal of the secular Kinderhookian excursion is dampened to absent. Dampening of the $\delta^{18}\text{O}$ can be attributed to diagenetic alteration. Without an independent framework, correlation based on similar excursions in $\delta^{13}\text{C}$ data has some weaknesses: $\delta^{13}\text{C}$ may be less prominent as a result of inefficient circulation that maintained the normal marine signature. Other possible explanations for a dampened $\delta^{13}\text{C}$ signal in shallow-water carbonates include diagenetic effects during deposition, and fractionation effects with contributions from aragonite, low-Mg calcite, and high-Mg calcite (Immenhauser et al., 2002). Though no evidence of subaerial exposure was observed in the outcrops in the current study, $\delta^{13}\text{C}$ signals

are strongly affected by variations in sea level, with as much as 90% of a carbon isotope signal lost due to overwriting or erosion at discontinuities (Strasser, 2015).

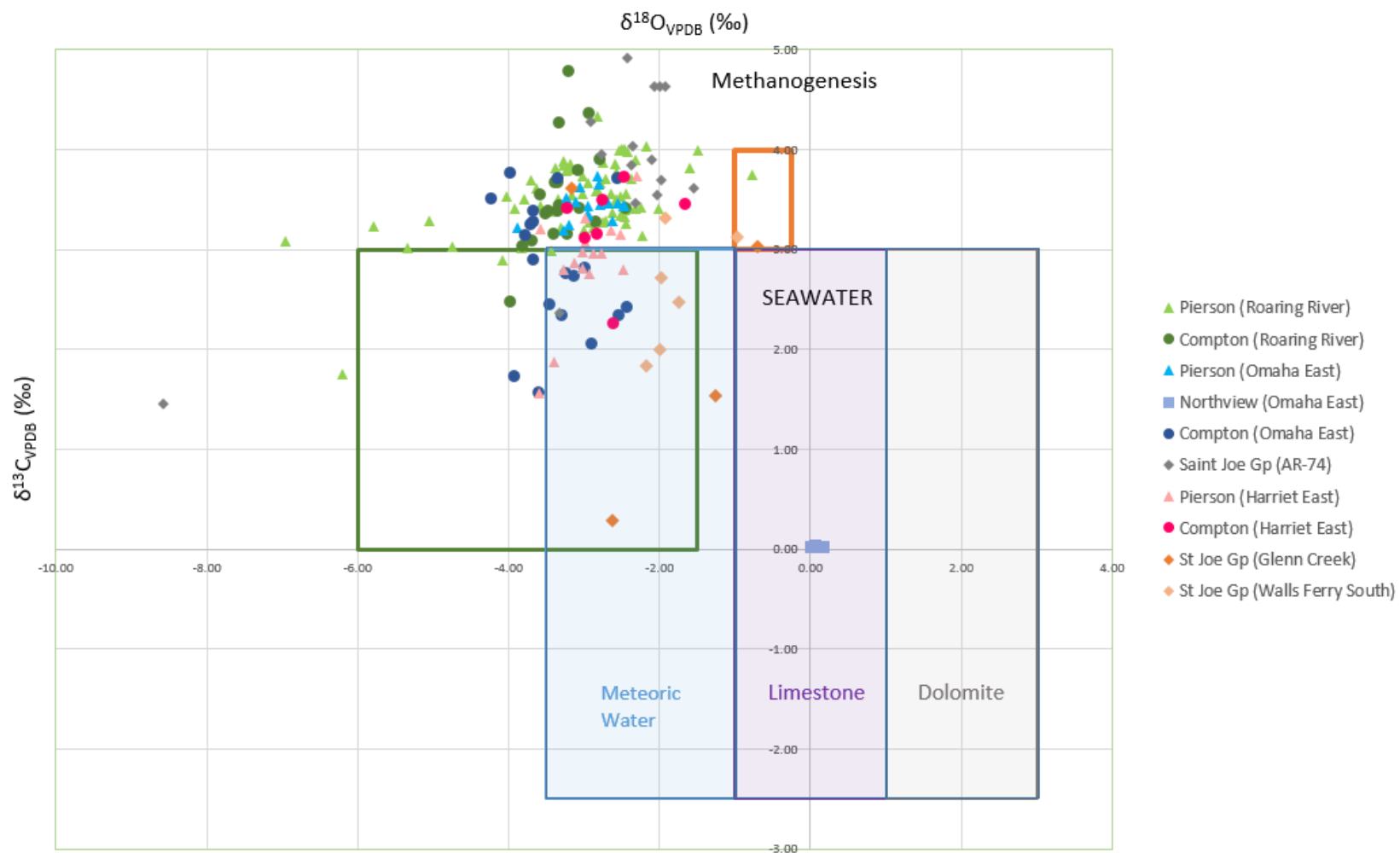


Figure 20. Current study isotope data plotted with expected ranges of values for select environments and diagenetic changes that affect isotopic signatures from Dupont (2019). Data collected in this study are depleted in oxygen relative to expected values for Mississippian carbonates deposited in marine environments as represented by the orange box from Frank and Lohmann (1995). Green box represents field of values reported by Koch et al. (2014) for subsurface samples from the Anadarko basin.

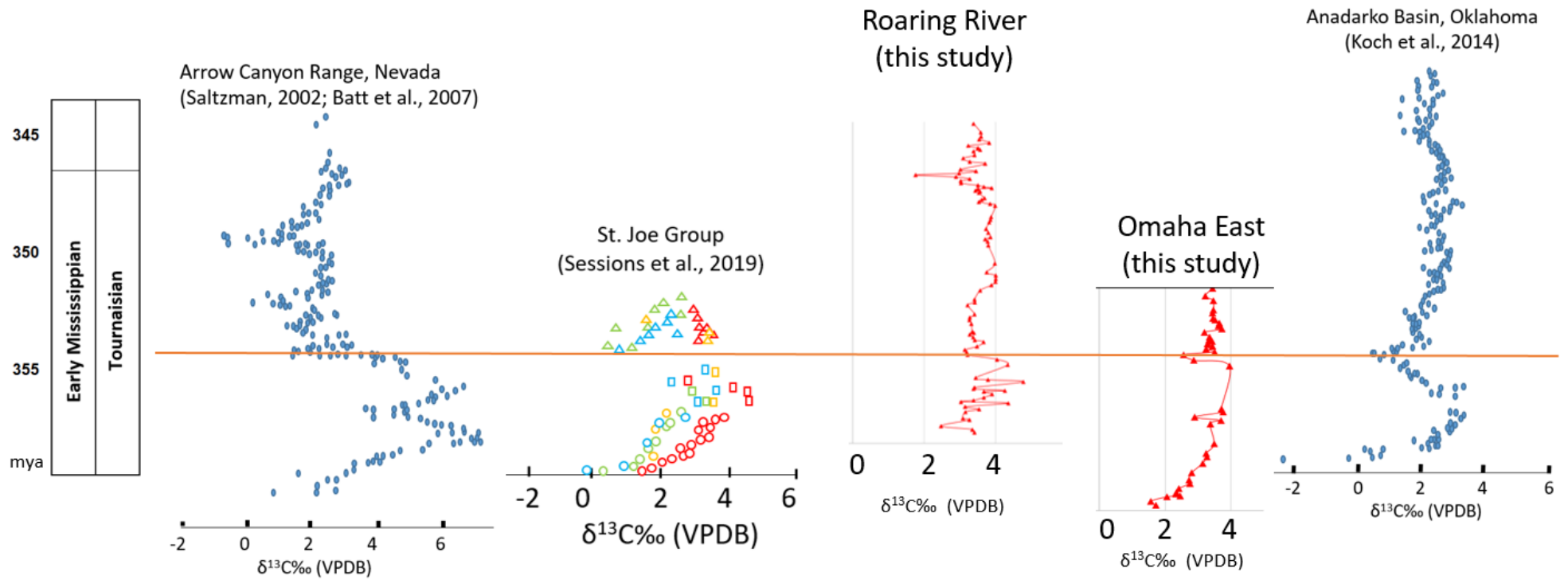


Figure 21. Correlation of carbon isotope profiles for the Mississippian including Arrow Canyon Range, Nevada (Saltzman 2003, Batt et al., 2007), St. Joe Group (Sessions et al, 2019), Roaring River, Missouri and Omaha East (this study) and Anadarko basin, Oklahoma (Koch et al., 2014). In the Sessions et al. (2019) profile, colors represent the four outcrops in the study: red represents data from the Jane, Missouri outcrop; orange represents data from the T-10 outcrop; blue represents data from the N-412 outcrop; and green represents data from the S-412 outcrop. Each formation is represented by a different shape: circles represent the Compton Formation; squares represent the Northview Formation; and triangles represent the Pierson Formation. Horizontal line represents contact between Kinderhookian and Osagean (Northview Formation and Pierson Formation).

CHAPTER VI

CONCLUSIONS and FUTURE WORK

This study used lithostratigraphy, petrography, published biostratigraphy and stable isotope geochemistry to investigate the St. Joe Group at six outcrops in southwestern Missouri and northwestern Arkansas. It built on previous work to confirm the presence/absence of the lithostratigraphic units that make up the St. Joe Group by integrating isotope chemostratigraphy, lithostratigraphy, and published conodont biostratigraphy. Based on this integration of several types of data, the following conclusions are proposed:

1. Isotope profiles across the St. Joe Group outcrops in this study document that the strong positive excursion of the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ curves recognized in the secular curve (Salzman, 2002; Batt et al., 2007 and Mii et al., 1999) for the Kinderhookian (Early Tournaisian) is not evident in the outcrop data.

2. A weak positive excursion is evident in the thicker outcrops at Roaring River and Omaha East that is comparable to the positive shift observed in data reported by Sessions et al. (2019) for several western Ozark outcrops. The weaker fractionation signal across the Kinderhookian in the Ozark outcrops compared to the secular curve could be the result of

increased meteoric influence and isolation from seawater with a more distinct fractionation signal, and/or influenced by the presence of crinoid and bryozoan fossils in the samples.

3. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ profiles across the Pierson Formation appear similar to data from Sessions et al. (2019) allowing confidence in the lithostratigraphic and chemostratigraphic correlations.

4. Integrated lithostratigraphy, chemostratigraphy and biostratigraphy support the inference that the St. Joe Group is intact at the study outcrops with no major unconformities disrupting the stratigraphy at the formation scale.

5. Decreasing thickness and increasing shale content of the Compton, Northview and Pearson formations to the south and east could indicate deepening water at the time of deposition, and fits the ramp depositional model.

6. Integrating conodont biostratigraphy from previous work, the age of the St. Joe Group can be constrained to the upper Tournaisian-Viséan, confirming that the St. Joe Group can be used as a reference section for Tournaisian-Viséan geochemical chronostratigraphy.

Constructing the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ curves revealed gaps in sampling that might influence results and interpretation. These gaps are especially important for the thin sections of the St. Joe Group in the eastern part of the study area. Additional sampling for chemostratigraphy, as well as a more detailed petrographic and biostratigraphic analyses could enhance the understanding of controls on deposition in the Ozark region during the Tournaisian. In particular, strontium isotope stratigraphy could potentially be used to correlate St. Joe Group carbonates independent of biostratigraphy and other isotope geochronological data (Kuznetsov et al, 2018). This is due to the consistency of strontium isotope data across ocean basins and its ability to record and preserve the ratio of $^{87}\text{Sr}/^{86}\text{Sr}$ in the sedimentation environment (Kuznetsov et al, 2018). This analysis is outside the scope of the current study but may yield insights into the history of the St. Joe Group.

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APPENDIX I

Stable Isotope geochemical data for samples analyzed by University of Miami Rosenstiel School of Marine and Atmospheric Science Stable Isotope Laboratory in Miami, Florida. Data is labeled by outcrop name and the bed designation is noted. One sample was collected per bedding unit. Blank data indicates no sample was analyzed for the indicated bed.

ROARING RIVER (refer to figure 14 for bed positions)				
Bed	$\delta^{13}\text{C}$	error	$\delta^{18}\text{O}$	error
0				
1				
2a	3.409662	0.018029	-2.4449	0.041191
2b	3.351286	0.018355	-3.51018	0.032446
2c	2.469212	0.017269	-3.97883	0.04824
2d	3.272745	0.025061	-2.8413	0.067843
2e	3.0854	0.018924	-3.68349	0.062324
2f				
3a	3.158835	0.018685	-3.40124	0.087501
3b	3.543813	0.025481	-3.58384	0.074877
3c	3.149035	0.02211	-3.21539	0.096471
3d	4.357137	0.018458	-2.93978	0.035651
3e	3.03204	0.019009	-3.80928	0.028514
3f	3.382539	0.027556	-3.34046	0.045309
3g	3.674326	0.023174	-3.3787	0.039903
3h	3.898336	0.01632	-2.78949	0.038627
3i	3.67405	0.018735	-3.34038	0.028478
3j	4.263495	0.018698	-3.32545	0.030715
3k	3.381987	0.011906	-3.47107	0.03451
3l	3.40961	0.016354	-3.05528	0.029542
3m	4.781728	0.018916	-3.19874	0.055968
3n	3.790203	0.027739	-3.07257	0.048274
3o	3.441508	0.0249	-3.33215	0.030257
4a				
4b				
5				
6	4.33736	0.019323	-2.82597	0.039385
7a	4.041263	0.012347	-2.18113	0.041273
7b	3.214194	0.020636	-2.88405	0.053519
7c	3.195534	0.017469	-3.00067	0.043979
8a	3.135472	0.02192	-2.23861	0.045288

Appendix I, cont.				
8b	3.483498	0.016642	-2.59561	0.030937
8c	3.668738	0.01728	-2.94863	0.032471
9a	3.414954	0.019854	-2.38292	0.04303
9b	3.372863	0.035736	-2.63073	0.183217
9c	3.27851	0.020737	-2.74781	0.029199
10a	3.393337	0.019453	-2.45952	0.049265
10b	3.345259	0.021514	-2.52247	0.04237
10c	3.322924	0.020024	-2.45947	0.025052
10d	3.267019	0.021441	-2.43941	0.027331
10e	3.282695	0.019136	-2.71505	0.037538
10f	3.41093	0.015224	-2.31863	0.03952
10g	3.218745	0.019767	-3.30071	0.046406
11a	3.419742	0.018358	-2.23957	0.042473
11b	3.408055	0.020009	-2.01264	0.023901
11c	3.565533	0.018587	-2.64704	0.036338
12a	3.87997	0.016582	-3.2797	0.032384
12b	3.999667	0.021272	-2.53384	0.026548
12c	4.005215	0.025347	-2.50294	0.071945
12d	4.00608	0.017099	-2.46594	0.041374
12e	3.754169	0.018194	-0.76876	0.043451
12f	3.982386	0.012843	-2.43292	0.042316
13a				
13b				
13c				
14a	3.794109	0.018016	-3.2291	0.036873
14b	3.782367	0.019593	-2.56577	0.043283
15a	3.710282	0.024748	-2.37618	0.026082
15b	3.861756	0.016341	-3.18379	0.019578
15c	3.799675	0.018844	-3.16741	0.032675
15d	3.734881	0.018264	-3.02914	0.021652
15e	3.823906	0.026012	-3.38322	0.037848
15f	3.860547	0.020063	-2.5966	0.030684
15g	3.873909	0.017234	-2.74989	0.041618
15h				
16a	3.991615	0.0309	-1.49432	0.044526
16b	3.848065	0.02912	-3.28179	0.060673
17a	3.536822	0.039529	-4.0205	0.029389
17b	3.616332	0.026161	-3.62576	0.027072
17c	3.690506	0.013567	-3.7132	0.049779
17d	3.532956	0.014399	-2.51822	0.047845

Appendix I, cont.				
17e	3.565554	0.020796	-2.45391	0.03967
17f	3.434511	0.020239	-3.58302	0.049206
17g	3.503678	0.026454	-2.56983	0.067675
17h	3.894989	0.021098	-2.32002	0.03734
17i	3.672184	0.013816	-2.79101	0.028498
17j	3.506552	0.316627	-3.79195	1.050671
17k	3.03191	0.027692	-4.74636	0.026025
18a	3.023118	0.022627	-5.33687	0.112749
18b	3.276851	0.023563	-2.93679	0.062663
18c	2.894624	0.017126	-4.08828	0.045223
18d	1.759627	0.028003	-6.20285	0.058911
18e	2.984126	0.021726	-3.44251	0.033808
18f	3.453957	0.01816	-3.33657	0.038417
18g	3.015606	0.027562	-3.82399	0.072846
19				
20a	3.711666	0.470923	-2.71674	1.60228
20b	3.283331	0.033511	-5.0594	0.871108
20c	3.091039	0.018928	-6.96179	0.152197
20d	3.40871	0.022702	-3.92679	0.057426
20e	3.388074	0.021663	-3.3924	0.084835
20f	3.564562	0.01339	-3.01634	0.04778
20g	3.507631	0.014022	-3.34039	0.039029
21a	3.235203	0.02387	-5.799	0.042024
21b	3.819083	0.025112	-1.60592	0.042656
21c	3.544876	0.019519	-3.16364	0.057024
21d	3.594771	0.025538	-2.82895	0.036731
21e	3.588101	0.022775	-2.83673	0.039207
22				
23	3.38839	0.025048	-2.95533	0.024378
OMAHA EAST (refer to figure 15 for bed positions)				
Bed	$\delta^{13}\text{C}$	error	$\delta^{18}\text{O}$	error
c1	1.724013	0.01148	-3.91848	0.035243
C2	1.55879	0.016148	-3.60371	0.052791
c3	2.058676	0.020095	-2.90144	0.027031
c4	2.453149	0.035714	-3.45242	0.050092
c5	2.33283	0.01747	-2.53271	0.041783

Appendix , cont.				
c6	2.341029	0.021414	-3.29922	0.05201
c7	2.419073	0.022453	-2.42909	0.043568
c8	2.759747	0.020096	-3.23436	0.030079
c9	2.725531	0.01761	-3.12226	0.04806
c10	2.80998	0.017731	-2.98947	0.070903
c11	3.142206	0.016391	-3.77181	0.056126
c12	3.280844	0.017907	-3.67182	0.037766
c13	3.245648	0.022214	-3.70141	0.019444
c14a	3.499376	0.023023	-4.21904	0.087396
c15	3.383469	0.022725	-3.666	0.062165
c16	3.708084	0.016484	-3.33837	0.0832
c17	2.900281	0.018916	-3.66639	0.041578
c18	3.762399	0.022408	-3.9782	0.04651
c19	3.714522	0.01233	-2.56206	0.072287
nv17	3.956576	0.016055	-2.43366	0.021282
nv18	2.876837	0.017286	-3.18194	0.052735
nv19	2.566309	0.022789	-2.74907	0.181597
nv21	3.509988	0.025845	-2.58518	0.064736
p1	3.24916	0.018124	-3.20078	0.032552
p2	3.443303	0.01823	-2.47432	0.051963
p3	3.283242	0.021449	-2.62231	0.039554
p5	3.431573	0.00839	-2.95088	0.038165
p6	3.335701	0.019453	-2.97451	0.050972
p7	3.35516	0.018875	-2.94204	0.046373
p8	3.193638	0.01206	-3.27817	0.028372
p9	3.730844	0.0234	-2.81714	0.067498
p10	3.631262	0.015665	-3.06627	0.043069
p11	3.657071	0.018748	-2.7988	0.050015
p12	3.520638	0.01955	-3.23314	0.033894
p13	3.459805	0.036313	-2.68389	0.045479
p14	3.442295	0.017271	-2.47256	0.044066
p15	3.475204	0.018656	-3.11872	0.05673
p18	3.468304	0.022455	-2.55777	0.055898
p19	3.224145	0.024884	-3.89016	0.036931
p22	3.446757	0.014645	-2.78032	0.040208

Appendix I, cont.				
AR 74 (refer to figure 16 for bed positions)				
Bed	$\delta^{13}\text{C}$	error	$\delta^{18}\text{O}$	error
bach ss 1	1.451767	0.020037	-8.58258	0.050972
sj1 C	4.63408	0.013316	-1.92564	0.039554
sj2 NV	4.626365	0.024396	-1.99921	0.050015
sj3 P1	4.91209	0.027679	-2.42057	0.033894
sj4 P2	4.278014	0.016157	-2.90811	0.046373
sj5 P3	3.94888	0.017125	-2.76494	0.043069
sj6 P4	4.635734	0.041321	-2.06131	0.109239
sj7 P5	4.030501	0.025879	-2.35011	0.067498
sj8 P6	3.544958	0.015543	-2.02456	0.043568
sj9 P7	3.46523	0.020334	-2.31391	0.05673
sj10 P8	3.620812	0.014115	-1.55424	0.028372
sj11 P9	3.89796	0.016074	-2.10889	0.032552
sj12 P10	2.368042	0.018093	-3.32543	0.044066
sj13 P11	3.701184	0.015649	-1.97301	0.038165
rs1	3.847437	0.021261	-2.37748	0.052791
HARRIET EAST (refer to figure 17 for bed positions)				
Bed	$\delta^{13}\text{C}$	error	$\delta^{18}\text{O}$	error
C1	3.452604	0.025935	-1.65171	0.033934
C2	3.724806	0.022134	-2.4619	0.060892
C3	2.262743	0.019877	-2.60914	0.050559
C4	3.11825	0.007825	-2.98047	0.058519
C5	3.148044	0.020143	-2.82993	0.049699
C6	3.493198	0.019695	-2.74492	0.028806
C7	3.415974	0.014005	-3.21487	0.043344
P1	3.199678	0.015419	-2.65167	0.049423
P2	3.203343	0.017055	-3.57514	0.055837
P3	3.314987	0.012557	-2.97755	0.048673
P4	2.977607	0.020524	-3.01435	0.075187
P5	2.79925	0.023228	-2.48246	0.064398
P6	3.150702	0.017759	-2.51683	0.031735
P7	2.963034	0.015585	-2.87253	0.043995
P8	2.967676	0.018382	-2.77635	0.045479
P9	3.065497	0.01743	-2.98027	0.047507
P10	2.764598	0.023997	-2.92649	0.038914

Appendix I, cont.				
P11	3.740211	0.016976	-2.30106	0.023965
P12/13	2.817937	0.032197	-3.01551	0.072962
P14/15	2.803162	0.025212	-3.27014	0.044277
P16	2.869165	0.015905	-3.1252	0.044734
P17	1.882503	0.012371	-3.39106	0.075881
P18	1.560183	0.021665	-3.59448	0.051963
rs1	2.255796	0.017903	-3.18916	0.027031
WALLS FERRY SOUTH (refer to figure 18 for bed positions)				
Bed	$\delta^{13}\text{C}$	error	$\delta^{18}\text{O}$	error
1	2.475982	0.028838	-1.74943	0.047507
3	2.001724	0.018525	-1.99635	0.023965
4	3.318184	0.035249	-1.93234	0.043995
5	2.719823	0.014134	-1.98691	0.031735
6	1.832642	0.01959	-2.17165	0.044277
7	3.121318	0.007847	-0.9723	0.044734
GLENN CREEK (refer to figure 19 for bed position)				
Bed	$\delta^{13}\text{C}$	error	$\delta^{18}\text{O}$	error
rs1	1.538174	0.02903	-1.25105	0.03302
3	0.291282	0.020656	-2.62875	0.075881
2	3.029886	0.026027	-0.70532	0.034088
1	3.613707	0.025385	-3.15835	0.043311

VITA

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2010-2011: Surface logging in the Anadarko Basin/Anadarko Shelf of Western Oklahoma for Horizon Well Logging and Geosearch/Empirica Well Logging.

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2013-2015: Operations Geologist, regulatory specialist, and geonavigation in the Anadarko Shelf/Basin of Western Oklahoma for Apache Corp.

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