GEOCHEMICAL EVALUATION OF THE MISSISSIPPIAN LIMESTONE

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Abstract: A multi-proxy geochemical investigation of the Mississippian Limestone interval in the STACK resource play area of the Anadarko Shelf was undertaken, in order to evaluate environmental conditions during deposition of sediments of the Mississippian Limestone interval within the Anadarko Shelf. Evaluation of the source rock potential of the interval was also undertaken in order to determine if the unit is capable of self-sourcing oil within the STACK. From the evaluation of stable nitrogen isotopes and redox sensitive elements, we concluded that redox conditions at time of deposition of sediments of the Mississippian Limestone interval within the Anadarko Shelf were oxic to suboxic, thereby ruling out anoxia as a factor that drove preservation of organic matter within the interval on the Anadarko Shelf. Analysis of organic carbon stable isotopes together with elemental proxies of paleoproductivity and detrital input suggests that there was lack of enhanced detrital input into the Anadarko Shelf, as well as an absence of heightened productivity within the Anadarko Shelf at time of deposition of sediments of the Mississippian Limestone interval. Finally, results from evaluation of organic geochemical analyses (Rock-Eval, saturate biomarkers) undertaken on Anadarko Shelf Mississippian Limestone rock extracts indicate presence of biomarkers said to be diagnostic of sediments of the Mississippian Limestone interval by previous investigations. Furthermore, biomarker analysis results support the paleoenvironmental interpretations obtained from stable isotope and elemental proxy results for sediments of the Mississippian Limestone interval within the Anadarko Shelf. Results from this study does not explicitly rule out that sediments of the Mississippian Limestone interval are capable of generating oil within the Anadarko Shelf, although pyrolysis results from the few samples examined in this study have poor source rock characteristics.

Insights from this study validate the utility of combining multiple geochemical proxies to tell a more nuanced story regarding paleoenvironmental conditions during deposition of mixed clastic-carbonate sediments, such as the Mississippian Limestone interval of the Anadarko Shelf, as well as the utility of some of these geochemical techniques (e.g., stable isotopes of nitrogen, elemental abundance of elemental proxies of redox, paleoproductivity and detrital input) in deciphering paleodepositional conditions in mixed clastic-carbonate sediments.

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CHAPTER I

INTRODUCTION

1.1 Background and Summary of Problem

The Mississippian Limestone interval in the mid-continent area of the U.S.A. was deposited in an ancient, continent-wide, epeiric sea during Mississippian time (Sloss, 1963; Gutschick and Sandberg, 1983). In addition, LeBlanc (2014) posited that Mississippian Limestone deposition occurred along a distally-steepened ramp and that lithological variation in this mixed carbonate-siliciclastic unit is a consequence of changes in eustasy and relative sea level controlled by Milankovitch cycle variations. Distally-steepened ramps have been described as possessing some characteristics of ramps and rimmed shelves, although they differ from rimmed shelves because their major slope break occurs several kilometres seaward of high-energy shoals (Read, 1985). Furthermore, the Mississippian has been described as a time of changing climate, with transitions from greenhouse to icehouse conditions (Haq and Schutter, 2008). Such climatic transitions would have influenced eustatic sea levels, which would in turn influence organic matter production and preservation (Huc et la., 2005). Hunt (2017) assigned an age range from middle Osagean to late Chesterian for the Mississippian Limestone in north-central Oklahoma, the location of the cores used in this study. Samples for the current study were obtained from two cores drilled in the Anadarko Shelf for petroleum exploration purposes. Lane and Dekeyser (1980) and Gutschick and Sandberg (1983) have described the Anadarko Shelf as a carbonate ramp environment located within 20° S of the paleoequator.

More than 900 million barrels of oil and over 6 tcf of natural gas have been produced from Mississippian Limestones of the Anadarko shelf (Koch et al., 2014) to date and the USGS estimates that an additional 31 million barrels of oil, 99 billion cubic feet of gas and 4 million barrels of natural gas liquids could yet be discovered within the Mississippian assessment unit of the Anadarko Basin Province (Higley, 2014). Several investigators suggest that the Mississippian Limestone interval is capable of self-sourcing oil and that the oil produced from the interval consists of oils sourced from the underlying Woodford shale, as well as oil generated by sediments of the Mississippian Limestone itself (e.g., Da Wang and Philp, 1997; Al Atwah, 2015). In recent times, there has been renewed petroleum industry interest in the Mississippian Limestone interval within the STACK resource play area of the Anadarko Shelf of Oklahoma driven by the prospect of producing hydrocarbons from source rocks through the combined application of horizontal drilling and hydraulic fracturing. Several authors have proposed that interactions between various factors, such as water column redox state, organic productivity and detrital input, are responsible for determining how much organic matter is produced and ultimately preserved in sediments (e.g., Pedersen and Calvert, 1990; Canfield, 1994; Tyson, 2005). Hence, the overall goal of this research project was to evaluate environmental conditions (redox, paleoproductivity and detrital input) at time of deposition of sediments of the Mississippian Limestone interval within the Anadarko Shelf using a combination of geochemical techniques including stable isotope geochemistry of organic carbon and nitrogen, analysis of elemental proxies for redox, paleoproductivity and detrital input, and evaluation of organic geochemical results (Rock-Eval and saturate biomarkers). Insights from geochemical evaluation of environmental conditions during deposition will then be utilised to decipher the source rock properties of the Mississippian Limestone interval within the Anadarko Shelf.

Bulk $\delta^{15}N$ values are a useful redox proxy because the process of denitrification predominates in suboxic waters. Denitrification preferentially removes light ^{14}N, resulting in the retention of the heavier ^{15}N isotope in sedimentary organic matter; consequently, bulk $\delta^{15}N$ values are higher in suboxic environments than in anoxic or oxic environments. In anoxic environments, nitrogen fixation (a process with minimal N isotope fractionation) is predominant and in oxic environments nitrification goes to completion. Consequently, lower bulk $\delta^{15}N$ values are associated with both oxic and anoxic environments (Mariotti et al., 1981; Quan et al., 2013). Authors such as Brandes and Devol (1997), Quan et al. (2008) and Rivera et al. (2015) have demonstrated the utility of $\delta^{15}N$ as a reliable water column redox proxy across a variety of environments. Stable carbon isotopes of organic matter ($\delta^{13}C_{org}$) are a useful proxy to determine organic matter provenance depending on which photosynthetic pathway plants utilize to incorporate C into organic matter during photosynthesis (e.g., Schoell, 1984; Meyers, 1994; Meyers, 1997; Ahmad and Davies, 2017). Most photosynthetic land plants preferentially incorporate ^{12}C into organic matter via the C_3 Calvin pathway thus, they consequently yield $\delta^{13}C_{org}$ of around -27‰ relative to PDB whereas, plants that utilize the C_4 Hatch-Slack pathway to incorporate C into organic matter have $\delta^{13}C_{org}$ of around -14‰ while marine organic matter yields $\delta^{13}C_{org}$ of between -22‰ and -20% relative to PDB (Meyers, 1994). Galimov (2006) reported that in formation of sapropelic organic matter, for instance petroleum source rocks, $\delta^{13}C_{org}$ values become isotopically light over time since the parent material from which this organic matter type is formed is initially isotopically light.

Elemental analysis was used to examine the elemental composition of sediments in this study. Since whole rock element signatures may be less representative of depositional environments (e.g., Abanda and Hannigan, 2006), a sequential extraction protocol was employed in this study. The carbonate fraction records information about seawater at time of formation of the carbonate fraction of the sediments, while the detrital fraction was used to evaluate detrital and nutrient input into the water column as these influence organic productivity and organic matter dilution (Huc et al., 2005). Certain trace elements (e.g., U, V, Mo., etc.) are enriched in anoxic environments and this property is what makes these elements useful as proxies of redox state (e.g., Koide et al., 1986; Emerson and

Huested, 1991; Crusius et al., 1996; Tribovillard et al., 2006; Steinmann et al., 2020). Other trace elements (e.g., Ag, Cu, Cd, Ni, etc) have an affinity for organic matter and these elements are usually delivered to sediments along with organic matter, consequently, rendering these elements as good productivity proxies (e.g., Eagle et al., 2003; Tribovillard et al., 2006; McKay and Pedersen, 2008). Enrichment factors were calculated for these elemental environmental proxies with enrichment defined as concentrations of an element in excess of its crustal abundance, where crustal abundance is usually taken to be concentration of the element in some "average lithology" (e.g., Post Archean Australian Shale (PAAS), Average shale, North American Shale Composite (NASC), etc). "Average carbonates" values as reported by Turekian and Wedepohl (1961) are used in our calculations of enrichment factors in this research project because of the mixed siliciclastic-carbonate nature of our samples. Enrichment factors greater than 1 are described as enriched relative to average carbonates and values less than 1 are depleted. Enrichment factor is calculated thus (Tribovillard et al., 2006):

$$\text{Enrichment Factor}_{\text{trace element}} = (\text{Trace metal}_{\text{sample}}/\text{Al}_{\text{sample}})/(\text{Trace metal}_{\text{average carbonate}}/\text{Al}_{\text{average carbonate}})$$

Biological markers (biomarkers) are organic compounds that are present in geologic compounds and whose structures can be unambiguously linked to the structures of precursor compounds occurring in original source materials (Philp, 1985). These fossil markers of previous life are composed of carbon, hydrogen and other elements and they are found in sediments, rocks and crude oils (Peters and Fowler, 2002; Peters et al., 2007). As a result of diagenesis and maturation changes, the biomarkers employed for organic geochemical studies have been converted from their oxygenated or unsaturated precursors into forms typically found in sediments. Consequently, biomarkers extracted from rocks and sediments provide direct evidence for prevailing environmental conditions in the geologic past during deposition of the sediments from which they were extracted (Philp, 1985). Various authors (e.g., Brooks et al., 1969; Didyk et al., 1978; Sofer, 1988; Hughes et al., 1995; Patranabis-Deb et al., 2016) have utilized biomarker parameters, such as the ratio of pristane to phytane, to interpret paleoenvironmental conditions under which sediments that formed rocks were deposited. Ratios < 1 are interpreted as indicating deposition under marine anoxic conditions. Values of the pristane to phytane ratio > 3 indicate deposition in oxic settings or are interpreted as indicating detrital sources of organic matter. Another biomarker parameter which has been used to discriminate provenance of preserved organic matter is the odd-even predominance of n-alkanes in the C_{15} to C_{33} range. Powell and McKirdy (1973), Dembicki Jr. et al. (1976) and Sofer (1988) have all demonstrated the utility of discriminating between carbonate-sourced organic matter (even predominance of n-alkanes) from clastic-sourced organic matter (odd predominance of n-alkanes) using this parameter.

1.2 Dissertation Layout

The dissertation is divided into three individual chapters bracketed by an introductory chapter (chapter I) and a chapter with conclusions and future work (chapter V). The chapters detail various aspects of the research project and are written as standalone manuscripts thus, they can be read on their own without reading the rest of the dissertation. Furthermore, one of these chapters is already published (chapter II) and the other two chapters will be submitted to peer-reviewed journals for publication imminently (chapters III and IV).

Chapter II is published as Adeboye, O. O., Riedinger, N., Wu, T., Grammer G. M. and Quan, T. M. (2020) in the journal Marine and Petroleum Geology and is titled Redox conditions on the Anadarko Shelf of Oklahoma during the deposition of the “Mississippian Limestone” (https://doi.org/10.1016/j.marpetgeo.2020.104345). This chapter evaluates redox conditions at time of deposition of the Mississippian Limestone interval on the Anadarko Shelf using a combination of stable nitrogen isotopes and elemental geochemistry.

Chapter III presents insights on paleoproductivity and detrital input at time of deposition of the Mississippian Limestone interval within the Anadarko Shelf of Oklahoma using stable carbon isotopes of organic carbon and elemental geochemistry data.

Chapter IV presents results from evaluation of environmental conditions during deposition of the Mississippian Limestone interval using Rock-Eval analysis and evaluation of saturate biomarkers, as well as evaluation of the oil source rock potential of the unit in the STACK resource play area within the Anadarko Shelf.

CHAPTER II

REDOX CONDITIONS ON THE ANADARKO SHELF OF OKLAHOMA DURING THE DEPOSITION OF THE MISSISSIPPIAN LIMESTONE

2.1 Abstract

A multiproxy approach including stable nitrogen isotopes and redox sensitive trace elements were employed in order to evaluate the impact of depositional redox conditions on organic matter accumulations within the Mississippian Limestone interval in the Anadarko Shelf of Oklahoma and also to investigate hydrocarbon source rock potential of the Mississippian Limestone in the study area. Nitrogen isotopes ($\delta^{15}N$), total organic carbon (TOC), and concentrations of redox-sensitive trace elements (Cu, Mn, Mo, Ni, U, V) were measured on samples from a core drilled in Canadian County, Oklahoma. TOC values are between 0-2.5 % and average 0.8 % in the studied interval of the core. The $\delta^{15}N$ data (3 ‰ to 14 ‰, average 8 ± 1 ‰) indicate sediment deposition under oxic to suboxic water conditions. This interpretation of depositional redox conditions is supported by elemental redox proxies which show no enrichment relative to average carbonate. Our geochemical data suggest that the Mississippian Limestone is unlikely to be a source rock for oil due to pervasively oxic to suboxic depositional redox conditions which would have resulted in oxidation of organic matter.

2.2 Introduction

The Mississippian Limestone is an informal name used extensively throughout the Anadarko and Arkoma Basins of Oklahoma. The term encompasses units of multiple ages within the Mississippian Period, often lumped together because of the scarcity of biostratigraphic control (Mazzullo et al., 2013). Significant quantities of hydrocarbons have been produced from various zones of the Mississippian Limestone in the Anadarko Basin and Shelf, historically via vertical well completions and more recently by combining horizontal drilling with hydraulic fracturing (Koch et al., 2014; Wilson et al., 2019). The majority of previous investigations carried out on the Mississippian Limestone interval of Oklahoma have focused on the sedimentology and sequence stratigraphy of the interval (e.g., LeBlanc, 2014; Flinton, 2016; Childress and Grammer, 2019; Price and Grammer, 2019; Shelley et al., 2019) while a subordinate amount of geochemical studies undertaken on this interval have focused on its source rock characteristics (e.g., Wang and Philp, 1997; Al Atwah, 2015; Al Atwah et al., 2019). Results from the available geochemical investigations of the Mississippian Limestone suggest that the interval is a hydrocarbon source rock and some of the hydrocarbons produced from the interval are self-sourced (e.g., Wang and Philp, 1997). The dearth of published studies focused on the source rock characteristics of the Mississippian Limestone is consistent with the relative paucity of geochemical source rock studies undertaken on carbonate rocks (e.g., Hunt, 1967; Malek-Aslani, 1980; Huo et al., 2019). Geochemical studies conducted on carbonate rocks tend to focus on outcrops or on those carbonate rocks that lack hydrocarbon source rock potential (e.g., Veizer, 1983; Cullers, 2002; Frimmel, 2009; Hamon et al., 2016; Tostevin, 2016; Owens et al., 2017). Similarly, recent studies of the Mississippian Limestone interval which incorporated geochemistry have focused almost exclusively on reservoir performance of the unit with less attention paid to investigating the source rock characteristics of the interval (e.g., Dupont and Grammer, 2019; Steinmann et al., 2020). Our study aims to characterize the Mississippian Limestone interval and to examine the source rock characteristics of this interval based on multiple geochemical proxies.

The deposition of rocks that are enriched in organic matter (and which are thus, potential hydrocarbon source rocks) is controlled by depositional redox conditions (e.g., Demaison and Moore, 1980), productivity (e.g., Pedersen and Calvert, 1990), and interactions of various other factors including dilution by non-organic matter detritus (e.g., Canfield, 1994; Bohacs et al., 2005; Tyson, 2005; Crombez et al., 2017). As part of a larger organic and inorganic geochemical study of the Mississippian Limestone interval of Oklahoma, we measured multiple redox proxies in order to characterize environmental conditions at the time of deposition of the unit in an area of the Anadarko Shelf. A secondary aim of this study was to determine if depositional redox conditions were responsible for organic richness in the Mississippian Limestone and hence, any possible hydrocarbon source rock potential of this interval within the study area. This paper presents findings on the investigation of depositional redox conditions of the Mississippian Limestone interval in an area of the Anadarko Shelf using bulk stable nitrogen isotopes ($\delta^{15}N$) and the elemental redox proxies copper, manganese, molybdenum, nickel, uranium and vanadium.

The utility of the $\delta^{15}N$ proxy as a reliable water column redox proxy has been demonstrated across a variety of environments (Brandes and Devol, 1997; Quan et al., 2008, 2013; Rivera et al., 2015; Kast et al., 2019). Bulk $\delta^{15}N$ values are a useful redox proxy because the process of denitrification predominates in suboxic waters. Denitrification preferentially removes light ^{14}N, resulting in the retention of the heavier ^{15}N isotope in sedimentary organic matter; consequently, bulk $\delta^{15}N$ values are higher in suboxic environments than in anoxic or oxic environments. In anoxic environments, nitrogen fixation (a process with minimal N isotope fractionation) is predominant and in oxic environments nitrification goes to completion. Consequently, lower bulk $\delta^{15}N$ values are associated with both oxic and anoxic environments (Mariotti et al., 1981; Quan et al., 2013). It is important to note that a negative shift in bulk $\delta^{15}N$ values could result from the transition from suboxic to oxic waters or from the transition from suboxic to anoxic waters. It is, thus, desirable to combine bulk nitrogen isotope results with results from other redox proxies, such as redox sensitive elements, in order to deduce robust interpretations of paleoenvironmental conditions. Elemental redox proxies have frequently been used to infer environmental conditions at time of deposition (e.g., Hatch and Leventhal, 1992; Jones and Manning, 1994; Algeo, 2004; Algeo and Maynard, 2004; Algeo and Lyons, 2006; McManus et al., 2006; Algeo and Rowe, 2012; Scott and Lyons, 2012; Hua et al., 2013). Elements such as copper, manganese, molybdenum, nickel, uranium and vanadium exhibit various oxidation states under different redox conditions and tend to be enriched in reducing environments, thereby making them useful redox proxies. In addition, some of these elements (e.g., copper, nickel) have a strong affinity with organic matter and have also been utilized as paleoproductivity proxies (e.g., Koide et al., 1986; Brumsack, 1991; Emerson and Huested, 1991; Crusius et al., 1996; Tribovillard et al., 2006; Little et al., 2015).

2.3 Samples and Methods

2.3.1 Geological Setting and Geographic Location of Samples

Sediments of the Mississippian Limestone interval were deposited in an ancient epeiric sea (Gutschick and Sandberg, 1983). The Mississippian Subsystem has been described as a period of changing climate with transitions from greenhouse to icehouse conditions (Haq and Schutter, 2008; LeBlanc, 2014). The climatic transitions and their consequences described by Haq and Schutter (2008) and LeBlanc (2014) would have influenced environmental conditions (e.g., oxygen concentrations) which would subsequently have influenced the production and preservation of organic matter during deposition of the Mississippian Limestone interval (cf., Huc et al., 2005). The samples for the current study were obtained from the cored interval of a petroleum exploration well drilled in the Anadarko Shelf of north central Oklahoma (Fig. 2.1). The Anadarko Shelf has been described as a carbonate ramp environment located within 20° S of the paleoequator (Lane and DeKeyser, 1980; Gutschick and Sandberg, 1983). Furthermore, it has been suggested that deposition of the Mississippian Limestone occurred along a distally-steepened ramp and the lithological variations observed in the interval are a result of changes in eustasy and relative sea level related to Milankovitch cycle variations (LeBlanc, 2014). Carbonate ramps, of which distally-steepened ramps are an end member, are widespread in geologic periods when framework builders were not abundant. Ramps have gentle slopes of 1° or less that extend for very long distances, on the order of kilometres and ramp development tends to be favoured in settings where sedimentation is not strongly differentiated between shallow waters with high carbonate productivity and deeper waters with lower carbonate production (Wright and Faulkner, 1990). Distally-steepened ramps possess characteristics of ramps and rimmed shelves but differ from rimmed shelves, because their major breaks in slope occur many kilometres seaward of high-energy shoals (Read, 1985).

The Mississippian Limestone interval is underlain by the Woodford Shale, a prolific Devonian source rock in the Mid-Continent region, and overlain by rocks of the Pennsylvanian Springer Formation (Wang and Philp, 1997). Age constraint on rocks of the Mississippian Limestone interval in our study area is poor because of the absence of conodonts within the interval, however, a study by Hunt (2017) carried out on the Mississippian Limestone to the east of our study area indicates that the Mississippian Limestone in north central Oklahoma is of Middle Osagean to Late Chesterian age (Uppermost Tournaisian to Latest Visean, ~ 346.7-330.9 Ma). The Mississippian Limestone interval in our study area is of heterogeneous lithology, and is comprised of calcareous, siliciclastic siltstones and carbonate packstones-grainstones.

2.3.2 Lithology Description of Facies

Wang et al. (2019) identified 7 distinct lithofacies in the Mississippian Limestone on the core examined for this geochemical study. Samples investigated in the present study encompass 6 of the identified lithofacies.

(1) Massive-bedded siltstone: described by Wang et al. (2019) as a low energy facies containing rare sedimentary or biogenic structures and interpreted as formed in distal outer ramp to basinal environments within generally restricted bottom waters.

(2) Laminated calcareous siltstone: described as deposited near storm wave base along more proximal outer ramp settings. The laminated calcareous siltstone lithofacies is characterized by millimetre-thick, alternating darker coloured and lighter coloured laminae, as well as the presence of millimetre-scale hummocky cross-stratification in the lighter coloured laminae.

(3) Burrowed calcareous siltstone: described as dominated by low diversity, high abundance *Phycosiphon* trace fossils, localised occurrences of *Zoophycos*, and occasional occurrence of *Teichichnus*. Intensity of bioturbation in this lithofacies is characterized as being relatively localised with isolated burrow clusters. This lithofacies is proposed as deposited in a proximal outer ramp to distal middle ramp environment close to storm wave base.

(4) Bioturbated calcareous siltstone: similar to the burrowed calcareous siltstone lithofacies; interpreted as deposited in a proximal outer ramp to distal middle ramp environment close to storm wave base and characterised by connected clusters of burrow networks that are homogenised. *Phycosiphon* traces dominate in this lithofacies although, similar to the burrowed calcareous siltstone lithofacies, there are localised occurrences of *Zoophycos*. Occasional *Teichichnus* traces also occur within this lithofacies.

(5) Massive-bedded packstone-grainstone: contains abundant peloids and skeletal debris (mostly crinoidal). Interpreted as storm- or earthquake-induced sediment liquefaction and storm transport in a proximal outer ramp to distal middle ramp setting around storm wave base. Presence of low energy mud drapes and burrowed zones indicate fluctuating energy levels at time of deposition.

(6) Hummocky cross-stratified (HCS)-planar laminated packstone-grainstone: deposited during rapid sedimentation precipitated by storms in a proximal outer ramp to distal middle ramp setting around storm wave base. This lithofacies contains abundant HCS and planar laminations and localized climbing ripples. Similar to the massive-bedded packstone-grainstone lithofacies, presence of low energy mud drapes and burrowed zones indicates fluctuating energy levels at time of deposition.

2.3.3 Sample Selection and Preparation

Samples were collected from a petroleum exploration well drilled in Canadian County, Oklahoma. The Mississippian Limestone interval in this well is between 2,955.95 m (9,698 ft) to 3,146.45 m (10,323 ft) as recorded in publicly accessible regulatory filings. Sampling was carried out based on the core descriptions from Wang et al. (2019).

A total of 143 samples were taken at intervals not exceeding approximately 0.61 m (2 ft) between 3,007.61 m (9,867.5 ft) and 3,049.68 m (10,005.5 ft) from the length of drill core which was split in half prior to sampling. One-third of each retrieved sample was manually pulverised to fine powder in an agate mortar and pestle. Pulverisation was carried out in the agate mortar to prevent metal contamination which could result in anomalous measurements of trace element concentrations of the samples.

2.3.4 Total Organic Carbon (TOC) Analysis

In order to determine the total organic carbon (TOC) content of the samples, approximately 50-55 mg of powdered rock samples were placed in silver capsules and dried for a period of 8 hours in an oven at a temperature of 50°C. Oven dried samples were acidified in silver capsules by sequential treatment with double deionised water (Sartorius), 25% hydrochloric acid until cessation of effervescence, and finally, concentrated hydrochloric acid until effervescence was no longer observed. Acidification was undertaken in order to eliminate inorganic carbon from the samples prior to TOC analysis. Acidified samples were subsequently dried in an oven at a temperature of 50°C for a period of 48 hours to ensure complete dryness. Once samples were dry, they were wrapped in tin capsules after which TOC was analysed using a Costech® ECS 4010 elemental combustion system. Acetanilide was used as a concentration standard for TOC, which is reported in units of weight % (wt. %).

2.3.5 Nitrogen Stable Isotope Redox Proxy

Approximately 50-55 mg of powdered rock samples were dried for a period of 8 hours in an oven at a temperature of 50°C. The dried rock samples were transferred into tin capsules and then analysed for N stable isotopes on the EA-IRMS. Bulk $\delta^{15}N$ results are reported relative to air in per mille units (‰) following the standard δ notation. Bulk nitrogen isotope ($\delta^{15}N$) measurements were carried out on a Thermo Finnigan Deltaplus XL® isotope ratio mass spectrometer interfaced with a Costech® ECS 4010 elemental combustion system (EA-IRMS). Isotope standards USGS 40 and NIST N3 were used for calibration and validation of $\delta^{15}N$ while acetanilide was used as a concentration standard for N in the study. Analytical error is ± 0.4 ‰ and is estimated from the standard deviation of a set of repeat measurements of the standards.

2.3.6 Elemental Redox Proxies

Whole rock trace element signatures may be less representative of depositional environment (Abanda and Hannigan, 2006) hence, we applied a sequential extraction and digestion protocol in this study. Crushed rocks underwent sequential digestion using a protocol modified from earlier works by Tessier et al. (1979), Tessier et al. (1996), and Poulton and Canfield (2005) in order to separate elements associated with the carbonate fraction of the rock from those associated with the non-carbonate fraction (Steinmann et al., 2020). A solution of 1M sodium acetate was prepared by dissolving anhydrous sodium acetate (trace metal grade) in double deionised water (MilliQ, Millipore) and brought up to a pH of 4 by the addition of glacial acetic acid. The solution was added to between 250-300 mg of crushed and homogenised rock samples and left to sit for an hour to react with the carbonate phase prior to shaking for 24 hours in an autoshaker. After the agitation step, the sodium acetate solution and rock mixture were centrifuged at 5500 rpm for 5 minutes and the supernatant was carefully transferred to polypropylene vials. The supernatant was analysed for trace elements associated with the carbonate fraction of the rock. The remaining solid, which was ultimately analysed for trace elements associated with the non-carbonate fraction, was rinsed in double deionised water and centrifuged at 5500 rpm for 5 minutes and the supernatant was removed. This step was carried out twice prior to three-acid digestion under heat and pressure using a PicoTrace® pressure digestion apparatus. Three mL of concentrated nitric acid, 1.5 mL of concentrated hydrofluoric acid, and 2 mL of concentrated perchloric acid (all acids were of trace metal grade) was added to the rinsed residue. Samples were left to soak in the multi-acid solution for 24 hours under normal atmospheric pressure and room temperature before the pressure digestion step. The samples were taken up in a 5 % nitric acid solution and stored cool. NIST standard reference material 1643f, USGS Brush Creek Shale SBC-1, and an in-house limestone standard were digested with the samples for quality control. Element contents were measured using a Thermo Scientific iCAP Qc® inductively coupled plasma-mass spectrometer (ICP-MS). The analytical error was better than 6 % for both carbonate fraction and non-carbonate fraction elemental content measurements. Total element content per sample was derived by calculating the sum of the measured contents of carbonate and non-carbonate fractions for the elemental redox proxies Cu, Mn, Mo, Ni, U and V for each sample. Enrichment factors of elemental redox proxies were calculated based on computed total element contents as described by Brumsack (2006) and Tribovillard et al. (2006): $\text{Enrichment Factor}_{\text{trace element}} = (\text{Trace element}_{\text{sample}}/\text{Al}_{\text{sample}})/(\text{Trace element}_{\text{average carbonate}}/\text{Al}_{\text{average carbonate}})$

Elements with enrichment factors greater than 1 are described as enriched while those with values less than 1 are considered to be depleted. Enrichment factors of elemental redox proxies derived in this study are compared to “average carbonates” values reported by Turekian and Wedepohl (1961) due to the high carbonate content of these samples. In comparison, enrichment factors relative to “average shale” values (Wedepohl, 1971) show a shift to slightly higher enrichment factor values.

For further discussion, water column redox conditions in this study are defined as oxic (> 2 ml O_2/l H_2O), suboxic (between 0.2 and 2 ml O_2/l H_2O), anoxic (< 0.2 ml O_2/l H_2O) or euxinic (0 ml O_2/l H_2O in the water column and presence of dissolved hydrogen sulphide, H_2S) after the parameters published by Tyson and Pearson (1991).

2.4 Results

Analytical results for bulk $\delta^{15}N$ and TOC measurements are presented in table 2.1 while results of the element contents analysis of non-carbonate fraction, redox-sensitive elements are presented in table 2.2. The redox-sensitive element contents of the carbonate fraction, redox-sensitive elements are presented in table 2.3 and table 2.4 contains total contents of redox-sensitive elements obtained by adding contents of redox-sensitive elements obtained from the carbonate and non-carbonate fractions of the investigated samples.

The TOC values in the studied core are between 0.0-2.5 % with an average value of 0.8 ± 0.5 %. Bulk $\delta^{15}N$ measurements averaged 8 ± 1 ‰ and ranged between 3 ‰ to 14 ‰ in the samples examined (Table 2.1, Fig. 2.2). In the non-carbonate fraction, measured Al contents were between 0.60 wt. % and 5.35 wt. %, Cu contents were between 1.07 ppm to 27.15 ppm, Mn contents varied from a low of 10.97 ppm to a high of 114.86 ppm, Mo contents ranged from 0.00 ppm to 35.19 ppm, Ni contents were between 2.72 ppm and 78.11 ppm, contents of U ranged between 0.67 ppm and 18.10 ppm and finally, contents of V were between 9.59 ppm and 760.08 ppm. In contrast, carbonate fraction contents of Al were between 0.00 wt. % to 0.03 wt. % (32.10 ppm to 283.19 ppm), those of Cu ranged from 0.00 ppm to 18.74 ppm, Mn carbonate fraction contents were between 9.73 ppm and 549.65 ppm, contents of Mo in the carbonate fraction were between 0.07 ppm and 16.10 ppm, Ni contents in the carbonate fraction were between 0.49 ppm and 47.00 ppm, carbonate fraction U contents ranged in value between 0.08 ppm and 1.68 ppm and lastly, carbonate fraction contents for V ranged from a low of 0.24 ppm to a high of 28.60 ppm.

The contents of the non-carbonate fractions of the redox sensitive elements Al, Cu, Mo, Ni, U and V (Table 2.2) are generally higher than the contents of these elements associated with the carbonate fraction of the rock (Table 2.3). This is in contrast to the element Mn, where its content in the carbonate associated fraction is higher than that in the non-carbonate fraction. Enrichment factors were calculated for total element concentrations. Calculated enrichment factors (EF) are presented in Table 2.5 and figure 2.5. The redox proxies Mn and U are depleted at every sampled depth whereas, calculated EF for Cu, Mo, Ni and V show varying levels of slight enrichment at various depths.

2.5 Discussion

Based upon the trends observed in the nitrogen isotope proxy and the general lack of enrichment observed in the elemental redox proxies, it is likely that redox conditions in the water column fluctuated between oxic and suboxic, during deposition of the sediments examined in this study (Fig. 2.3). Results from the stable nitrogen isotope measurements ($\delta^{15}N$ values between 3‰ and 14‰, average $\delta^{15}N$ values of 8 ± 1 ‰) suggest that suboxic conditions, shown by higher $\delta^{15}N$ values, were intermittent in the water column during deposition of sediments in the study area. Lower $\delta^{15}N$ values indicate periods when either nitrification or nitrogen fixation predominated in the water column reflecting either oxic or anoxic water column conditions (Quan et al., 2013). The overall data indicates, however, that denitrification (and resulting suboxia) was moderate in the water column at the time of deposition of these sediments. We are unable to ascribe observed variations in lithology or petrophysically significant facies (defined by Wang et al., 2019) to changes in depositional redox conditions inferred from bulk $\delta^{15}N$ values (Figs. 2.2 and 2.3). This suggests that another factor (e.g., Milankovich sea level cycles and/or intermittent storm deposition as proposed by LeBlanc, 2014; Wang et al., 2019) other than water column redox is responsible for the lithological and facies variations observed in this core. The nitrogen isotope redox proxy stays fairly consistent irrespective of sea level cycle, in the area of the Anadarko Shelf where these sediments were deposited. Since the nitrogen stable isotope proxy is unable to conclusively resolve the state of depositional redox, elemental redox proxies were examined to further constrain bottom water redox conditions at time of deposition in the study area.

Similar to the results of Steinmann et al. (2020), we found that contents of elemental redox proxies Mo, U and V are higher in the non-carbonate fraction than in the carbonate fraction (Tables 2.2

and 2.3). These findings suggest that the origins of these elements are likely primarily detrital and these elements were supplied into the ocean via continental runoff (cf. Bruland et al., 2014 and references therein). The paleo proxies Cu and Ni also display higher contents in the non-carbonate fraction, when compared to their carbonate fraction contents, however no correlation with Al or Ti was observed (Fig. 2.4 and Tables 2.2 and 2.3). This lack of correlation with Al or Ti, while not completely ruling out detrital input as the main input source for these paleo proxies to the study area, could indicate diagenetic modifications including remobilisation of specific elements (e.g., Abanda and Hannigan, 2006; Riedinger et al., 2014; Hood et al., 2018). Manganese in the carbonate fraction is higher than the in the non-carbonate fraction suggesting that delivery of Mn to the study area might be associated with water column processes, especially since Mn is known to substitute for Ca and Mg in carbonates (Calvert and Price, 1970; Veizer, 1983; Soldati et al., 2016).

Enrichment factors of all elemental redox proxies examined in this study (Cu, Mn, Mo, Ni, U and V) indicate that there is lack of overall enrichment above the "average carbonates" values of Turekian and Wedepohl (1961) (Table 2.5 and Fig. 2.5) suggesting the presence of ventilated bottom waters. Previous studies have reported that depletion or lack of significant enrichment of elemental redox proxies such as Cu, Mn, Mo, Ni, U and V, relative to "average shales", is a hallmark of oxic environments (e.g., Koide et al., 1986; Rimmer, 2004; Borchers et al., 2005; Brumsack, 2006; Tribovillard et al., 2006; Arnaboldi and Meyers, 2007; Ross and Bustin, 2009). While the enrichment factors in the current study were calculated with respect to "average carbonates", the depletion or lack of significant enrichment described by these various authors was observed in the current study for the elemental redox proxies Cu, Mn, Ni, U, Mo and, V in the vast majority of samples (Fig. 2.5).

Although we observed slight enrichment and relatively high concentrations of Mo in certain samples examined in this study (Table 2.4 and Fig. 2.5), a comparison with the enrichment factors and concentrations of Mo in another lithologically heterogeneous rock unit with petroleum source rock potential, such as the Monterey Formation, indicates that the values seen in the Mississippian Limestone are not particularly high. The Monterey Formation, California is an organic rich, petroleum source rock characterized by heterogeneous (carbonaceous, calcareous and siliceous) lithologies similar to the Mississppian Limestone interval, with reported Mo EFs of greater than 350 relative to "average shale" (Hancock et al., 2019). A similar situation is observed for the elemental redox proxy V, which shows slight enrichment (EF no greater than 5) in this study compared to enrichment factors up to 29 in the Monterey Shale (Hancock et al., 2019). Studies by Rimmer (2004), Borchers et al. (2005) and Scott et al. (2017) also report Mo concentrations that are greater than 1000 ppm, concentrations of V greater than 500 ppm, and enrichment factors of 100 or greater for these redox sensitive elements (relative to "average shale") in studies on shales and modern sediments from settings where these redox sensitive elements are significantly enriched due to anoxic or euxinic environmental conditions.

Results from the current study in the Anadarko Shelf showing depletion or lack of significant enrichment above "average carbonates" values for the investigated elemental redox proxies (Cu, Mn, Mo, Ni, U, V) are in agreement with the results of a study on the Mississippian Limestone by Steinmann et al. (2020) who examined Mississippian Limestone outcrops in Jane, Missouri, an area to the east of the location where the well from which the samples for our study spudded. Our results and those reported by Steinmann et al. (2020) indicate that conditions were oxic to suboxic at time of deposition of the Mississippian Limestone interval (cf. Brumsack, 2006). The study of Steinmann et al. (2020) noted the depletion or lack of significant enrichment of the elemental redox proxies (Mo, U and V). The results from Steinmann et al. (2020) and the current study suggest that oxic-suboxic bottom water conditions were widespread and extended eastward from modern day north-central Oklahoma to south-west Missouri during deposition of the Mississippian Limestone interval. Unlike the study by Steinmann et al. (2020), minimal enrichments of Mo and V were observed at multiple depths in this study (Fig. 2.4, Tables 2.4 and 2.5) although these enrichments are still well below those reported by Borchers et al. (2005) who report enrichment factors of over 100 for Molybdenum relative to "average shale" ("average shale" concentrations are documented in Wedepohl, 1971).

Mo contents of 70 ppm or greater, previously thought to occur only in euxinic environments, have been described as occurring under nitrogenous, hence, suboxic conditions (cf. Canfield and Thamdrup, 2009) via a particulate shuttle associated with Mn and Fe (Scholz et al., 2017). Results from the current study (Mo contents of up to approximately 51 ppm at sample depth 3024.38m, Table 2.4) suggest that a similar particulate shuttle may have been operational, at least intermittently, in our Anadarko Shelf study area based on a combination of measured Mo contents and bulk stable nitrogen isotope signatures, which are suggestive of suboxic water column conditions during deposition. Similarly, Huang et al. (2015) report that V is incorporated into sediments through organic matter or in oxygen-depleted (suboxic) environments. We do not observe any correlation between organic matter (proxied by TOC) and V, neither do we observe any correlation between TOC and the other paleo proxies examined in this study (Cu, Mn, Mo, Ni, U). This suggests that total V content of up to approximately 497 ppm (sample depth 3022.88m, Table 2.4) observed in our study are likely due to suboxic depositional redox conditions.

Very elevated Mo enrichments can also be associated with the presence of sulfurised organic matter as observed in limestones of the Orbagnoux Formation of France, the Bancs Jumeaux Formation of France, and the Kashpir oil shales of Russia (Tribovillard et al., 2004). Furthermore, it was reported by Tribovillard et al. that Mo enrichment factors relative to “average shale” did not exceed 20 in rock intervals that lacked sulfurised organic matter whereas, Mo enrichment factors in the presence of sulfurised organic matter was well over 500 and even exceeded 1000 in some cases. Similarly, slight Mo enrichments (EF up to 20) have been observed in sediments and rocks deposited under fully oxic water columns (e.g., Tribovillard et al., 2004; Scott and Lyons, 2012). Although we did not explicitly investigate the character of the organic matter present in the Mississippian Limestone for this study, we believe that it is likely to be non-sulfurised since previous studies by Kim and Philp (2001) and Al Atwah (2015) did not report the presence of sulfurised organic matter in the Mississippian Limestone. Determining the amounts of sulfurised organic matter and pyritic Sulphur, if any, that may be present in the Mississippian Limestone interval of the U.S. Mid-Continent region, although beyond the scope of the present study, would be a worthwhile endeavour.

Varying intensities of burrows and bioturbation observed in multiple lithofacies (e.g, in the burrowed calcareous siltstone, bioturbated calcareous siltstone and in the massive-bedded packstone-grainstone lithofacies) and described by Wang et al. (2019) is indicative of the presence of oxygen in the study area at time of deposition. Other outcrop and subsurface studies undertaken on the Mississippian Limestone interval throughout the Mid-Continent region of the USA have also documented the presence of bioturbation (e.g., Flinton, 2016), thus lending further support to the inference that the area of the Anadarko Shelf examined in this study was ventilated at the time these sediments were deposited. That these studies reported low diversity in type of burrows suggests less than optimal oxygen levels (or perhaps some other limiting factor). When these previous results are examined in addition to the results of water column redox state determined from bulk stable nitrogen isotopes (Fig. 2.3) as well as the depletion and/or lack of significant enrichment of the suite of measured elemental redox proxies investigated in this study (Fig. 2.5), they strongly suggest that this our study site was oxygenated (fully oxic to suboxic) at time of deposition of these sediments.

2.5.1 Implications for the Mississippian Limestone Interval as a Source Rock

It has been suggested that rocks of the Mississippian Limestone have hydrocarbon source rock potential and show a distinct geochemical signature different from that of the underlying Woodford Shale - an important source rock which is present within the Anadarko Basin and shelf (Wang and Philp, 1997; Kim and Philp, 2001; Al Atwah, 2015 and Wang and Philp, 2019). The amount of organic carbon in the investigated Mississippian Limestone sediments averages 0.8 wt. % (with maximum contents up to 2.5 wt. %, Table 2.1). Thus, this level of organic richness is theoretically high enough in the rocks in order to be considered as having fair to good hydrocarbon source potential (cf. Peters and Cassa, 1994; Sorkhabi, 2016). However, additional parameters such as thermal maturity evaluation, rock eval pyrolysis and visual kerogen analysis should be taken into account in the course of evaluating the source rock potential.

Deposition of source rocks are thought to be influenced by the combined effects of depositional redox, productivity and dilution (e.g., Demaison and Moore, 1980; Pedersen and Calvert, 1990; Canfield, 1994; Tyson, 2005). In this study, depositional redox conditions were evaluated in an area of the Anadarko Shelf using stable nitrogen isotopes and elemental redox proxies. Our results indicate that there is a lack of correlation between TOC and water column redox state proxied by bulk $\delta^{15}N$ (Fig. 2.6, $R^2 = 0.45$). Similarly, no correlation is observed between TOC and concentration of Mo, the benthic zone redox proxy, which showed the greatest, albeit minimal enrichment, of the suite of elemental redox proxies considered in this study (Fig. 2.7, $R^2 = 0.29$). These findings suggest that depositional redox state was not the dominant control on organic matter preservation within the Mississippian Limestone in this area of the Anadarko Shelf. This explanation is predicated on the combination of water column and elemental redox proxies that indicate suboxic to oxic redox conditions at time of deposition of the Mississippian Limestone sediments in our study area. Alternatively, our results indicate that organic matter preserved within the rocks of the Mississippian Limestone in this area of the Anadarko Shelf may consist of both autochthonous and allochthonous types. Furthermore, our results could also indicate that heightened productivity may well be another possible factor which is responsible for deposition and preservation of organic matter-rich intervals in the Mississippian Limestone in this area of the Anadarko Shelf. This has been alluded to by previous studies undertaken by Kim and Philp (2001) and Al Atwah (2015). These workers suggest that algal bloom events may have been responsible for organic matter-rich zones in the Mississippian Limestone interval. Although we can neither confirm nor deny the presence of algae-derived organic matter in the samples examined for the current study because we did not conduct visual kerogen analysis, we observed depletion of the elemental paleo proxies Cu and Ni which can both serve as productivity proxies (cf. Tribovillard et al., 2006). While the depletion of Cu and Ni does not support the assertion that heightened productivity is responsible for organic rich intervals in the

Mississippian Limestone, Cu and Ni depletion might not necessarily preclude the incidence of heightened productivity since these elemental proxies are also sensitive to depositional redox conditions. This is because Cu and Ni depletion reported in the current study may be due to oxygenated environmental conditions during deposition or diagenetic modifications or remobilisation of these paleo proxies post deposition (e.g., Abanda and Hannigan, 2006; Hood et al., 2018).

The apparent paradox of potential source rocks occurring in generally oxygenated settings is not uncommon. Bustin (1988) reported similar findings from the Tertiary Niger Delta and concluded by stating that source rocks of marginal quality (< 3% TOC) were viable due to their great volume (brought about by heightened productivity of the delta), rapid maturation rates and short migration distances (due to interbedded source rocks and permeable reservoir units). Kim and Philp (2001) suggested that the relationship between detrital input and organic richness warrants further study so as to unravel, and perhaps, be able to predict organic matter enrichment and consequent source rock potential in the Mississippian Limestone interval and we agree with this assertion. Despite observing high TOC in certain intervals of the Mississippian Limestone in the samples we examined for this study, the totality of our results from investigating depositional redox conditions of the Mississippian Limestone point towards the presence of low quality organic matter. This is because the organic matter present within the unit at our study site was oxidised as a result of the pervasive oxic to suboxic environmental conditions at time of deposition of the Mississippian Limestone and as such, will result in the lack of potential of this organic matter to generate oil. Additional studies that incorporate results from Rock-Eval pyrolysis analysis, visual kerogen analysis, stable isotopes of organic carbon as well as both saturate and aromatic biomarkers could help to further refine the assessments and conclusions regarding the source rock potential of the Mississippian Limestone sediments within the Anadarko Shelf.

2.6 Conclusions and Summary

Results from stable nitrogen isotopes and a suite of redox sensitive elements suggest that water column redox conditions at time of deposition of the Mississippian Limestone interval in the area of the Anadarko Shelf of Oklahoma was oxic to suboxic. Furthermore, no relationship is observed between depositional redox conditions and organic richness (proxied by TOC) suggesting that depositional redox state was not the dominant factor which influenced organic matter accumulation in this area of the Anadarko Shelf during deposition or that perhaps, there are two populations of organic matter present within the Mississippian Limestone. An alternative explanation is needed for intervals of the Mississippian Limestone that are enriched in organic matter (intervals with > 0.5-1 % TOC). Findings from our study indicate that the Mississippian Limestone interval, at least in this area of the Anadarko Shelf, has poor source rock potential. This is because of poor preservation of organic matter present within the unit at our study site due to pervasive oxic to suboxic depositional conditions; the organic matter in the Mississippian Limestone is likely oxidised and as such, will result in the lack of potential of this organic matter to generate oil. Further studies that integrate results from Rock Eval pyrolysis, visual kerogen assessment, stable isotopes of organic carbon and biomarkers could help to further confirm the assessments and conclusions regarding the source rock potential of Mississippian Limestone sediments of the Anadarko Shelf and will be complimentary to this study which is based on analysis of TOC content, bulk stable nitrogen isotopes and elemental proxies of depositional redox.

2.7 Acknowledgements

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Figures

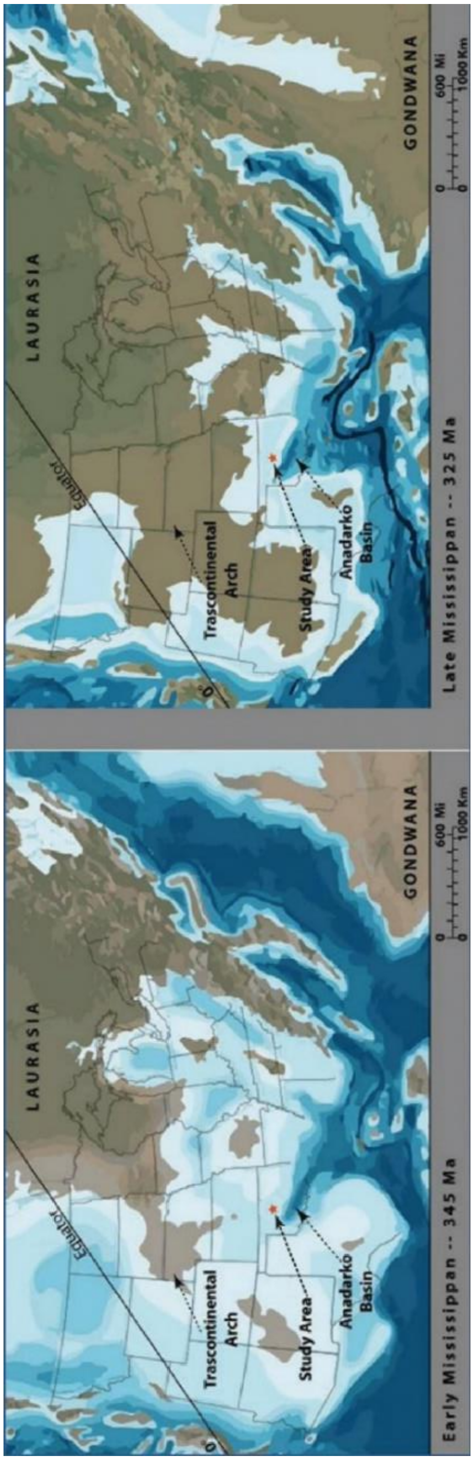


Figure 2.1: Paleogeography of Oklahoma during the Early (left) and Late (right) Mississippian showing the extent of the Mississippian epeiric sea and the equatorial paleogeographic setting of the Anadarko Shelf. Red star depicts location of the well from which samples examined in this study were collected (after Blakey, 2011 and Al Atwah, 2015).

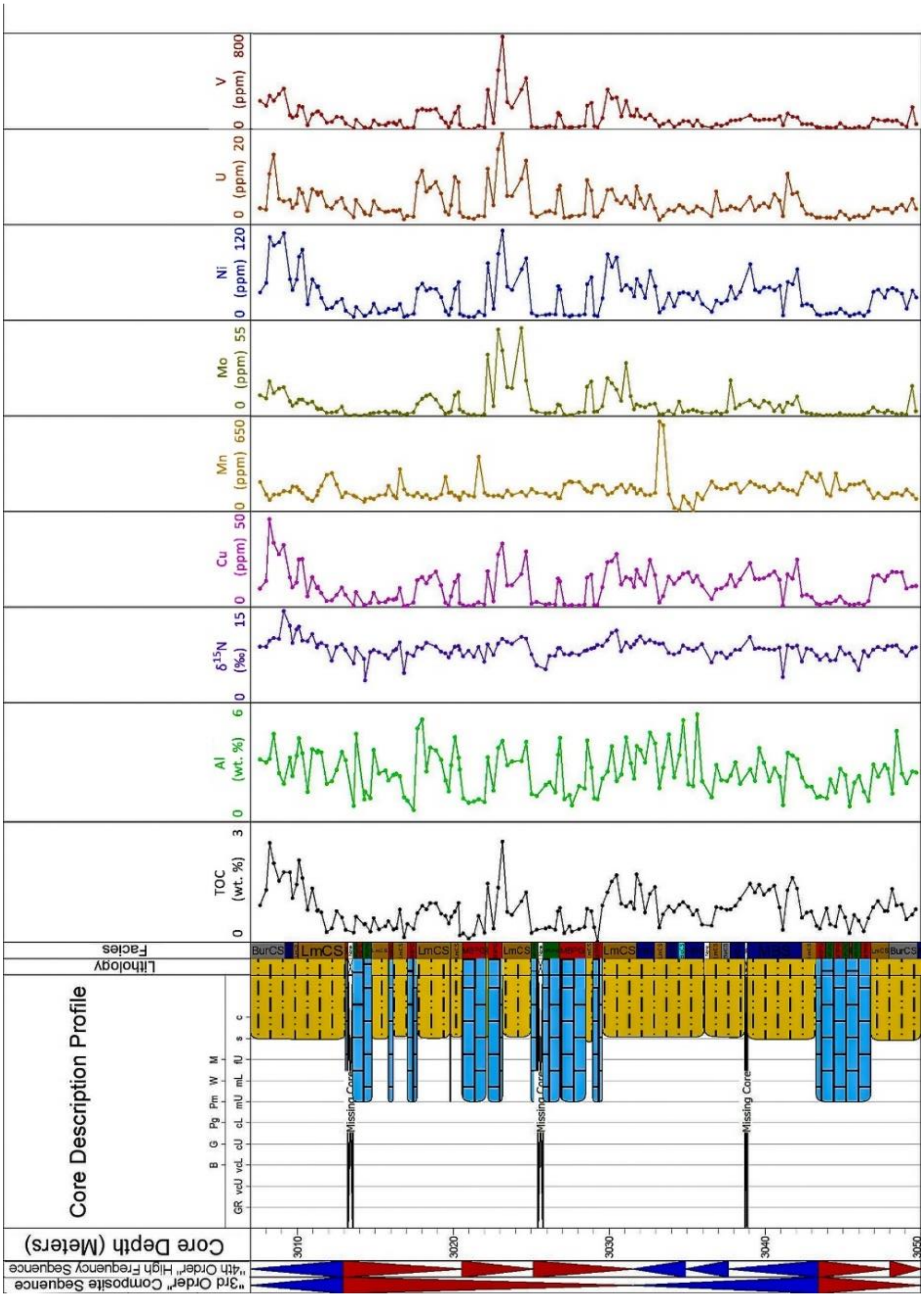


Figure 2.2: Summary figure showing variation of total concentrations of elemental paleo proxies with depth, lithology, sequences and lithofacies inferred from core descriptions. Total concentrations of elemental paleo proxies calculated by adding carbonate fraction and non-carbonate fraction concentrations of elemental paleo proxies. Core descriptions, subdivisions of lithofacies and sequence stratigraphic framework based on Wang et al. (2019). Red triangles indicate a shallowing upward trend while blue triangles indicate a deepening upward trend.

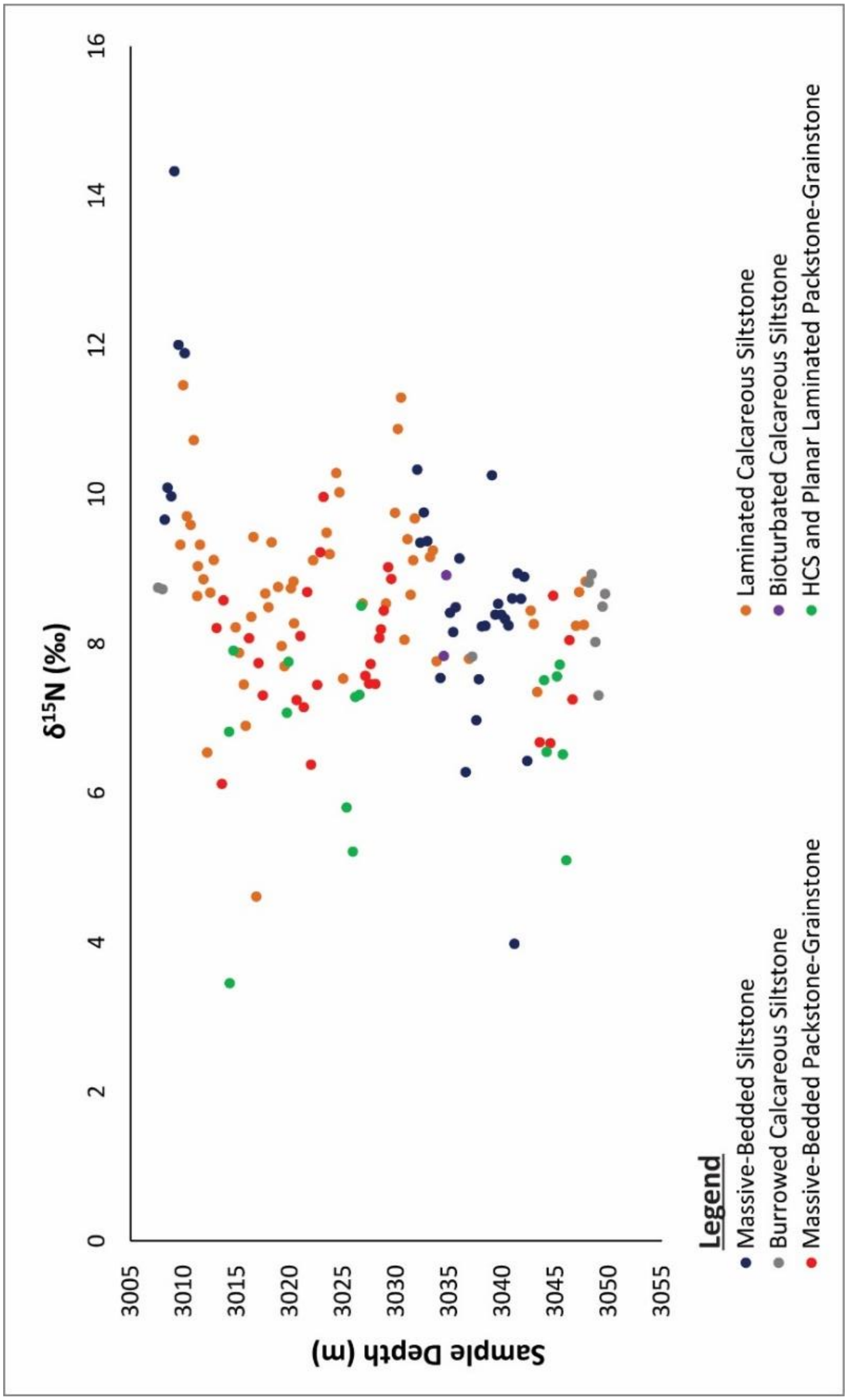


Figure 2.3: Bulk stable nitrogen isotopes results for all samples investigated in this study discriminated by lithofacies showing lack of a discernible variation in nitrogen isotope values and lithology.

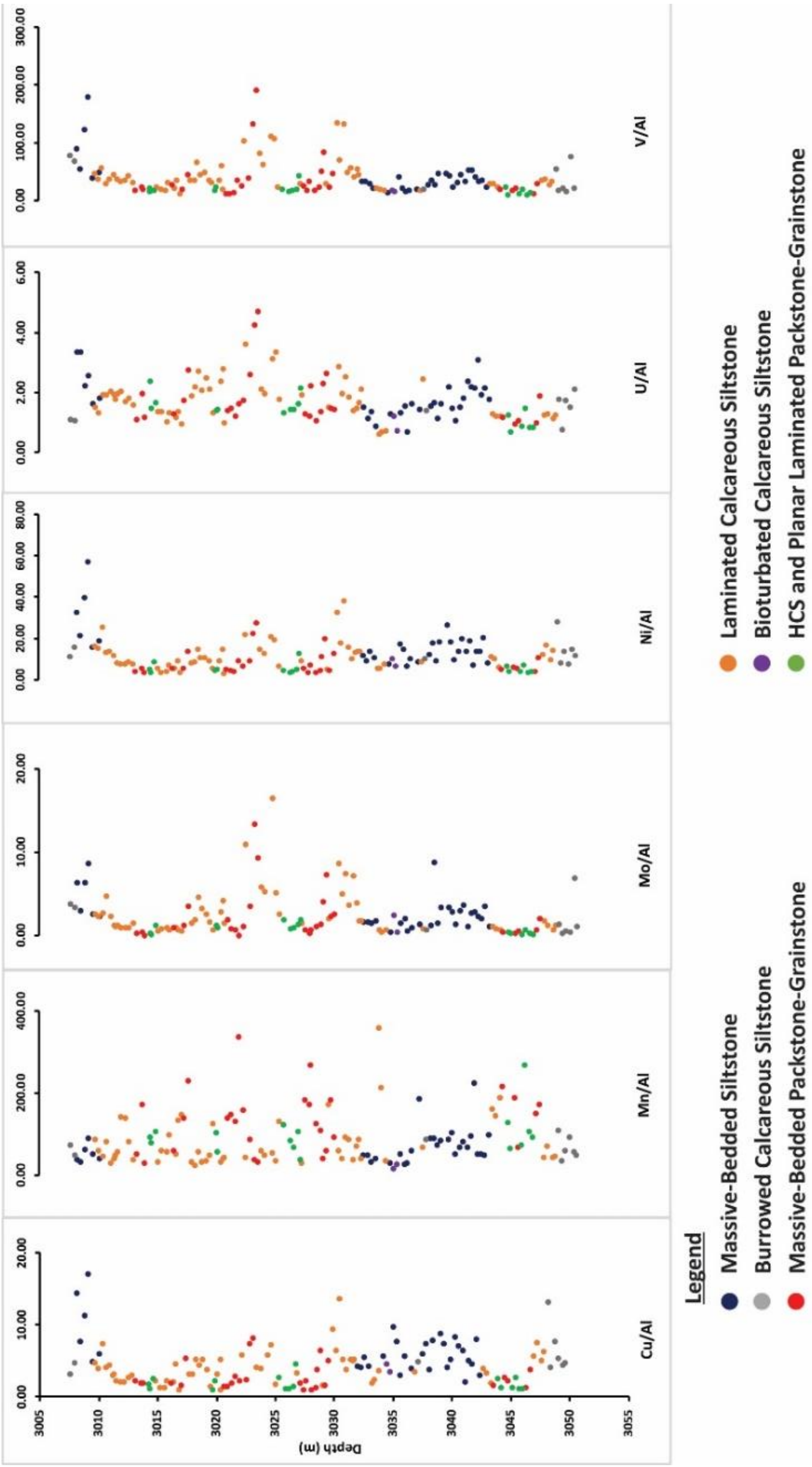


Figure 2.4: Plots of total redox-sensitive element content/Al by depth.

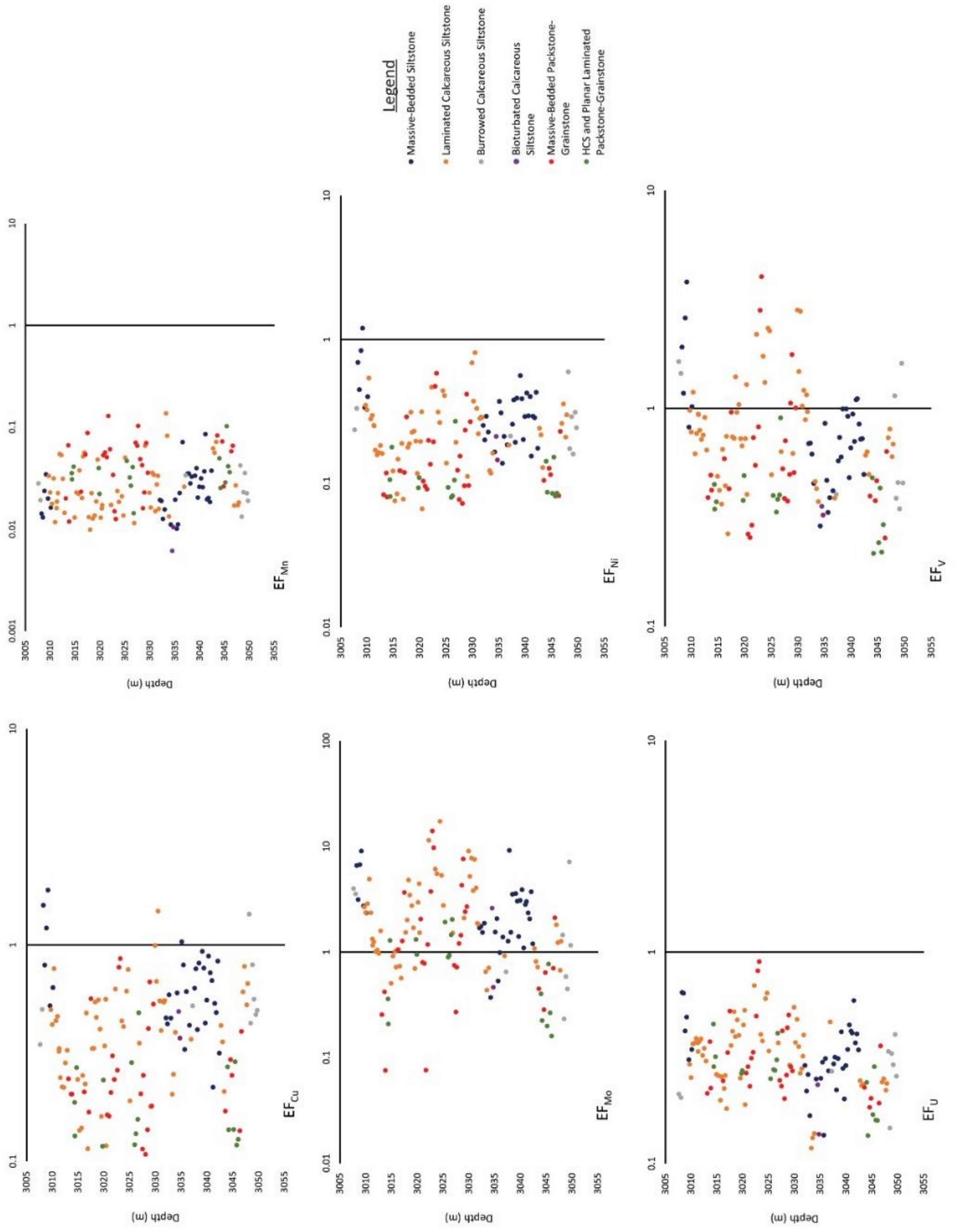


Figure 2.5: Enrichment factors of elemental redox proxies Cu, Mn, Mo, Ni, U and V showing depletion (Cu, Mn, Ni and U) or slight enrichment (Mo and V) and absence of a relationship between enrichment factor of redox sensitive trace element and lithofacies.

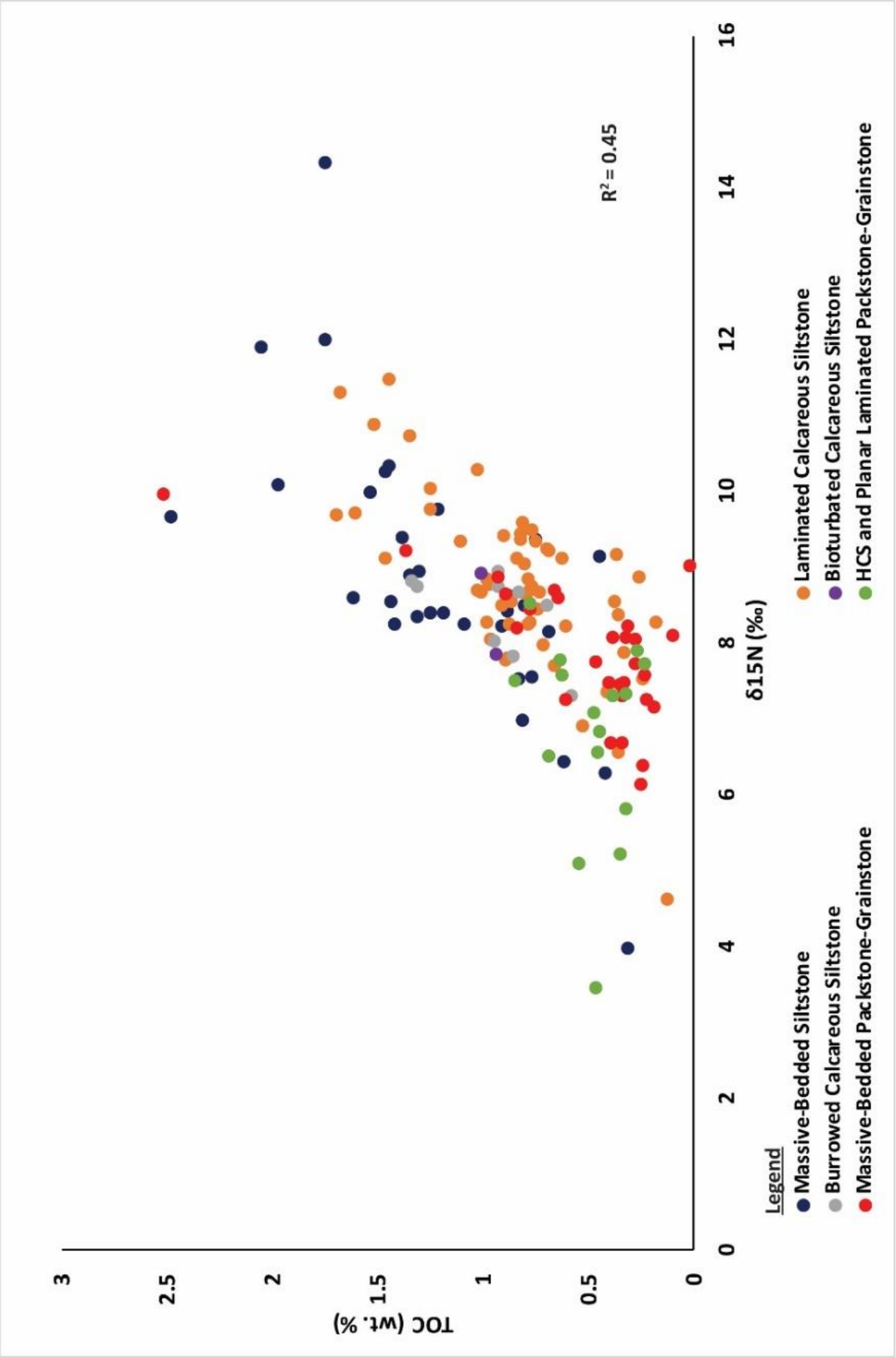


Figure 2.6: Relationship between stable nitrogen isotope measurements and TOC for samples in this study. Note that there is lack of correlation between stable nitrogen isotope (a proxy for water column redox state) and TOC.

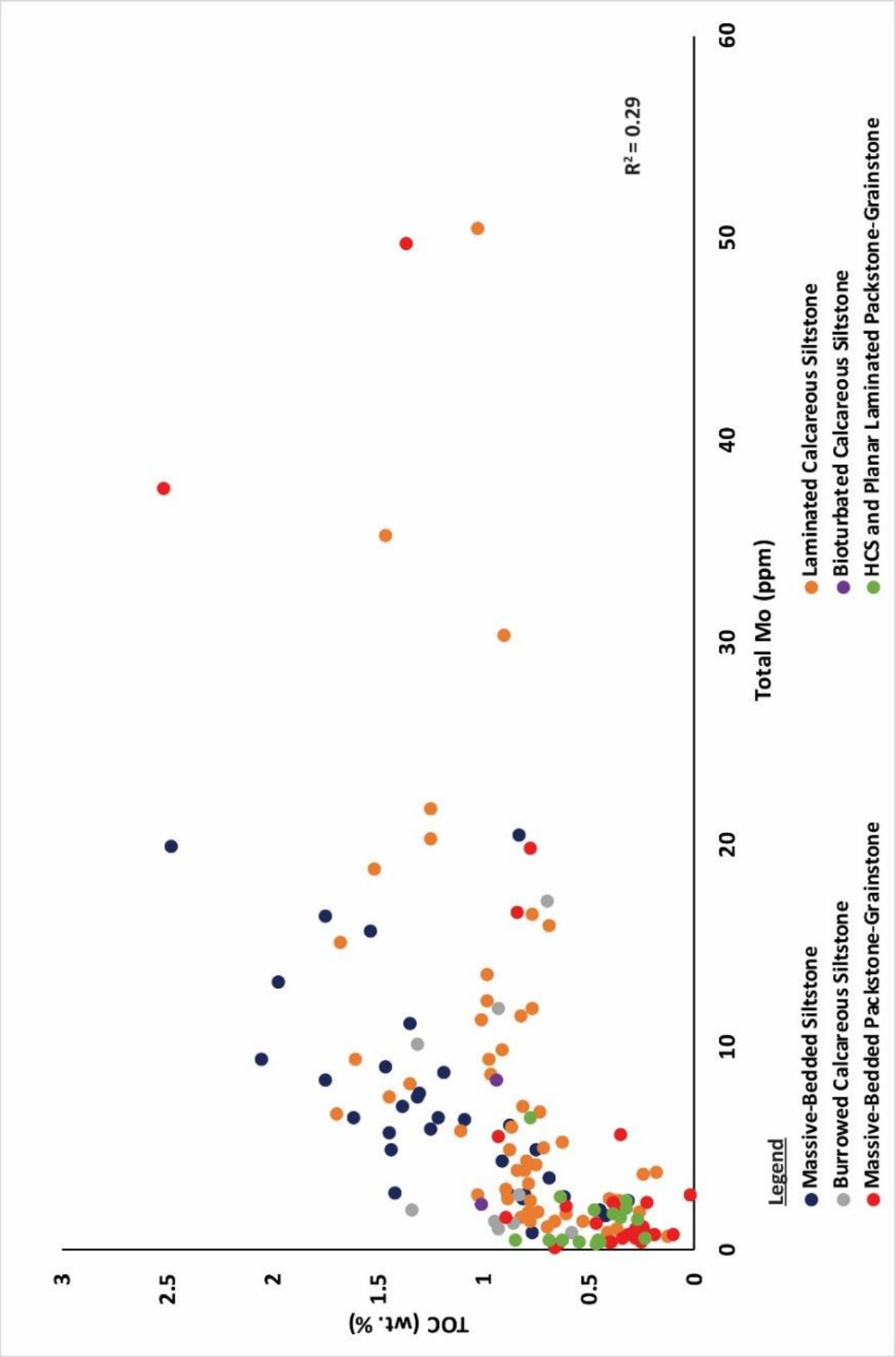


Figure 2.7: Relationship between total Mo concentration and TOC for samples in this study. Note that there is no correlation between Mo concentration (proxy for benthic redox conditions) and TOC.

Tables

Table 2.1: Bulk nitrogen stable isotope (δ15N) and total organic carbon (TOC) content in the investigated samples at Canadian County, Oklahoma Anadarko Shelf study site. Samples for which analyses were not run are denoted by "-".

Sample Depth (m)	$\delta^{15}N$ (‰)	TOC (wt. %)
3007.61	9	0.9
3008.01	9	1.3
3008.22	10	2.5
3008.50	10	2.0
3008.83	10	1.5
3009.14	14	1.8
3009.53	12	1.7
3009.69	9	1.1
3009.96	11	1.4
3010.11	12	2.1
3010.33	10	1.6
3010.66	10	0.8
3010.97	11	1.3
3011.27	9	0.8
3011.33	9	0.8
3011.55	9	0.7
3011.88	9	0.3
3012.22	7	0.4
3012.52	9	0.8
3012.86	9	0.6
3013.10	8	0.3
3013.62	6	0.2
3013.77	9	0.6
3014.29	7	0.5
3014.35	3	0.5
3014.69	8	0.3
3014.90	8	0.6
3015.23	8	0.3
3015.66	7	0.4
3015.84	7	0.5
3016.18	8	0.3
3016.36	8	0.4
3016.58	9	0.8
3016.85	5	0.1
3017.06	8	0.5
3017.46	7	0.3

Sample Depth (m)	$\delta^{15}N$ (‰)	TOC (wt. %)
3017.70	9	0.7
3018.01	8	0.9
3018.28	9	0.8
3018.53	-	1.0
3018.89	9	1.0
3019.23	8	0.7
3019.50	8	0.7
3019.71	7	0.5
3019.87	8	0.6
3020.11	9	0.8
3020.34	9	1.0
3020.42	8	0.2
3020.64	7	0.2
3020.99	8	0.1
3021.33	7	0.2
3021.63	9	0.7
3022.00	6	0.2
3022.21	9	1.5
3022.58	7	0.3
3022.88	9	1.4
3023.16	10	2.5
3023.46	9	0.8
3023.77	9	0.7
3024.38	10	1.0
3024.68	10	1.2
3025.02	8	0.2
3025.35	6	0.3
3025.93	5	0.4
3026.18	7	0.4
3026.54	7	0.3
3026.72	9	0.8
3026.85	9	0.9
3027.12	8	0.2
3027.46	7	0.4
3027.61	8	0.3
3028.07	7	0.3
3028.43	8	0.4
3028.58	8	0.8
3028.86	8	0.8
3029.04	9	0.4
3029.25	9	0.0

Sample Depth (m)	$\delta^{15}N$ (‰)	TOC (wt. %)
3029.56	9	0.9
3029.89	10	1.3
3030.17	11	1.5
3030.47	11	1.7
3030.78	8	1.0
3031.08	9	0.9
3031.39	9	1.0
3031.60	9	0.8
3031.75	10	1.7
3032.00	10	1.4
3032.30	9	0.7
3032.61	10	1.2
3032.94	9	1.4
3033.22	9	0.4
3033.46	9	0.7
3033.83	8	0.9
3034.16	8	0.8
3034.50	8	0.9
3034.74	9	1.0
3035.08	8	0.9
3035.38	8	0.7
3035.63	8	0.8
3035.96	9	0.4
3036.57	6	0.4
3036.87	8	0.9
3037.18	8	0.9
3037.55	7	0.8
3037.79	8	0.8
3038.09	8	0.9
3038.40	8	1.1
3039.04	10	1.5
3039.34	8	1.2
3039.62	9	1.4
3039.92	8	1.2
3040.26	8	1.3
3040.59	8	1.4
3040.93	9	0.9
3041.14	4	0.3
3041.45	9	1.3
3041.75	9	1.6
3042.06	9	1.3

Sample Depth (m)	δ^{15}N (‰)	TOC (wt. %)
3042.36	6	0.6
3042.67	8	0.7
3042.97	8	0.8
3043.31	7	0.4
3043.52	7	0.3
3043.95	8	0.9
3044.17	7	0.5
3044.53	7	0.4
3044.80	9	0.9
3045.13	8	0.6
3045.41	8	0.2
3045.71	7	0.7
3046.02	5	0.5
3046.32	8	0.3
3046.63	7	0.6
3046.93	8	0.9
3047.24	9	1.0
3047.66	8	0.8
3047.85	9	0.8
3048.15	9	1.3
3048.43	9	0.9
3048.76	8	0.9
3049.07	7	0.6
3049.43	8	0.7
3049.68	9	0.8

Table 2.2: Redox-sensitive element contents in the non-carbonate fraction.

Sample Depth (m)	Al (Wt. %)	Cu (ppm)	Mn (ppm)	Mo (ppm)	Ni (ppm)	U (ppm)	V (ppm)
3007.61	3.11	7.77	87.57	9.21	20.79	3.08	225.67
3008.01	2.97	12.00	59.52	8.12	33.03	2.58	193.69
3008.22	3.14	27.15	64.29	16.91	78.11	9.84	282.17
3008.50	4.39	19.91	71.48	10.21	70.58	13.57	237.11
3008.83	2.44	16.64	69.09	11.47	57.96	4.78	291.58
3009.14	1.90	18.10	103.89	12.68	62.41	4.23	337.65
3009.53	3.20	10.15	76.19	6.38	36.17	4.37	119.59
3009.69	2.29	7.80	82.82	4.42	29.08	2.62	100.07
3009.96	3.31	10.53	89.85	5.82	37.83	3.49	114.67
3010.11	4.17	16.56	105.00	7.56	49.39	6.53	195.15
3010.33	3.43	16.80	106.35	7.97	60.12	5.91	190.50
3010.66	1.51	3.92	16.91	5.91	14.18	2.34	41.42
3010.97	3.62	10.54	48.80	6.82	33.24	6.11	129.52
3011.27	3.45	10.33	48.94	3.85	34.66	5.11	143.75
3011.33	3.53	10.87	71.08	3.39	35.79	4.70	145.75
3011.55	3.46	7.38	40.11	3.48	19.69	5.48	110.13
3011.88	1.90	3.96	35.36	1.52	11.42	2.75	49.82
3012.22	2.02	4.27	47.30	1.79	13.02	2.47	56.61
3012.52	2.58	6.86	65.34	2.00	17.23	4.02	93.33
3012.86	3.48	9.03	48.59	4.29	16.38	5.11	99.27
3013.10	3.07	5.72	40.60	0.52	7.61	3.09	50.57
3013.62	0.82	1.36	11.10	0.22	3.39	1.27	12.91
3013.77	4.38	5.89	50.71	0.21	9.15	4.98	80.17
3014.29	1.13	1.78	14.62	0.26	4.05	2.37	21.90
3014.35	1.52	1.84	23.75	0.19	4.69	1.95	22.50
3014.69	1.19	2.41	14.86	1.11	8.47	1.69	18.14
3014.90	3.58	6.92	47.53	1.25	13.36	4.69	76.30
3015.23	2.42	2.86	31.05	1.60	6.28	3.04	41.34
3015.66	2.56	3.14	29.36	1.90	7.72	2.43	37.59
3015.84	2.07	4.37	57.90	1.16	9.32	2.48	49.62
3016.18	2.34	4.00	54.73	1.70	9.16	2.74	59.05
3016.36	2.39	4.79	33.31	1.81	10.38	2.56	43.91
3016.58	2.27	9.93	34.53	1.32	13.20	2.73	52.67
3016.85	1.24	1.10	24.76	0.34	3.23	0.89	13.48
3017.06	1.07	1.48	16.57	1.02	4.37	1.59	19.28
3017.46	0.60	3.06	15.60	1.82	6.85	1.41	24.16
3017.70	4.65	11.53	94.93	5.39	24.65	8.32	154.94
3018.01	5.10	11.78	65.60	7.44	26.89	10.72	169.21

Sample Depth (m)	Al (Wt. %)	Cu (ppm)	Mn (ppm)	Mo (ppm)	Ni (ppm)	U (ppm)	V (ppm)
3018.28	2.50	9.98	76.94	8.79	20.42	6.28	159.08
3018.53	3.69	13.72	59.66	10.03	25.58	7.17	162.00
3018.89	3.56	14.02	59.29	7.04	23.11	8.25	169.26
3019.23	3.09	9.70	49.05	3.75	18.30	5.93	91.02
3019.50	2.06	2.76	49.65	0.97	7.81	2.31	46.10
3019.71	1.54	1.61	28.22	1.54	5.44	1.87	24.06
3019.87	2.82	5.50	36.52	1.89	10.24	3.71	53.34
3020.11	4.22	9.97	80.24	8.96	21.58	9.51	138.51
3020.34	3.19	12.17	81.98	9.68	25.10	8.34	189.43
3020.42	2.61	2.66	27.77	2.67	5.49	2.26	42.80
3020.64	1.18	1.79	11.13	1.89	4.47	1.36	11.10
3020.99	0.97	1.21	10.97	0.47	3.12	1.16	9.59
3021.33	1.03	1.46	12.87	0.55	2.72	1.01	12.41
3021.63	1.14	2.15	28.01	0.00	5.04	1.71	25.63
3022.00	1.01	1.35	16.40	0.73	3.59	1.43	20.84
3022.21	3.21	11.04	88.35	23.57	33.36	11.18	324.22
3022.58	1.57	2.04	15.99	4.11	8.81	3.70	53.86
3022.88	3.69	19.00	78.52	33.60	43.01	15.25	479.21
3023.16	4.02	20.05	80.90	24.72	67.15	18.10	760.08
3023.46	2.83	6.91	77.38	11.78	20.27	5.60	219.95
3023.77	3.02	7.51	50.69	12.52	20.03	5.60	176.70
3024.38	3.04	11.74	96.86	35.19	29.80	9.10	329.08
3024.68	3.98	17.72	72.36	13.85	51.95	12.79	421.74
3025.02	1.40	2.00	19.97	2.85	6.08	2.13	26.69
3025.35	1.31	3.21	17.07	2.03	4.71	1.36	18.34
3025.93	1.86	1.77	32.26	1.24	5.18	2.40	25.63
3026.18	1.99	2.00	26.03	1.43	5.35	2.58	32.13
3026.54	1.48	1.92	18.96	1.47	5.54	2.12	21.64
3026.72	3.34	9.20	60.30	4.76	20.31	6.97	137.08
3026.85	4.18	8.60	60.11	4.26	18.76	7.90	119.11
3027.12	1.15	1.98	23.39	0.62	5.57	1.17	16.88
3027.46	1.35	1.07	29.76	0.13	3.63	1.33	17.12
3027.61	0.84	1.64	32.47	0.41	4.74	1.61	22.28
3028.07	1.80	1.82	22.29	1.79	4.90	1.66	24.05
3028.43	1.68	1.75	34.88	1.85	5.73	2.03	34.56
3028.58	4.06	9.07	86.38	12.67	19.99	9.03	192.37
3028.86	2.71	9.74	66.19	14.07	22.03	6.87	212.00
3029.04	1.18	1.80	26.13	1.93	5.01	1.51	26.79
3029.25	1.15	1.68	21.56	2.01	4.83	1.39	21.38
3029.56	2.15	8.36	47.12	4.34	19.56	2.52	92.43

Sample Depth (m)	Al (Wt. %)	Cu (ppm)	Mn (ppm)	Mo (ppm)	Ni (ppm)	U (ppm)	V (ppm)
3029.89	2.51	13.40	68.29	15.66	38.47	6.74	320.98
3030.17	3.77	15.72	77.19	14.75	36.80	6.97	252.85
3030.47	2.04	19.67	106.95	11.40	53.97	4.62	261.48
3030.78	2.37	9.10	80.97	6.65	23.48	3.89	106.52
3031.08	4.20	10.43	65.37	23.89	21.69	5.61	229.15
3031.39	2.92	11.13	59.15	9.37	24.64	3.85	112.92
3031.60	2.16	9.68	75.07	3.32	24.47	2.87	110.60
3031.75	3.78	15.45	70.37	5.56	41.39	7.07	167.10
3032.00	3.58	12.07	77.85	4.60	34.44	4.64	111.60
3032.30	2.96	10.42	48.96	3.74	22.82	2.73	91.54
3032.61	4.44	21.34	71.63	5.34	53.56	4.82	125.48
3032.94	3.91	15.41	55.24	6.22	37.17	2.82	78.08
3033.22	1.67	3.22	61.56	0.71	8.20	0.67	23.75
3033.46	2.70	6.48	45.62	0.90	13.08	1.22	35.38
3033.83	4.35	14.68	91.13	2.51	29.69	2.89	76.49
3034.16	2.23	11.27	27.94	0.64	16.45	2.80	30.51
3034.50	3.33	12.57	44.02	7.21	25.10	4.04	56.34
3034.74	5.06	15.19	98.78	2.03	30.52	3.59	77.79
3035.08	1.88	16.51	49.38	2.61	29.49	2.37	76.23
3035.38	1.79	10.68	29.10	2.92	18.16	2.74	39.79
3035.63	5.35	14.87	103.01	2.39	30.82	3.63	84.30
3035.96	2.03	10.26	32.53	1.39	18.82	3.18	36.54
3036.57	1.23	4.25	25.03	1.32	9.63	1.48	21.19
3036.87	2.84	7.32	64.00	2.03	19.02	6.22	48.08
3037.18	2.09	8.99	36.04	1.11	18.67	2.82	36.13
3037.55	2.04	11.06	50.28	2.25	22.29	2.67	51.72
3037.79	2.32	13.14	59.61	17.67	29.86	3.08	75.32
3038.09	2.98	9.87	71.52	3.62	21.49	2.77	75.80
3038.40	1.91	11.97	64.99	5.17	27.95	2.50	84.76
3039.04	2.63	13.11	114.86	7.19	46.06	4.88	118.39
3039.34	2.05	10.82	66.79	4.63	27.93	2.48	82.36
3039.62	3.68	10.83	74.04	3.94	25.97	3.46	78.63
3039.92	2.95	11.65	69.25	6.63	27.91	3.92	85.59
3040.26	2.02	12.99	57.83	5.81	30.27	3.07	85.36
3040.59	2.68	14.81	58.34	2.36	32.25	5.70	84.86
3040.93	2.25	13.34	62.89	4.95	36.12	4.30	104.92
3041.14	0.85	1.10	22.80	1.90	4.07	1.42	18.74
3041.45	3.44	10.86	68.90	5.42	28.34	10.03	129.19
3041.75	3.30	10.43	63.10	4.87	29.68	5.89	105.81
3042.06	3.12	18.08	71.32	9.21	46.35	6.25	103.20

Sample Depth (m)	Al (Wt. %)	Cu (ppm)	Mn (ppm)	Mo (ppm)	Ni (ppm)	U (ppm)	V (ppm)
3042.36	2.23	5.56	59.40	1.96	15.46	3.64	45.98
3042.67	1.77	6.90	40.24	1.54	17.38	1.91	40.51
3042.97	1.76	5.25	50.93	1.07	13.91	1.89	45.60
3043.31	1.23	2.20	28.79	0.69	5.96	1.22	25.04
3043.52	1.29	1.82	32.43	0.43	5.27	1.25	20.26
3043.95	1.19	2.92	26.59	0.30	6.39	1.31	25.51
3044.17	2.13	2.65	24.28	0.34	7.00	1.28	20.42
3044.53	1.49	2.98	27.62	0.31	7.15	1.20	21.83
3044.80	2.65	6.03	39.83	1.11	12.49	2.55	52.04
3045.13	2.34	2.75	28.99	0.28	6.79	1.89	24.99
3045.41	0.79	1.90	20.91	0.51	4.72	0.95	14.10
3045.71	1.96	2.08	24.67	0.33	5.97	1.41	18.34
3046.02	2.30	2.68	43.60	0.22	7.64	1.71	29.00
3046.32	1.52	1.88	33.14	0.77	5.31	1.26	16.37
3046.63	1.05	3.55	27.00	1.71	8.93	1.75	29.35
3046.93	2.86	12.85	60.35	4.28	25.64	3.42	97.12
3047.24	2.25	13.20	81.66	2.39	31.66	2.62	84.74
3047.66	2.84	12.82	62.87	1.51	25.06	2.86	80.45
3047.85	2.65	14.84	57.41	2.73	32.88	2.72	85.77
3048.15	1.42	16.58	79.65	1.81	37.27	2.19	76.82
3048.43	4.53	16.53	89.67	0.89	34.28	3.28	82.89
3048.76	2.41	15.21	44.22	1.13	27.61	3.57	51.32
3049.07	1.94	8.43	31.64	0.61	12.49	2.53	30.80
3049.43	2.51	6.78	48.84	11.56	18.03	4.99	181.62
3049.68	2.46	8.55	43.44	2.24	20.98	2.74	52.40

Table 2.3: Redox-sensitive element contents in the carbonate fraction.

Sample Depth (m)	Al (Wt. %)	Cu (ppm)	Mn (ppm)	Mo (ppm)	Ni (ppm)	U (ppm)	V (ppm)
3007.61	0.01	2.56	142.79	2.71	14.29	0.42	18.27
3008.01	0.01	2.31	91.12	2.00	13.99	0.62	11.31
3008.22	0.01	18.74	53.24	3.02	26.05	0.81	4.67
3008.50	0.01	13.91	79.06	3.00	23.26	1.15	8.69
3008.83	0.01	11.30	83.22	4.26	39.69	0.66	11.07
3009.14	0.01	14.61	68.95	3.84	47.00	0.71	8.21
3009.53	0.01	5.89	92.14	2.02	15.33	0.86	6.11
3009.69	0.01	3.18	117.68	1.45	9.08	0.93	7.04
3009.96	0.01	3.03	109.60	1.68	13.44	0.94	8.36
3010.11	0.01	8.76	73.00	1.84	30.29	1.07	7.65
3010.33	0.01	8.69	53.72	1.45	28.32	0.72	3.86
3010.66	0.00	2.52	108.13	1.21	6.02	0.61	3.21
3010.97	0.01	5.68	62.82	1.36	18.09	1.34	3.30
3011.27	0.03	0.34	97.48	0.57	7.29	1.68	11.91
3011.33	0.02	0.37	102.54	0.54	6.67	1.60	12.72
3011.55	0.03	0.71	165.96	0.67	8.55	1.41	21.43
3011.88	0.02	0.07	239.38	0.33	2.97	1.15	15.79
3012.22	0.02	0.00	238.51	0.25	2.90	1.01	16.85
3012.52	0.03	0.22	148.07	0.42	5.48	0.77	19.38
3012.86	0.02	1.84	84.11	1.01	10.50	0.49	8.07
3013.10	0.02	1.35	121.81	0.23	4.65	0.38	6.74
3013.62	0.00	0.25	132.74	0.11	1.26	0.37	6.52
3013.77	0.01	2.66	85.84	0.11	7.63	0.25	7.85
3014.29	0.01	0.24	90.92	0.13	1.69	0.35	2.32
3014.35	0.00	0.06	99.46	0.11	1.18	0.34	2.57
3014.69	0.01	0.69	114.28	0.37	1.75	0.32	3.16
3014.90	0.02	1.26	75.07	0.48	7.50	0.29	7.25
3015.23	0.01	0.37	115.12	0.53	2.46	0.28	7.41
3015.66	0.01	0.36	120.78	0.58	2.65	0.26	7.01
3015.84	0.02	0.57	148.02	0.27	5.30	0.33	14.75
3016.18	0.01	0.71	89.36	0.67	4.58	0.31	6.92
3016.36	0.01	0.44	94.41	0.62	3.61	0.30	6.65
3016.58	0.02	0.66	276.54	0.28	7.49	0.40	28.60
3016.85	0.00	0.25	158.88	0.33	1.36	0.29	2.25
3017.06	0.00	0.25	135.63	0.29	1.75	0.30	2.64
3017.46	0.01	0.22	125.33	0.32	1.60	0.27	3.86
3017.70	0.02	3.24	65.80	1.45	14.97	0.53	9.45
3018.01	0.02	4.47	67.19	2.40	19.08	0.61	8.25

Sample Depth (m)	Al (Wt. %)	Cu (ppm)	Mn (ppm)	Mo (ppm)	Ni (ppm)	U (ppm)	V (ppm)
3018.28	0.02	3.12	72.37	2.80	17.16	0.64	8.56
3018.53	0.02	2.67	63.83	2.27	14.48	0.59	7.72
3018.89	0.02	5.01	68.60	2.36	16.22	0.72	8.23
3019.23	0.02	2.39	102.89	1.27	10.77	0.65	16.35
3019.50	0.01	0.44	212.54	0.41	3.80	0.45	20.49
3019.71	0.01	0.12	133.09	0.40	1.40	0.29	3.73
3019.87	0.02	0.93	128.57	0.68	4.58	0.39	13.07
3020.11	0.01	3.81	63.56	2.98	17.92	0.53	7.94
3020.34	0.02	5.01	52.16	3.93	22.93	0.61	7.20
3020.42	0.02	0.29	90.42	1.16	2.82	0.35	7.56
3020.64	0.01	0.06	153.97	0.43	1.38	0.31	3.86
3020.99	0.00	0.29	133.31	0.27	1.31	0.31	2.25
3021.33	0.00	0.59	124.88	0.22	1.76	0.25	1.94
3021.63	0.01	1.22	361.86	0.08	5.87	0.19	14.59
3022.00	0.01	0.95	145.17	0.41	2.95	0.35	5.55
3022.21	0.02	8.21	57.77	11.68	38.35	0.56	12.07
3022.58	0.01	1.92	124.88	1.53	5.76	0.41	7.91
3022.88	0.01	8.88	66.71	16.10	40.45	0.60	17.68
3023.16	0.02	13.32	52.56	12.88	45.20	1.00	14.09
3023.46	0.01	5.15	98.36	4.80	22.05	0.46	14.41
3023.77	0.01	4.61	96.47	3.46	18.14	0.43	12.74
3024.38	0.01	6.05	70.79	15.28	34.21	0.53	9.49
3024.68	0.01	11.62	70.40	6.48	25.71	0.63	9.69
3025.02	0.00	0.54	165.14	0.86	3.16	0.38	6.49
3025.35	0.01	0.36	143.86	0.38	1.15	0.37	6.54
3025.93	0.01	0.35	124.65	0.35	1.90	0.32	4.02
3026.18	0.01	0.55	113.98	0.35	2.45	0.32	4.28
3026.54	0.01	0.30	139.53	0.61	1.93	0.29	6.74
3026.72	0.01	6.33	65.99	1.77	22.83	0.31	7.38
3026.85	0.01	5.46	66.19	1.82	19.85	0.28	7.48
3027.12	0.01	0.29	191.27	0.21	1.24	0.33	12.28
3027.46	0.01	0.39	204.21	0.22	1.35	0.32	7.77
3027.61	0.01	0.38	196.47	0.17	1.49	0.28	6.34
3028.07	0.00	0.02	207.71	0.28	1.32	0.26	8.09
3028.43	0.01	0.49	152.05	0.47	1.96	0.28	5.29
3028.58	0.01	6.87	85.03	4.02	25.49	0.32	12.49
3028.86	0.01	7.80	97.50	5.77	32.11	0.33	16.93
3029.04	0.01	0.23	178.68	0.45	1.30	0.31	8.33
3029.25	0.00	0.30	190.54	0.65	0.49	0.35	6.54
3029.56	0.01	2.64	156.56	1.26	8.13	0.60	11.36

Sample Depth (m)	Al (Wt. %)	Cu (ppm)	Mn (ppm)	Mo (ppm)	Ni (ppm)	U (ppm)	V (ppm)
3029.89	0.01	10.54	82.53	6.13	44.40	0.51	18.40
3030.17	0.01	8.73	84.18	4.04	30.30	0.43	12.84
3030.47	0.01	8.38	85.73	3.82	25.17	0.55	11.20
3030.78	0.01	3.42	131.69	2.05	14.15	0.57	9.85
3031.08	0.01	5.74	100.52	6.49	22.64	0.30	13.96
3031.39	0.01	4.20	152.10	2.01	14.92	0.47	11.08
3031.60	0.01	1.57	114.47	0.56	5.37	0.79	8.59
3031.75	0.01	4.53	86.79	1.10	10.45	0.99	7.34
3032.00	0.01	3.68	104.11	1.21	8.81	0.84	6.35
3032.30	0.01	1.83	98.76	1.23	5.54	0.70	6.63
3032.61	0.02	3.67	75.81	1.21	8.59	1.36	5.57
3032.94	0.02	1.79	105.72	0.82	5.47	0.66	6.60
3033.22	0.03	0.10	549.65	0.35	1.71	0.38	13.63
3033.46	0.02	0.07	542.79	0.23	2.21	0.67	20.18
3033.83	0.01	1.75	61.53	0.44	4.03	0.28	1.09
3034.16	0.01	1.55	37.33	0.16	1.18	0.14	0.30
3034.50	0.01	3.13	9.73	1.14	8.72	0.09	0.26
3034.74	0.01	2.78	40.38	0.22	4.67	0.08	0.64
3035.08	0.01	2.15	47.10	0.18	3.95	0.14	0.57
3035.38	0.01	3.18	18.54	0.64	8.33	0.10	0.24
3035.63	0.02	1.94	53.72	0.34	4.40	0.20	0.78
3035.96	0.01	1.59	88.53	0.54	1.81	0.18	1.26
3036.57	0.01	0.77	207.53	0.32	1.29	0.30	3.53
3036.87	0.01	2.64	130.62	0.48	6.01	0.77	4.52
3037.18	0.01	1.48	150.07	0.19	2.67	0.19	4.24
3037.55	0.01	1.31	138.64	0.24	2.91	0.52	4.50
3037.79	0.01	4.11	155.29	2.81	12.33	0.81	6.42
3038.09	0.01	1.69	148.98	0.78	5.99	0.72	9.39
3038.40	0.01	3.10	99.52	1.30	7.81	0.66	6.09
3039.04	0.01	10.36	116.43	1.83	24.47	0.91	6.32
3039.34	0.01	4.53	147.84	1.34	10.12	0.57	7.82
3039.62	0.01	4.48	123.53	1.01	9.42	0.45	5.96
3039.92	0.01	4.04	133.09	2.09	13.20	0.59	7.31
3040.26	0.01	4.22	109.71	1.75	10.90	0.62	5.69
3040.59	0.01	4.25	123.62	0.45	5.52	0.68	5.51
3040.93	0.02	1.48	156.82	1.17	7.30	0.74	13.40
3041.14	0.01	0.69	168.52	0.55	2.20	0.43	26.20
3041.45	0.01	6.81	108.85	2.33	19.79	0.65	10.25
3041.75	0.01	5.00	113.01	1.66	15.57	0.58	8.24
3042.06	0.01	7.09	80.67	1.96	17.80	0.50	5.30

Sample Depth (m)	Al (Wt. %)	Cu (ppm)	Mn (ppm)	Mo (ppm)	Ni (ppm)	U (ppm)	V (ppm)
3042.36	0.01	1.19	160.78	0.60	3.23	0.41	7.07
3042.67	0.01	0.33	250.21	0.31	3.15	0.39	11.28
3042.97	0.01	0.78	209.82	0.31	4.44	0.28	7.73
3043.31	0.01	0.29	205.10	0.17	1.65	0.32	4.34
3043.52	0.01	0.29	249.14	0.13	1.19	0.31	4.14
3043.95	0.01	0.20	129.24	0.16	1.73	0.21	1.87
3044.17	0.00	0.19	117.58	0.12	1.81	0.24	1.56
3044.53	0.01	1.23	256.55	0.10	1.92	0.25	5.00
3044.80	0.01	0.29	143.00	0.52	2.04	0.28	6.87
3045.13	0.00	0.39	147.73	0.17	2.74	0.21	2.10
3045.41	0.00	0.29	193.31	0.07	1.06	0.25	2.29
3045.71	0.00	0.14	189.05	0.16	1.67	0.24	2.16
3046.02	0.00	0.09	175.17	0.13	1.72	0.22	3.09
3046.32	0.00	0.13	199.37	0.25	0.65	0.28	2.07
3046.63	0.01	0.48	155.91	0.43	2.67	0.25	2.66
3046.93	0.01	3.77	67.87	0.69	10.08	0.24	3.10
3047.24	0.02	4.02	78.16	0.27	6.89	0.38	2.08
3047.66	0.01	1.56	65.49	0.31	3.45	0.46	1.07
3047.85	0.02	2.00	70.22	0.50	5.17	0.63	1.27
3048.15	0.01	2.35	78.85	0.17	3.36	0.35	0.96
3048.43	0.01	2.30	68.29	0.12	3.41	0.23	0.84
3048.76	0.01	3.47	102.08	0.23	5.93	0.63	1.32
3049.07	0.01	2.00	150.04	0.22	2.37	0.47	1.34
3049.43	0.01	4.67	99.92	5.66	19.40	0.39	11.41
3049.68	0.01	3.22	79.80	0.50	7.77	0.62	1.20

Table 2.4: Total* redox-sensitive element content in samples.

Sample Depth (m)	Al (Wt. %)	Cu (ppm)	Mn (ppm)	Mo (ppm)	Ni (ppm)	U (ppm)	V (ppm)
3007.61	3.12	10.33	230.36	11.92	35.08	3.50	243.94
3008.01	2.98	14.31	150.64	10.12	47.02	3.20	205.00
3008.22	3.15	45.89	117.53	19.93	104.16	10.65	286.84
3008.50	4.40	33.82	150.54	13.21	93.84	14.72	245.8
3008.83	2.45	27.94	152.31	15.73	97.65	5.44	302.65
3009.14	1.91	32.71	172.84	16.52	109.41	4.94	345.86
3009.53	3.21	16.04	168.33	8.40	51.5	5.23	125.70
3009.69	2.30	10.98	200.50	5.87	38.16	3.55	107.11
3009.96	3.32	13.56	199.45	7.50	51.27	4.43	123.03
3010.11	4.18	25.32	178.00	9.40	79.68	7.60	202.80
3010.33	3.44	25.49	160.07	9.42	88.44	6.63	194.36
3010.66	1.51	6.44	125.04	7.12	20.20	2.95	44.63
3010.97	3.63	16.22	111.62	8.18	51.33	7.45	132.82
3011.27	3.48	10.67	146.42	4.42	41.95	6.79	155.66
3011.33	3.55	11.24	173.62	3.93	42.46	6.30	158.47
3011.55	3.49	8.09	206.07	4.15	28.24	6.89	131.56
3011.88	1.92	4.03	274.74	1.85	14.39	3.90	65.61
3012.22	2.04	4.27	285.81	2.04	15.92	3.48	73.46
3012.52	2.61	7.08	213.41	2.42	22.71	4.79	112.71
3012.86	3.50	10.87	132.70	5.30	26.88	5.60	107.34
3013.10	3.09	7.07	162.41	0.75	12.26	3.47	57.31
3013.62	0.82	1.61	143.84	0.33	4.65	1.64	19.43
3013.77	4.39	8.55	136.55	0.32	16.78	5.23	88.02
3014.29	1.14	2.02	105.54	0.39	5.74	2.72	24.22
3014.35	1.52	1.90	123.21	0.30	5.87	2.29	25.07
3014.69	1.20	3.10	129.14	1.48	10.22	2.01	21.30
3014.90	3.60	8.18	122.60	1.73	20.86	4.98	83.55
3015.23	2.43	3.23	146.17	2.13	8.74	3.32	48.75
3015.66	2.57	3.50	150.14	2.48	10.37	2.69	44.60
3015.84	2.09	4.94	205.92	1.43	14.62	2.81	64.37
3016.18	2.35	4.71	144.09	2.37	13.74	3.05	65.97
3016.36	2.40	5.23	127.72	2.43	13.99	2.86	50.56
3016.58	2.29	10.59	311.07	1.60	20.69	3.13	81.27
3016.85	1.24	1.35	183.64	0.67	4.59	1.18	15.73
3017.06	1.07	1.73	152.20	1.31	6.12	1.89	21.92
3017.46	0.61	3.28	140.93	2.14	8.45	1.68	28.02
3017.70	4.67	14.77	160.73	6.84	39.62	8.85	164.39
3018.01	5.12	16.25	132.79	9.84	45.97	11.33	177.46
3018.28	2.52	13.10	149.31	11.59	37.58	6.92	167.64
3018.53	3.71	16.39	123.49	12.30	40.06	7.76	169.72

Sample Depth (m)	Al (Wt. %)	Cu (ppm)	Mn (ppm)	Mo (ppm)	Ni (ppm)	U (ppm)	V (ppm)
3018.89	3.58	19.03	127.89	9.40	39.33	8.97	177.49
3019.23	3.11	12.09	151.94	5.02	29.07	6.58	107.37
3019.50	2.07	3.20	262.19	1.38	11.61	2.76	66.59
3019.71	1.55	1.73	161.31	1.94	6.84	2.16	27.79
3019.87	2.84	6.43	165.09	2.57	14.82	4.10	66.41
3020.11	4.23	13.78	143.80	11.94	39.5	10.04	146.45
3020.34	3.21	17.18	134.14	13.61	48.03	8.95	196.63
3020.42	2.63	2.95	118.19	3.83	8.31	2.61	50.36
3020.64	1.19	1.85	165.10	2.32	5.85	1.67	14.96
3020.99	0.97	1.50	144.28	0.74	4.43	1.47	11.84
3021.33	1.03	2.05	137.75	0.77	4.48	1.26	14.35
3021.63	1.15	3.37	389.87	0.08	10.91	1.90	40.22
3022.00	1.02	2.30	161.57	1.14	6.54	1.78	26.39
3022.21	3.23	19.25	146.12	35.25	71.71	11.74	336.29
3022.58	1.58	3.96	140.87	5.64	14.57	4.11	61.77
3022.88	3.70	27.88	145.23	49.70	83.46	15.85	496.89
3023.16	4.04	33.37	133.46	37.60	112.35	19.1	774.17
3023.46	2.84	12.06	175.74	16.58	42.32	6.06	234.36
3023.77	3.03	12.12	147.16	15.98	38.17	6.03	189.44
3024.38	3.05	17.79	167.65	50.47	64.01	9.63	338.57
3024.68	3.99	29.34	142.76	20.33	77.66	13.42	431.43
3025.02	1.40	2.54	185.11	3.71	9.24	2.51	33.18
3025.35	1.32	3.57	160.93	2.41	5.86	1.73	24.88
3025.93	1.87	2.12	156.91	1.59	7.08	2.72	29.65
3026.18	2.00	2.55	140.01	1.78	7.80	2.90	36.41
3026.54	1.49	2.22	158.49	2.08	7.47	2.41	28.38
3026.72	3.35	15.53	126.29	6.53	43.14	7.28	144.46
3026.85	4.19	14.06	126.3	6.08	38.61	8.18	126.59
3027.12	1.16	2.27	214.66	0.83	6.81	1.50	29.16
3027.46	1.36	1.46	233.97	0.35	4.98	1.65	24.89
3027.61	0.85	2.02	228.94	0.58	6.23	1.89	28.62
3028.07	1.80	1.84	230.00	2.07	6.22	1.92	32.14
3028.43	1.69	2.24	186.93	2.32	7.69	2.31	39.85
3028.58	4.07	15.94	171.41	16.69	45.48	9.35	204.86
3028.86	2.72	17.54	163.69	19.84	54.14	7.20	228.93
3029.04	1.19	2.03	204.81	2.38	6.31	1.82	35.12
3029.25	1.15	1.98	212.10	2.66	5.32	1.74	27.92
3029.56	2.16	11.00	203.68	5.60	27.69	3.12	103.79
3029.89	2.52	23.94	150.82	21.79	82.87	7.25	339.38
3030.17	3.78	24.45	161.37	18.79	67.10	7.40	265.69
3030.47	2.05	28.05	192.68	15.22	79.14	5.17	272.68
3030.78	2.38	12.52	212.66	8.70	37.63	4.46	116.37

Sample Depth (m)	Al (Wt. %)	Cu (ppm)	Mn (ppm)	Mo (ppm)	Ni (ppm)	U (ppm)	V (ppm)
3031.08	4.21	16.17	165.89	30.38	44.33	5.91	243.11
3031.39	2.93	15.33	211.25	11.38	39.56	4.32	124.00
3031.60	2.17	11.25	189.54	3.88	29.84	3.66	119.19
3031.75	3.79	19.98	157.16	6.66	51.84	8.06	174.44
3032.00	3.59	15.75	181.96	5.81	43.25	5.48	117.95
3032.30	2.97	12.25	147.72	4.97	28.36	3.43	98.17
3032.61	4.46	25.01	147.44	6.55	62.15	6.18	131.05
3032.94	3.93	17.20	160.96	7.04	42.64	3.48	84.68
3033.22	1.70	3.32	611.21	1.06	9.91	1.05	37.38
3033.46	2.72	6.55	588.41	1.13	15.29	1.89	55.56
3033.83	4.36	16.43	152.66	2.95	33.72	3.17	77.58
3034.16	2.24	12.82	65.27	0.80	17.63	2.94	30.81
3034.50	3.34	15.70	53.75	8.35	33.82	4.13	56.60
3034.74	5.07	17.97	139.16	2.25	35.19	3.67	78.43
3035.08	1.89	18.66	96.48	2.79	33.44	2.51	76.80
3035.38	1.80	13.86	47.64	3.56	26.49	2.84	40.03
3035.63	5.37	16.81	156.73	2.73	35.22	3.83	85.08
3035.96	2.04	11.85	121.06	1.93	20.63	3.36	37.80
3036.57	1.24	5.02	232.56	1.64	10.92	1.78	24.72
3036.87	2.85	9.96	194.62	2.51	25.03	6.99	52.60
3037.18	2.10	10.47	186.11	1.30	21.34	3.01	40.37
3037.55	2.05	12.37	188.92	2.49	25.20	3.19	56.22
3037.79	2.33	17.25	214.90	20.48	42.19	3.89	81.74
3038.09	2.99	11.56	220.50	4.40	27.48	3.49	85.19
3038.40	1.92	15.07	164.51	6.47	35.76	3.16	90.85
3039.04	2.64	23.47	231.29	9.02	70.53	5.79	124.71
3039.34	2.06	15.35	214.63	5.97	38.05	3.05	90.18
3039.62	3.69	15.31	197.57	4.95	35.39	3.91	84.59
3039.92	2.96	15.69	202.34	8.72	41.11	4.51	92.9
3040.26	2.03	17.21	167.54	7.56	41.17	3.69	91.05
3040.59	2.69	19.06	181.96	2.81	37.77	6.38	90.37
3040.93	2.27	14.82	219.71	6.12	43.42	5.04	118.32
3041.14	0.86	1.79	191.32	2.45	6.27	1.85	44.94
3041.45	3.45	17.67	177.75	7.75	48.13	10.68	139.44
3041.75	3.31	15.43	176.11	6.53	45.25	6.47	114.05
3042.06	3.13	25.17	151.99	11.17	64.15	6.75	108.5
3042.36	2.24	6.75	220.18	2.56	18.69	4.05	53.05
3042.67	1.78	7.23	290.45	1.85	20.53	2.30	51.79
3042.97	1.77	6.03	260.75	1.38	18.35	2.17	53.33
3043.31	1.24	2.49	233.89	0.86	7.61	1.54	29.38
3043.52	1.30	2.11	281.57	0.56	6.46	1.56	24.40
3043.95	1.20	3.12	155.83	0.46	8.12	1.52	27.38

Sample Depth (m)	Al (Wt. %)	Cu (ppm)	Mn (ppm)	Mo (ppm)	Ni (ppm)	U (ppm)	V (ppm)
3044.17	2.13	2.84	141.86	0.46	8.81	1.52	21.98
3044.53	1.50	4.21	284.17	0.41	9.07	1.45	26.83
3044.80	2.66	6.32	182.83	1.63	14.53	2.83	58.91
3045.13	2.34	3.14	176.72	0.45	9.53	2.10	27.09
3045.41	0.79	2.19	214.22	0.58	5.78	1.20	16.39
3045.71	1.96	2.22	213.72	0.49	7.64	1.65	20.50
3046.02	2.30	2.77	218.77	0.35	9.36	1.93	32.09
3046.32	1.52	2.01	232.51	1.02	5.96	1.54	18.44
3046.63	1.06	4.03	182.91	2.14	11.60	2.00	32.01
3046.93	2.87	16.62	128.22	4.97	35.72	3.66	100.22
3047.24	2.27	17.22	159.82	2.66	38.55	3.00	86.82
3047.66	2.85	14.38	128.36	1.82	28.51	3.32	81.52
3047.85	2.67	16.84	127.63	3.23	38.05	3.35	87.04
3048.15	1.43	18.93	158.50	1.98	40.63	2.54	77.78
3048.43	4.54	18.83	157.96	1.01	37.69	3.51	83.73
3048.76	2.42	18.68	146.30	1.36	33.54	4.20	52.64
3049.07	1.95	10.43	181.68	0.83	14.86	3.00	32.14
3049.43	2.52	11.45	148.76	17.22	37.43	5.38	193.03
3049.68	2.47	11.77	123.24	2.74	28.75	3.36	53.60

*Total redox-sensitive element content calculated by adding redox-sensitive element contents in the non-carbonate (Table 2.2) and carbonate (Table 2.3) fractions for each sample depth.

Table 2.5: Calculated enrichment factors for measured total element concentrations as compared to “average carbonates” (Turekian and Wedepohl, 1961) for elemental redox proxies.

Sample Depth (m)	EF_{Cu}	EF_{Mn}	EF_{Mo}	EF_{Ni}	EF_{U}	EF_{V}
3007.61	0.35	0.03	4.00	0.24	0.21	1.64
3008.01	0.50	0.02	3.57	0.33	0.21	1.45
3008.22	1.53	0.01	6.64	0.69	0.64	1.91
3008.50	0.81	0.01	3.15	0.45	0.64	1.17
3008.83	1.20	0.02	6.75	0.84	0.42	2.60
3009.14	1.80	0.03	9.07	1.20	0.49	3.80
3009.53	0.52	0.02	2.75	0.34	0.31	0.82
3009.69	0.50	0.03	2.68	0.35	0.29	0.98
3009.96	0.43	0.02	2.37	0.32	0.26	0.78
3010.11	0.64	0.02	2.36	0.40	0.35	1.02
3010.33	0.78	0.02	2.88	0.54	0.37	1.19
3010.66	0.45	0.03	4.93	0.28	0.37	0.62
3010.97	0.47	0.01	2.36	0.30	0.39	0.77
3011.27	0.32	0.02	1.34	0.25	0.37	0.94
3011.33	0.33	0.02	1.16	0.25	0.34	0.94
3011.55	0.24	0.02	1.25	0.17	0.38	0.79
3011.88	0.22	0.05	1.01	0.16	0.39	0.72
3012.22	0.22	0.05	1.05	0.16	0.32	0.76
3012.52	0.29	0.03	0.97	0.18	0.35	0.91
3012.86	0.33	0.01	1.59	0.16	0.31	0.64
3013.10	0.24	0.02	0.26	0.08	0.22	0.39
3013.62	0.20	0.07	0.42	0.12	0.38	0.49
3013.77	0.20	0.01	0.08	0.08	0.23	0.42
3014.29	0.19	0.04	0.36	0.11	0.46	0.45
3014.35	0.13	0.03	0.21	0.08	0.29	0.35
3014.69	0.27	0.04	1.29	0.18	0.32	0.37
3014.90	0.24	0.01	0.51	0.12	0.26	0.49
3015.23	0.14	0.02	0.92	0.08	0.26	0.42
3015.66	0.14	0.02	1.01	0.08	0.20	0.36
3015.84	0.25	0.04	0.72	0.15	0.26	0.65
3016.18	0.21	0.02	1.05	0.12	0.25	0.59
3016.36	0.23	0.02	1.06	0.12	0.23	0.44
3016.58	0.49	0.05	0.74	0.19	0.26	0.74
3016.85	0.11	0.06	0.57	0.08	0.18	0.27
3017.06	0.17	0.05	1.28	0.12	0.34	0.43
3017.46	0.56	0.09	3.68	0.29	0.53	0.96
3017.70	0.33	0.01	1.54	0.18	0.36	0.74

Sample Depth (m)	$\mathrm{EF}_{\mathrm{Cu}}$	$\mathrm{EF}_{\mathrm{Mn}}$	$\mathrm{EF}_{\mathrm{Mo}}$	$\mathrm{EF}_{\mathrm{Ni}}$	EF_{U}	EF_{V}
3018.01	0.33	0.01	2.02	0.19	0.42	0.73
3018.28	0.55	0.02	4.82	0.31	0.52	1.40
3018.53	0.46	0.01	3.48	0.23	0.40	0.96
3018.89	0.56	0.01	2.76	0.23	0.48	1.04
3019.23	0.41	0.02	1.70	0.20	0.40	0.73
3019.50	0.16	0.05	0.70	0.12	0.25	0.67
3019.71	0.12	0.04	1.32	0.09	0.27	0.38
3019.87	0.24	0.02	0.95	0.11	0.28	0.49
3020.11	0.34	0.01	2.96	0.20	0.45	0.73
3020.34	0.56	0.02	4.45	0.31	0.53	1.29
3020.42	0.12	0.02	1.53	0.07	0.19	0.40
3020.64	0.16	0.05	2.06	0.10	0.27	0.27
3020.99	0.16	0.06	0.80	0.10	0.29	0.26
3021.33	0.21	0.05	0.78	0.09	0.23	0.29
3021.63	0.31	0.13	0.08	0.20	0.32	0.73
3022.00	0.24	0.06	1.18	0.14	0.34	0.55
3022.21	0.63	0.02	11.47	0.47	0.69	2.19
3022.58	0.26	0.03	3.76	0.19	0.50	0.82
3022.88	0.79	0.01	14.08	0.47	0.82	2.82
3023.16	0.87	0.01	9.76	0.58	0.90	4.02
3023.46	0.45	0.02	6.14	0.31	0.41	1.74
3023.77	0.42	0.02	5.54	0.26	0.38	1.31
3024.38	0.61	0.02	17.38	0.44	0.60	2.33
3024.68	0.77	0.01	5.34	0.41	0.64	2.27
3025.02	0.19	0.05	2.77	0.14	0.34	0.50
3025.35	0.29	0.05	1.93	0.09	0.25	0.40
3025.93	0.12	0.03	0.90	0.08	0.28	0.33
3026.18	0.13	0.03	0.94	0.08	0.28	0.38
3026.54	0.16	0.04	1.46	0.11	0.31	0.40
3026.72	0.49	0.01	2.04	0.27	0.41	0.90
3026.85	0.35	0.01	1.52	0.19	0.37	0.63
3027.12	0.21	0.07	0.75	0.12	0.25	0.53
3027.46	0.11	0.07	0.27	0.08	0.23	0.39
3027.61	0.25	0.10	0.72	0.15	0.42	0.71
3028.07	0.11	0.05	1.21	0.07	0.20	0.38
3028.43	0.14	0.04	1.45	0.10	0.26	0.50
3028.58	0.41	0.02	4.31	0.23	0.44	1.06
3028.86	0.68	0.02	7.65	0.42	0.50	1.77
3029.04	0.18	0.07	2.11	0.11	0.29	0.62
3029.25	0.18	0.07	2.42	0.10	0.29	0.51

Sample Depth (m)	EF_{Cu}	EF_{Mn}	EF_{Mo}	EF_{Ni}	EF_{U}	EF_{V}
3029.56	0.53	0.04	2.71	0.27	0.27	1.01
3029.89	1.00	0.02	9.06	0.69	0.55	2.82
3030.17	0.68	0.02	5.22	0.37	0.37	1.48
3030.47	1.44	0.04	7.78	0.81	0.48	2.79
3030.78	0.55	0.03	3.83	0.33	0.36	1.03
3031.08	0.40	0.02	7.57	0.22	0.27	1.21
3031.39	0.55	0.03	4.07	0.28	0.28	0.89
3031.60	0.54	0.03	1.88	0.29	0.32	1.15
3031.75	0.55	0.02	1.85	0.29	0.41	0.97
3032.00	0.46	0.02	1.70	0.25	0.29	0.69
3032.30	0.43	0.02	1.75	0.20	0.22	0.69
3032.61	0.59	0.01	1.54	0.29	0.26	0.62
3032.94	0.46	0.02	1.88	0.23	0.17	0.45
3033.22	0.20	0.14	0.65	0.12	0.12	0.46
3033.46	0.25	0.08	0.44	0.12	0.13	0.43
3033.83	0.40	0.01	0.71	0.16	0.14	0.37
3034.16	0.60	0.01	0.37	0.17	0.25	0.29
3034.50	0.49	0.01	2.62	0.21	0.24	0.36
3034.74	0.37	0.01	0.47	0.15	0.14	0.32
3035.08	1.04	0.02	1.55	0.37	0.25	0.85
3035.38	0.81	0.01	2.08	0.31	0.30	0.47
3035.63	0.33	0.01	0.53	0.14	0.14	0.33
3035.96	0.61	0.02	0.99	0.21	0.31	0.39
3036.57	0.43	0.07	1.39	0.19	0.27	0.42
3036.87	0.37	0.03	0.93	0.18	0.47	0.39
3037.18	0.52	0.03	0.65	0.21	0.27	0.40
3037.55	0.63	0.04	1.27	0.26	0.30	0.57
3037.79	0.78	0.04	9.22	0.38	0.32	0.74
3038.09	0.41	0.03	1.55	0.19	0.22	0.60
3038.40	0.83	0.03	3.54	0.39	0.31	0.99
3039.04	0.94	0.03	3.60	0.56	0.42	0.99
3039.34	0.78	0.04	3.04	0.39	0.28	0.92
3039.62	0.44	0.02	1.41	0.20	0.20	0.48
3039.92	0.56	0.03	3.09	0.29	0.29	0.66
3040.26	0.89	0.03	3.91	0.43	0.35	0.94
3040.59	0.74	0.03	1.10	0.29	0.45	0.71
3040.93	0.69	0.04	2.83	0.40	0.42	1.09
3041.14	0.22	0.09	3.02	0.15	0.41	1.11
3041.45	0.54	0.02	2.36	0.29	0.59	0.85
3041.75	0.49	0.02	2.07	0.29	0.37	0.72

Sample Depth (m)	EF_{Cu}	EF_{Mn}	EF_{Mo}	EF_{Ni}	EF_{U}	EF_{V}
3042.06	0.84	0.02	3.74	0.43	0.41	0.73
3042.36	0.32	0.04	1.20	0.18	0.35	0.50
3042.67	0.42	0.06	1.08	0.24	0.25	0.61
3042.97	0.36	0.06	0.82	0.22	0.23	0.63
3043.31	0.21	0.07	0.72	0.13	0.24	0.50
3043.52	0.17	0.08	0.45	0.10	0.23	0.40
3043.95	0.27	0.05	0.40	0.14	0.24	0.48
3044.17	0.14	0.03	0.23	0.09	0.14	0.22
3044.53	0.30	0.07	0.28	0.13	0.18	0.38
3044.80	0.25	0.03	0.64	0.11	0.20	0.47
3045.13	0.14	0.03	0.20	0.09	0.17	0.24
3045.41	0.29	0.10	0.77	0.15	0.29	0.43
3045.71	0.12	0.04	0.27	0.08	0.16	0.22
3046.02	0.13	0.04	0.16	0.09	0.16	0.29
3046.32	0.14	0.06	0.70	0.08	0.19	0.25
3046.63	0.40	0.07	2.12	0.23	0.36	0.63
3046.93	0.61	0.02	1.82	0.26	0.24	0.73
3047.24	0.80	0.03	1.23	0.36	0.25	0.80
3047.66	0.53	0.02	0.67	0.21	0.22	0.60
3047.85	0.66	0.02	1.27	0.30	0.24	0.69
3048.15	1.39	0.04	1.45	0.60	0.34	1.14
3048.43	0.44	0.01	0.23	0.17	0.15	0.39
3048.76	0.81	0.02	0.59	0.29	0.33	0.46
3049.07	0.56	0.04	0.45	0.16	0.29	0.35
3049.43	0.48	0.02	7.18	0.31	0.41	1.61
3049.68	0.50	0.02	1.16	0.24	0.26	0.45

CHAPTER III

ON ORGANIC MATTER ENRICHMENT IN THE MISSISSIPPIAN LIMESTONE OF THE ANADARKO SHELF OF OKLAHOMA

3.1 Abstract

To date, over 900 million barrels of oil and 6.4 trillion cubic feet (tcf) of gas have been produced from the Anadarko Shelf and Basin of Oklahoma. Recently, there has been a resurgence in activity in this petroleum province due to the application of modern completion techniques to organic-rich rock intervals, including heterogeneous lithologies such as the Mississippian Limestone within the Anadarko Shelf in central Oklahoma. Furthermore, previous work on the Mississippian Limestone interval in the Anadarko shelf suggest that depositional redox does not appear to impact organic matter accumulation and abundance within the interval. Consequently, additional investigation of factors responsible for organic matter enrichment and deposition of potential source rock segments in the Anadarko shelf is warranted. Utilizing samples collected from a cored petroleum exploration well drilled in Kingfisher County, Oklahoma, we investigated the effects of paleoproductivity and detrital input on organic matter enrichment in the Mississippian Limestone interval of the Anadarko shelf using a combination of measurements of stable carbon isotopes of organic carbon ($\delta^{13}C_{org}$) as well as various elemental geochemical proxies of paleoproductivity and detrital input. Total organic carbon (TOC) values are between 0-2.1 wt. % and average 0.4 wt. % in the studied core interval. The $\delta^{13}C_{org}$ values were between

– 38.6 ‰ and – 24.7 ‰ (average -28.3 ± 2.9 ‰). Taken together, TOC values and $\delta^{13}C_{org}$ signatures suggest that the Mississippian Limestone interval is unlikely to have generated liquid hydrocarbons at our Anadarko Shelf study site. Furthermore, calculated enrichment factors for elemental geochemical proxies for paleoproductivity and detrital input are not significantly enriched above their content in average carbonate. Likewise, there is no relationship between TOC and detrital input proxies or between TOC and paleoproductivity proxies. Our results do not indicate heightened contribution of nutrients into the Anadarko Shelf at time of deposition of sediments of the Mississippian Limestone. Similarly, our results suggest that there was lack of enhanced organic matter productivity in the Mississippian Limestone interval in our Anadarko Shelf study site during deposition. Thus, results from our study suggest that the organic matter found in the Mississippian Limestone in our study area within the STACK (Sooner Trend, Anadarko Basin, Canadian and Kingfisher Counties) is likely allochthonous and is mostly of terrestrial provenance. Consequently, the Mississippian Limestone interval in our study site is unlikely to have self-sourced any oil.

3.2 Introduction

Significant quantities of hydrocarbons have been produced over several decades from the Anadarko Shelf and Basin of Oklahoma (Harris, 1975; Koch et al., 2014). In recent times, hydrocarbon exploration and exploitation in various onshore locations in North America, such as the Sooner Trend, Anadarko Basin, Canadian and Kingfisher Counties (STACK) resource play within the Anadarko Shelf and Basin of Oklahoma (Fig. 3.1), have experienced a renaissance due to the advent of modern completion techniques which combine horizontal drilling and hydraulic fracturing. The United States Geological Survey (USGS) estimates that up to 31 million barrels of oil, 99 billion cubic feet of gas and 4 million barrels of natural gas liquids could yet be discovered within the Mississippian assessment unit of the Anadarko Basin Province (Higley, 2014). Furthermore, various previous studies suggest that the hydrocarbon resources hosted within the Mississippian Limestone interval are a mixture of hydrocarbons generated by the regionally extensive, underlying Woodford Shale and hydrocarbons self-sourced from sediments of the Mississippian Limestone interval itself (Kim and Philp, 2001; Al Atwah et al., 2019; Symcox and Philp, 2019; Wilson et al., 2019). Past studies, suggesting that the Mississippian Limestone interval is a source rock unit, have utilized biomarker geochemistry of produced oil and rock extracts, Rock-Eval source rock screening as well as organic petrography to arrive at their conclusions (e.g., Atwah et al., 2019; Atwah et al., 2020; Wang and Philp, 1997; Wang and Philp, 2019). The lithological heterogeneity of the Mississippian Limestone interval and lack of well constrained biostratigraphic control further complicates investigations of the Mississippian Limestone interval because specific zones within the interval are unable to be correlated with significant confidence from one study area to the other and as a result, source rock zones within the interval are not well constrained, if in fact they are present at all (Atwah et al., 2020 and references therein). Petroleum source rocks, as well as other rocks and sediments which are enriched in organic matter, are typically inferred to be deposited based on one of 3 end-member models: deposition under anoxic conditions (e.g., Demaison and Moore, 1980), deposition as a result of heightened productivity of organic matter (e.g., Parrish, 1982; Parrish and Curtis, 1982; Waples, 1983; Pedersen and Calvert, 1990; Caplan and Bustin, 1998), and deposition associated with very low levels of dilution by non-organic matter sediments (e.g., Canfield, 1994; Tribovillard et al., 2005). Other authors have proposed that a combination of these various end members is responsible for organic matter enrichments in sediments and source rocks (e.g., Huc et al., 1992; Ramanampisoa and Disnar, 1994; Hedges and Keil, 1995; Meyers, 1997; Tyson, 2001; Curiale and Curtis, 2016; Li et al., 2020). A previous study of depositional redox conditions of the Mississippian Limestone interval within the Anadarko Shelf found that redox conditions at time of deposition were oxic to suboxic (Adeboye et al., 2020). These authors consequently called into question the self-sourcing potential and source rock characteristics of the Mississippian Limestone interval within the Anadarko Shelf because organic matter accumulation in the Mississippian Limestone could not be ascribed to depositional anoxia. Since anoxia cannot explain organic matter accumulation in the Mississippian Limestone interval, the present study attempts to investigate organic productivity and detrital input into the Anadarko Shelf and the impact of these factors, individually or in concert, on organic matter accumulation during deposition of sediments of the Mississippian Limestone. Past studies suggest that enhanced productivity can result in heightened organic matter accumulation in various modern and ancient environments (e.g., Pedersen and Calvert, 1990; Brumsack, 2006).

Elemental geochemistry has been utilized to decipher paleoproductivity and detrital input in various ancient and modern sediments, from various basins across the globe (e.g., Borchers et al., 2005; Brumsack, 2006; Ross and Bustin, 2009; Boning et al., 2015; Sweere et al., 2016; Steinmann et al., 2020). The genesis and fate of sedimentary organic matter is able to be deduced from the examination of a variety of elements that are associated with organic matter or, which are essential (micro-) nutrients. Hence, high concentrations of elements such as Ag, Cd, Cu, Ni, P and Zn have been successfully utilised as proxies for heightened paleoproductivity in assorted sediments of different ages, across various basins (e.g., Loring, 1979; Koide et al., 1986; Tribovillard et al., 2006; McKay and Pedersen, 2008; Wagner et al., 2013; Li et al., 2020; Steinmann et al., 2020). Al is transported into the oceans via continental runoff in rivers or through aeolian means and is usually immobile during diagenesis. Furthermore, elements that show positive covariation with Al, such as Co, Cr, K and Ti, are usually interpreted to be of detrital provenance (e.g., Ross and Bustin, 2009; Tribovillard et al., 2006 and references therein). Measurements of stable carbon isotope of organic matter ($\delta^{13}C_{org}$) have been used to distinguish between various populations and/or types of organic matter due to the observation that various populations of organic matter display distinct $\delta^{13}C_{org}$ values (e.g., Craig, 1953; Hayes et al., 1989; Kenig et al., 1994; Mackensen and Schmiedl, 2019) consequently, this parameter will be used to discriminate organic matter type in this study.

In order to evaluate paleoproductivity and detrital input within the Anadarko Shelf at time of deposition of sediments of the Mississippian Limestone interval, we measured stable isotopes of organic carbon ($\delta^{13}C_{org}$) and abundance of a suite of elemental proxies for paleoproductivity (Ag, Cd, Cu, Ni, P and Zn) and detrital input (Co, Cr, K and Ti) on Mississippian Limestone samples collected from a hydrocarbon exploration well drilled in Kingfisher County, Oklahoma. Our study could help to refine ideas on hydrocarbon exploration within the Anadarko Shelf by providing insights into those factors that were responsible for deposition of intervals having heightened organic matter (inferred from TOC content) within the Mississippian Limestone interval in the STACK resource play area.

3.3 Samples and Methods

3.3.1 Geological and Paleogeographic Setting

The Mississippian Limestone interval in the Mid-Continent region of the U.S.A. is considered to be part of the 2nd order Kaskaskia supersequence as defined by Sloss (1963). Sediments making up the Mississippian Limestone interval were deposited close to the equator, along a distally steepened ramp, in an ancient epeiric sea during a period of climate transition (Gutschick and Sandberg, 1983; Haq and Schutter, 2008; LeBlanc, 2014). The changing climate during Mississippian time would have impacted levels of paleoproductivity and detrital input, factors which would both exert an influence on the genesis and fate of sedimentary organic matter preserved in the Mississippian Limestone interval. The Mississippian Limestone interval is underlain by the Woodford Shale, a Devonian petroleum source rock in the US Mid-Continent region, and overlain by rocks of the Pennsylvanian Springer Formation (Wang and Philp, 1997). There is poor age constraint on rocks of the Mississippian Limestone interval in our study area due to the lack of conodonts within the interval, although Hunt (2017) reports ages of ~ 346.7 to 330.9 Ma (Middle Osagean to Late Chesterian, Uppermost Tournaisian to Latest Visean) for Mississippian Limestone samples obtained to the east of our study site.

In our study area, the Mississippian Limestone interval is of heterogeneous lithology, and is comprised of calcareous, siliciclastic siltstones and carbonate packstones-grainstones. Wang et al. (2019) identified a total of 7 distinct lithofacies within the Mississippian Limestone on the core examined for the current study as follows: (1) glauconitic siltstone-fine sandstone (2) massive-bedded siltstone (3) laminated calcareous siltstone (4) burrowed calcareous siltstone (5) bioturbated calcareous siltstone (6) massive-bedded packstone-grainstone (7) hummocky cross stratified (HCS) and planar laminated packstone-grainstone. All lithofacies, except the glauconitic siltstone-fine sandstone, are present in the samples employed for the current study.

Although briefly summarised above, Wang et al. (2019) and Adeboye et al. (2020) provide greater details about the geology and paleogeography of the Mississippian Limestone interval, as well as the facies classification of the Mississippian Limestone interval which is employed in the current study. It is pertinent to note that the core examined in this study is different from that which was utilised for the Adeboye et al. (2020) study, although Wang et al. (2019) provided the underlying lithological descriptions for both cores studied by Adeboye et al. (2020) and in the current study and the general lithological construction is similar in these cores, even though they were drilled in different locations within the Anadarko Shelf of Oklahoma.

3.3.2 Sample Selection and Preparation

Samples for the current study were obtained from the cored interval of a petroleum exploration well drilled in Kingfisher County, Oklahoma (Fig. 3.1) and sampling was conducted based on the core descriptions of Wang et al. (2019). A total of 81 samples were collected between 2685.20 m (8809.7 ft) and 2706.62 m (8880 ft) at intervals not exceeding approximately 0.61 m (2 ft). The sampled drill core examined in the current study was split in half prior to sampling and a third of each sample was crushed and homogenised to fine powder in an agate mortar and pestle in order to prevent any metal contamination (for details see Adeboye et al., 2020).

3.3.3 Total Organic Carbon Measurements

In order to determine the total organic carbon (TOC) content of the samples (reported in units of weight %, wt. %), approximately 50-55 mg of powdered rock samples were placed in silver capsules and dried for a period of 8 hours in an oven at a temperature of 50°C. Oven dried samples were acidified in silver capsules by sequential treatment with double deionised water (Sartorius), 25% hydrochloric acid until cessation of effervescence, and finally, concentrated hydrochloric acid until effervescence was no longer observed. Acidification was undertaken in order to get rid of inorganic carbon from the samples prior to the TOC analysis. Acidified samples were subsequently dried in an oven at a temperature of 50°C for a period of 48 hours to ensure complete dryness. Once samples were dry, they were wrapped in tin capsules along with some vanadium pentoxide combustion catalyst then, TOC was analysed using a Costech® ECS 4010 elemental combustion system. Acetanilide was used as a concentration standard for TOC.

3.3.4 Organic Carbon Isotope Measurements

Organic carbon stable isotope ($\delta^{13}C_{org}$) measurements were carried using a Thermo Finnigan Deltaplus XL® isotope ratio mass spectrometer interfaced with a Costech® ECS 4010 elemental analyser (EA-IRMS). Approximately 20-30 mg of powdered rock samples were placed in silver capsules and dried for a period of 8 hours in an oven at a temperature of 50°C. Oven dried samples were acidified in silver capsules by sequential treatment with double deionised water (Sartorius), 25% hydrochloric acid until cessation of effervescence, and finally, concentrated hydrochloric acid until effervescence was no longer observed. Acidification was undertaken in order to remove inorganic carbon from the samples prior to analysis for organic carbon stable isotopes. Acidified samples were subsequently dried in an oven at a temperature of 50°C for a period of 48 hours to ensure complete dryness. Once samples were dry, they were wrapped in tin capsules after which stable organic carbon isotope measurements were made using the EA-IRMS. $\delta^{13}C_{org}$ results are computed using standard δ notation and are reported relative to VPDB in units of per mille (‰).

Isotope standards USGS 40 and Urea-1 were used for calibration and validation of $\delta^{13}C_{org}$ while acetanilide was used as a concentration standard for C in the study. Analytical error is ± 0.4 ‰ and is estimated from the standard deviation of a set of repeat measurements of standards. Standard deviation of duplicate samples of $\delta^{13}C_{org}$ is 0.49.

3.3.5 Measurements of Elemental Contents and Enrichment Factor Calculations

Contents of elements used to investigate paleoproductivity and detrital input contributions at time of deposition of the Mississippian Limestone interval were measured on a Thermo Scientific iCAP Qc® inductively coupled plasma-mass spectrometer (ICP-MS) as described in detail in Adeboye et al. (2020). Briefly, 250-300 mg of crushed rocks were sequentially digested using a sodium acetate solution (trace metal grade) followed by multi-acid digestion under heat and pressure. Thus, elements associated with the carbonate fraction of the rock were separated from those associated with the non-carbonate fraction, respectively. Analyses of trace elements associated with the carbonate fraction of the rock and those associated with the non-carbonate fraction were carried out separately and total element content per sample was derived by computing the sum of the measured contents of carbonate and non-carbonate fractions for the various elemental proxies of paleoproductivity (Ag, Cd, Cu, Ni, P and Zn) and detrital input (Co, Cr, K and Ti) assessed in this study. All reagents used in this step were of trace metal grade and the analytical error is better than 6% for both carbonate fraction and non-carbonate fraction elemental content measurements based on repeated measurements of reference standard materials. Enrichment factors of elemental proxies were calculated based on computed total element contents as described by Adeboye et al. (2020) and references therein: $\text{Enrichment Factor}_{\text{trace element}} = (\text{Trace element}_{\text{sample}}/\text{Al}_{\text{sample}})/(\text{Trace element}_{\text{average carbonate}}/\text{Al}_{\text{average carbonate}})$

3.4 Results

3.4.1 TOC and $\delta^{13}C_{org}$ Measurements

Measurements of TOC and $\delta^{13}C_{org}$ measurements are presented in Table 1. TOC values in the studied core are between 0.0-2.1 wt. % with an average value of 0.4 ± 0.4 wt. %. (Table 1). The following is a breakdown of TOC values within individual lithofacies identified in the sampled interval of core: Average TOC values are 1.0 wt. % in samples classified as massive bedded siltstone lithofacies and TOC values range from 0.1 wt. % to 2.1 wt. %. TOC values are between 0.1 wt. % and 0.7 wt. % in samples of the laminated calcareous siltstone lithofacies (average TOC values of 0.4 wt. %). The 3 samples described as being burrowed calcareous siltstone lithofacies have maximum TOC contents of 0.2 wt. % (average TOC values of 0.1 wt. %) while TOC values are up to 0.5 wt. % in samples of the bioturbated calcareous siltstone lithofacies (average 0.2 wt. % TOC). Massive-bedded packstone-grainstone lithofacies samples have TOC values between 0.1 wt. % and 0.8 wt. % (average TOC values of 0.2 wt. %), and in samples belonging to the HCS and planar laminated packstone to grainstone lithofacies, TOC values reach a maximum of 1.2 wt. % with an average value of 0.7 wt. % TOC (Fig. 3.2). Measured $\delta^{13}C_{org}$ values were between – 38.6 ‰ and – 24.7 ‰ with an average of - 28 ± 3 ‰ in the samples analysed for this study (Table 3.1). An examination of the $\delta^{13}C_{org}$ trend with lithofacies (Fig. 3.2) reveals that average $\delta^{13}C_{org}$ values are around - 27 ‰ for samples classified as belonging to the burrowed calcareous siltstone (average $\delta^{13}C_{org}$ values of – 27.3 ‰), bioturbated calcareous siltstone (average $\delta^{13}C_{org}$ values of – 26.9 ‰) and massive-bedded packstone-grainstone lithofacies (average $\delta^{13}C_{org}$ values of – 26.5 ‰), while the samples described as being massive bedded siltstone lithofaces have average of $\delta^{13}C_{org}$ values of – 28.0 ‰. Finally, samples belonging to the laminated calcareous siltstone (average $\delta^{13}C_{org}$ values of – 30.9 ‰) and HCS and planar laminated packstone to grainstone lithofaces (average $\delta^{13}C_{org}$ values of – 30.8 ‰) have average $\delta^{13}C_{org}$ values of – 31.0 ‰.

3.4.2 Elemental Proxy Contents

Results from measurements of total contents (non-carbonate fractions + carbonate fraction contents) of elemental proxies of detrital input (Fig. 3.3) and paleoproductivity are presented in Tables 2 and 3 respectively. Total contents of elemental proxies of detrital input measured for this study are as follows: Al contents in samples ranged from 0.73 wt. % to 4.32 wt. %, total Co contents were between 1.05 ppm and 7.70 ppm, total Cr abundance in these samples were between 20.24 ppm and 290.49 ppm, contents of K in these samples were between 0.18 wt. % and 1.84 wt. %, finally, contents of Ti varied between 0.12 wt. % and 0.48 wt. %. Similarly, total contents of elemental proxies of paleoproductivity considered in this study are as follows: Ag contents were between 0.07 ppm to 2.64 ppm, Cd contents ranged from 0.11 ppm to 17.41 ppm, Cu contents were between 1.07 ppm and 21.45 ppm, Ni contents varied from 3.19 ppm to 51.92 ppm, contents of P ranged from 0.04 wt. % to 5.28 wt. % and contents of Zn were between 12.63 ppm to 301.99 ppm.

3.5 Discussion

Organic matter enrichment is defined based on the parameters published by Peters and Cassa (1994) and Sorkhabi (2016). These authors report that sedimentary organic matter content that is ≥ 0.5 wt. % is considered to be fairly enriched in sediments and sedimentary rocks. Thus, of all the samples examined in this study, samples classified as being massive bedded siltstone lithofacies (average TOC values of 1.0 wt. %) and HCS and planar laminated packstone to grainstone lithofacies (average TOC values of 0.7 wt. %) can generally be considered as having heightened TOC values, while those samples belonging to the laminated calcareous siltstone, burrowed calcareous siltstone, bioturbated calcareous siltstone and massive-bedded packstone-grainstone lithofacies have low organic matter contents, since the average TOC contents in these lithofacies are below 0.5 wt. % (Fig. 3.2, Table 3.1). Similarly, there appears to be a consistency in the measured values of $\delta^{13}C_{org}$ in most of those lithofacies which have low average TOC values (average TOC values of no more than 0.2 wt. %) with average $\delta^{13}C_{org}$ values of between – 26.5 ‰ to – 27 ‰, whereas the lithofacies intervals with higher TOC contents (≥ 0.5 wt. %) have different average $\delta^{13}C_{org}$ values (average $\delta^{13}C_{org}$ value of – 28.0 ‰ in massive bedded siltstone lithofacies vs. average $\delta^{13}C_{org}$ value of – 30.8 ‰ for HCS and planar laminated packstone to grainstone).

It is worth pointing out that average $\delta^{13}C_{org}$ values are different in both of these intervals with higher organic matter content. The only exception to these overall trends would be samples classified as belonging to the laminated calcareous siltstone lithofacies, where samples have average TOC values of 0.4 wt. %, a value which is higher than those found in samples classified as belonging to burrowed calcareous siltstone, bioturbated calcareous siltstone and massive-bedded packstone-grainstone lithofacies, where average TOC contents are between 0.1 and 0.2 wt. %. Similarly, the average $\delta^{13}C_{org}$

value of – 30.9 ‰ measured in samples described as being laminated calcareous siltstone lithofacies are different from those measured in the other lithofacies subdivisions that have TOC contents of < 0.5 wt. %, where average $\delta^{13}C_{org}$ values are about – 27 ‰.

The differences in TOC and $\delta^{13}C_{org}$ measured in samples examined in this study suggests that different types of organic matter were contributed to, and subsequently preserved in the various lithofacies groupings present within the studied interval of core. It has been reported that $\delta^{13}C_{org}$ values of type I organic may be up to - 35 ‰, those of type II organic matter are up to – 32 ‰ while type III organic matter $\delta^{13}C_{org}$ values are about – 27 ‰ (Whiticar, 1996). Type I organic matter is typically thought of as being composed of algal material and being of lacustrine provenance, type III organic matter is usually composed of continental plants and is of terrestrial provenance and type II organic matter is usually interpreted as being of marine provenance and is composed of zooplankton, phytoplankton and bacteria. Similarly, $\delta^{13}C_{org}$ values of between ~ - 25 ‰ to – 27 ‰ have been reported for terrestrial organic matter of Devonian- to Carboniferous-aged coals and kerogen (e.g., Redding et al., 1980; Warwick and Ruppert, 2016) and values of $\delta^{13}C_{org}$ of at least between ~ -30 ‰ and ~ -32 ‰ for marine organic matter of Devonian to Carboniferous aged kerogens have also been reported (Maynard, 1981; Formolo et al., 2014). Based on the reported $\delta^{13}C_{org}$ values for the different types of organic matter, it appears that there are contributions of types II and III organic matter to the samples examined in this study. Average $\delta^{13}C_{org}$ values of around – 27 ‰ suggests inputs of type III organic matter to samples belonging to the various lithofacies with TOC contents < 0.2 wt. %. Samples of the laminated calcareous siltstone lithofacies (average TOC content of 0.4 wt. %), even though they are classified as being low TOC since their average TOC content is < 0.5 wt. %, appear to have contributions of largely type II organic matter, as reflected in the different average value (- 30.9 ‰) of the $\delta^{13}C_{org}$ signatures of the samples belonging to this lithofacies. In those lithofacies with TOC contents ≥ 0.5 wt. %, there appears to be contributions of different types of organic matter based on measured $\delta^{13}C_{org}$ values: massive bedded siltstone lithofacies (average TOC value of 1.0 wt. %) have $\delta^{13}C_{org}$ values showing likely contributions of mixed type II-III organic matter because the average $\delta^{13}C_{org}$ value of - 28.0 ‰ calculated for this lithofacies class lies on the border between the reported $\delta^{13}C_{org}$ values for type II and type III organic matter, perhaps due to having different proportions of the different types of organic matter (e.g., Ahmad and Davies, 2017). This is in contrast to the average $\delta^{13}C_{org}$ value of – 30.8 ‰ for HCS and planar laminated packstone to grainstone (average TOC value of 0.7 wt. %), which seem to signify greater contribution of type II organic matter to samples classified as being of this lithofacies. The $\delta^{13}C_{org}$ values measured in our current study of organic matter from the Mississippian Limestone interval of the Anadarko Shelf of Oklahoma are similar to previously reported $\delta^{13}C_{org}$ values of terrestrial and marine organic matter of Devonian to Carboniferous age (e.g., Redding et al., 1980; Maynard, 1981; Formolo et al., 2014; Warwick and Ruppert, 2016). Consequently, our findings suggest that there was contribution of organic matter from a variety of marine and terrestrial sources into this area of the Anadarko Shelf during deposition of sediments of the Mississippian Limestone interval. Furthermore, it could be the case that in those lithofacies with average TOC < 0.2 wt. %, the constituent sediments of these lithofacies groups perhaps did not receive sufficient input of organic matter during deposition or whatever organic matter was in fact deposited in these sediments was not preserved over time as these sediments became lithified and subjected to diagenetic processes (e.g., bioturbation, burrowing). It has been reported previously that lithological variations within the Mississippian Limestone interval are a consequence of changes in eustasy and relative sea level overprinted by Milankovitch cycle variations (LeBlanc, 2014; Dupont and Grammer, 2019) thus, it is likely that inputs of different organic matter type observed in the lithofacies groupings in this study are ultimately controlled by these basin- and shelf-wide factors (cf. Huc et al., 2005). We speculate that during periods of lower relative sea level, those lithofacies with predominant type III organic matter, such as the burrowed calcareous siltstone lithofaces, were deposited and processes that expose organic matter to oxygen (e.g., burrowing, bioturbation) were more widespread thus, leading to the lower average TOC content and type III $\delta^{13}C_{org}$ signatures observed in these lithofacies. Sediments belonging to lithofacies with higher TOC contents were deposited at times of higher relative sea levels or during periods of sediment starvation, leading to greater preservation of organic matter (in the case of the massive bedded siltstone lithofacies, cf. Wang et al., 2019) or input and preservation of a different type of organic matter (in the case of laminated calcareous siltstone lithofacies and HCS and planar laminated packstone-grainstone, cf. Wang et al., 2019). It is important to note that the reported $\delta^{13}C_{org}$ values of Devonian and Carboniferous age organic matter (both marine and terrestrial) including those presented in this paper, as well as those reported by Formolo et al. (2014) and Warwick and Ruppert (2016), are different from the values of $\delta^{13}C_{org}$ reported for modern organic matter, such as those published by Peters et al. (1978) and Meyers (1994; 1997). Properties of the various organic matter types (I, II, III and IV) are expounded upon in greater detail in papers by Meyers (1994), Peters and Cassa (1994) and Whiticar (1996), amongst others.

So as to further investigate the sources of organic matter in the studied interval of core, we examined contents (Tables 3.2 and 3.3) and enrichment factors (Tables 3.4 and 3.5) of the elemental proxies of detrital input Co, Cr, K and Ti, as well as paleoproductivity proxies Ag, Cd, Cu, Ni, P and Zn within individual lithofacies groupings (Figs. 3.4 and 3.5). These proxies allow us to determine whether the organic matter in those lithofacies with higher TOC contents are autochthonous or allochthonous. No elevated enrichment of detrital input proxies was observed in any lithofacies groups regardless of TOC content, except for a slight enrichment in Co (enrichment factor up to 10), suggesting that there was at best, only a slight contribution of detrital material from continental sources to the study site at time of deposition (Fig. 3.4 and Table 3.4). Our findings regarding the slight enrichment of the Co detrital input proxy (Table 3.4) are similar to those reported in the study of Steinmann et al. (2020) who examined outcrops of the Mississippian Limestone in Jane, Missouri, a distance of over 400 kilometres away from our Anadarko Shelf study site in Oklahoma. Steinmann and coworkers identified the presence of, and enrichment (Enrichment factors up to 10, with respect to average shale) of, the detrital input proxies Co, Cr and Ti. The findings from both studies suggest that there was some level of detrital input influx at time of deposition of sediments of the Mississippian Limestone and this detrital input was likely extensive enough that it is reflected in the mixed clastic-carbonate lithology preserved within the Mississippian

Limestone interval, both in the Anadarko Shelf of Oklahoma (this study) as well as in Missouri (Steinmann et al., 2020).

Similarly, in all lithofacies subdivisions, irrespective of TOC content, there is a uniform lack of enrichment above background values for the paleoproductivity proxies, except for Cd, which has enrichment factors of up to 60 in the massive bedded siltstone lithofacies (average TOC content is 1.0 wt. % in this lithofacies interval) and enrichment factors of up to 49 in the laminated calcareous siltstone lithofacies, where average TOC content is 0.4 wt. %. Paradoxically, the heightened enrichment of Cd observed within the massive bedded siltstone and laminated calcareous siltstone lithofacies is not observed within the HCS and planar laminated packstone to grainstone lithofaces where average TOC content is 0.7 wt. % (Fig. 3.5 and Table 3.5). Enrichment of Cd in Mississippian Limestone samples was observed in an outcrop study of the Mississippian Limestone in Jane, Missouri, where it was speculated that Cd was likely bound in extraneous organic matter that was transported to the study area and then was released in pore waters during decay to be incorporated into authigenic minerals (Steinmann et al., 2020 and references therein). Enrichment factors reported for Cd by Steinmann et al. (2020) in their Mississippian Limestone outcrop study were greater than 200 thus, it is likely that the process they described for Cd enrichment in their Mississippian Limestone study was operating to a lesser extent in our Anadarko Shelf study site during deposition of sediments of the Mississippian Limestone interval. The paleoproductivity proxies (Ag, Cd, Cu, Ni, P, Zn) we examined in this study are generally depleted relative to average carbonate at most depths within the studied core interval although P did display slight enrichments (enrichment factors no greater than 20) in 2 instances, one each in the laminated calcareous siltstone and in the massive-bedded packstone-grainstone lithofacies (Table 3.5). This depletion of paleoproductivity proxies is different from the findings of Steinmann et al. (2020), who noticed slight enrichments of the elemental paleoproductivity proxies P, Ni and Zn (enrichment factors up to 10, with respect to average shale) in their outcrop study of the Mississippian Limestone. Additionally, there is no evidence for upwelling at time of deposition of the Mississippian Limestone interval observed from our current study in our Anadarko Shelf study site due to the lack of significant enrichment in elemental proxies of paleoproductivity (e.g., Cd, P) which are typically highly enriched in upwelling zones (cf. Brumsack, 2006). The lack of significant enrichments of the vast majority of paleoproductivity proxies, in both the current Mississippian Limestone study from the Anadarko Shelf, and in the outcrop study of the Mississippian Limestone conducted by Steinmann et al. (2020), may be due to oxic conditions at time of deposition of these sediments in both study sites (e.g., Tribovillard et al., 2006; Adeboye et al., 2020) or, may be a consequence of remobilisation and/or diagenesis (e.g., Abanda and Hannigan, 2006). Cu and Ni were employed as redox proxies by Adeboye et al. (2020) during their investigation of depositional redox on the Anadarko Shelf however, Tribovillard et al. (2006) state that these elemental proxies are also useful as paleoproductivity proxies due to their affinity with organic matter. The depletion observed for both Cu and Ni in all lithofacies groupings in the current study supports the findings of Adeboye et al. (2020), that redox conditions at time of deposition of sediments of the Mississippian Limestone interval on the Anadarko Shelf were oxygenated and, from a paleoproductivity standpoint, there was lack of enhanced organic matter productivity within the Anadarko Shelf when these sediments were being deposited. The lack of heightened enrichment in the paleoproductivity proxies considered in this study, combined with the $\delta^{13}C_{org}$ measurements which show signatures of type II and III organic matter, suggests that the organic matter within the studied core is allochthonous and was sourced outside our study. No correlation was observed between Al and the paleoproductivity proxies Ag, Cd, Cu, P, Ni and Zn, nor was there any correlation between TOC and Al (Fig. 3.6). These findings are likely because the organic matter preserved in the Mississippian Limestone samples examined in our study appears to be predominantly type III organic matter, thus indicative of terrestrial origin, and are most likely allochthonous. The measured $\delta^{13}C_{org}$ values support the assertion that organic matter contained in these samples are predominantly of terrestrial origin (Fig. 3.2) and, the lack of correlation between TOC and elemental proxies of productivity (Fig. 3.7) and detrital input proxies (Fig. 3.8) lend support to the idea that the organic matter is non-indigenous to the Mississippian Limestone interval in our Anadarko Shelf study location. Taken together, the insights provided by the $\delta^{13}C_{org}$ values indicating presence of terrestrial organic matter, the lack of correlation between TOC and elemental proxies of detrital input and paleoproductivity, as well as the lithological descriptions provided by Wang et al. (2019), which describe the presence of burrows and bioturbation in the vast majority of the various lithofacies present in the Mississippian Limestone interval, provide evidence that the Mississippian Limestone interval is unlikely to be a self-sourcing interval for liquid hydrocarbons. The low levels of detrital input contributions inferred from lack of significant enrichment of detrital input proxies mean that lower amounts of nutrients are being contributed to the water column (cf. Tribovillard et al., 2006). This in turn will result in lower levels of productivity, which is seen in the lack of significant enrichment of productivity proxies observed in our study. Coupled with the oxic depositional redox conditions inferred from those elemental proxies of redox (e.g., Cu, Ni) and the presence of bioturbation in these sediments, the meagre amounts of organic matter that would be indigenous to the Mississippian Limestone interval will likely be degraded and would be unlikely to generate oil, a situation confirmed by the largely terrestrial signature of the $\delta^{13}C_{org}$ measured on the organic matter present in the Mississippian Limestone samples we studied. The findings of Adeboye et al. (2020), indicating oxic to suboxic depositional redox conditions in the Mississippian Limestone interval within the Anadarko Shelf, further support the assertion that the Mississippian Limestone is a poor source rock. This is because any organic matter contained in the unit, whether the organic matter is allochthonous or autochthonous, would have been oxidised, and this is reflected in the large majority of $\delta^{13}C_{org}$ measurements carried out on Mississippian Limestone organic matter measured for this study showing signatures consistent with those of type III (terrestrial, gas-prone) or type IV (inert/oxidised) organic matter. The lack of correlation between TOC and detrital input proxies (Fig. 3.8) observed in the current study also preclude contribution of nutrients via continental processes (e.g. via riverine input or aeolian means) into the Anadarko Shelf at time of deposition of the Mississippian Limestone in our study site hence, the organic matter preserved within the Mississippian Limestone interval is likely allochthonous. The type of organic matter and the amount of organic matter present within samples of the Mississippian Limestone interval examined for this study, as well as the lack of significant nutrient input and absence of heightened productivity, are supportive of our conclusion that the Mississippian Limestone interval in our Anadarko Shelf study site is likely not a source rock for oil.

The findings from the current study, and those of Wang et al. (2019) and Adeboye et al. (2020), are not in agreement with reports of investigations undertaken on the Mississippian Limestone by Al Atwah (2019) and Atwah et al. (2019, 2020) who suggested, based on organic geochemical techniques, that the Mississippian Limestone interval has likely self-sourced some of the oil resources hosted within the interval. In fact, Xia et al. (2019) surmised that carbonate source rocks are predominantly composed of types I and II organic matter, even if their organic matter content generally tends to be no greater than a maximum of 4 wt. % TOC. The Mississippian Limestone interval in our Anadarko Shelf study area appears to be composed predominantly of type III organic matter which is probably allochthonous, thus lending credence to the assertion by Symcox and Philp (2019) that the Mississippian Limestone is not a self-sourcing interval for oil. Rather, the Mississippian Limestone interval within the STACK play in the Anadarko Basin and Shelf is likely charged by the regionally extensive Argillaceous Woodford shale. The differences in results reported by these various authors could be a consequence of examining samples of the Mississippian Limestone interval from various locations across the US mid-continent since it is widely known that the Mississippian Limestone interval is very heterogeneous both laterally and vertically (e.g., Harris, 1975; Wang et al., 2019). Additional factors not investigated in this paper which would further shed light on source rock properties of the Mississippian Limestone interval within the STACK, and which are potential directions for future studies include maturity evaluation, visual kerogen analyses and pyrolysis evaluation to estimate the amount of hydrocarbons that have been generated and that are potentially able to be generated from rocks of the Mississippian Limestone interval.

3.6 Conclusions and Future Work

Results from $\delta^{13}C_{org}$ and elemental proxies of detrital input and paleoproductivity indicate that the Mississippian Limestone interval in the area of Kingfisher County, Oklahoma from which we sourced the samples for this study do not support the assertion that the Mississippian Limestone interval is capable of self-sourcing oil within the Anadarko Shelf, at least in our study area. While there is fair to good TOC content within certain lithofacies within the examined core interval, the $\delta^{13}C_{org}$ results indicate that the organic matter that is present is of largely of terrestrial origin. Moreover, there is a lack of correlation between TOC and elemental proxies of detrital input and paleoproductivity, strongly suggesting that the organic matter present in these Mississippian Limestone samples are allochthonous. Findings from this study and other recent studies (e.g., Symcox and Philp, 2019; Adeboye et al., 2020) suggest that the Mississippian Limestone interval is unlikely to have self-sourced hydrocarbons based on the character of the preserved organic matter inferred from stable organic carbon isotope geochemistry and biomarker evidence. Further work examining the biomarkers extracted from Mississippian Limestone samples is underway so as to confirm the provenance of the organic matter hosted in the Mississippian Limestone interval and also to estimate maturity of the interval in our study site. Biomarker results will be reported in a future manuscript.

3.7 Acknowledgements

Discussions with several researchers on how to improve the ideas presented in the paper are gratefully acknowledged. We would also like to thank Newfield Exploration (since purchased by the former Encana Corporation, which currently trades under the name Ovintiv Inc.) for providing access to the core from which we collected the samples used in this study. OOA is grateful to the Oklahoma Geological Foundation (OGF) for the Herbert G. and Shirley A. Davis Geology Fellowship, the National Association of Black Geoscientists (NABG) for the Mack Gipson Scholarships and the American Association of Petroleum Geologists (AAPG) for the Grants-in-Aid awards without which this work, and the overall project which it is a part of, would have been impossible. We are also grateful to the Oklahoma State University Mississippian Consortium as well as the Boone Pickens School of Geology for providing additional funding which enabled us to undertake this study. This is Oklahoma State University – Boone Pickens School of Geology contribution # XXXX-XXX

Figures

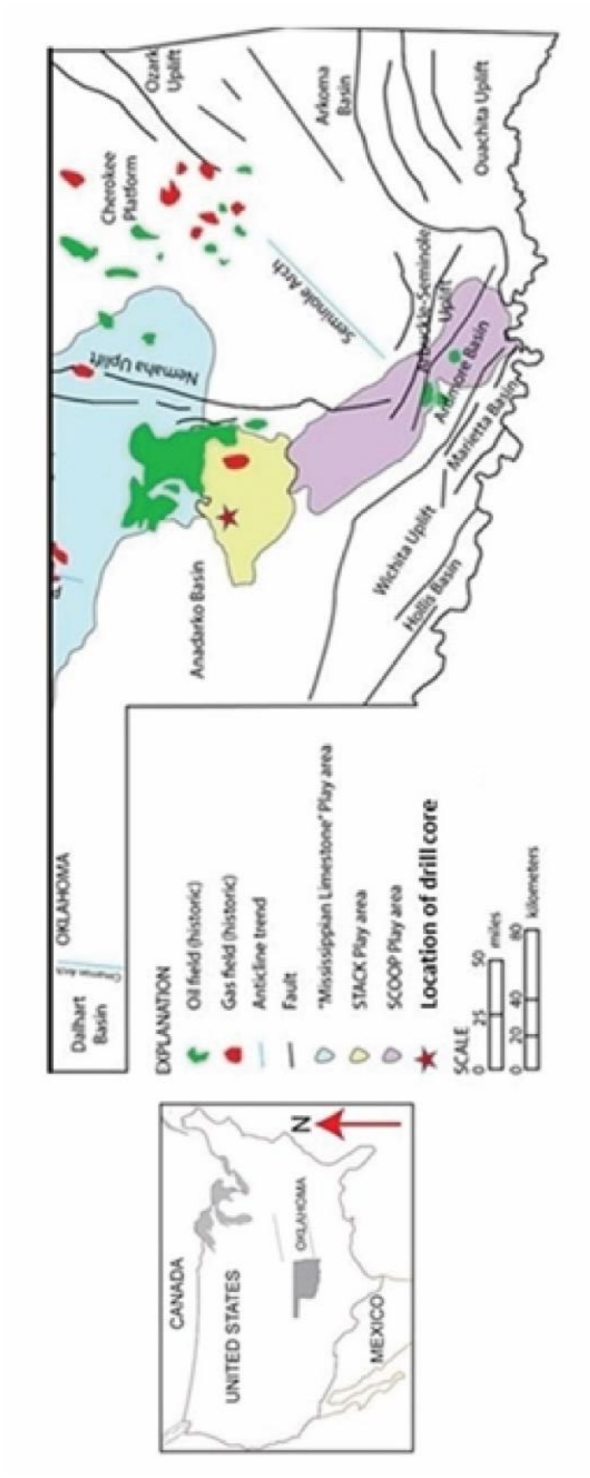


Figure 3.1: Location of well from which samples were obtained as well as various hydrocarbon producing fields of the State of Oklahoma (After Hunt, 2017).

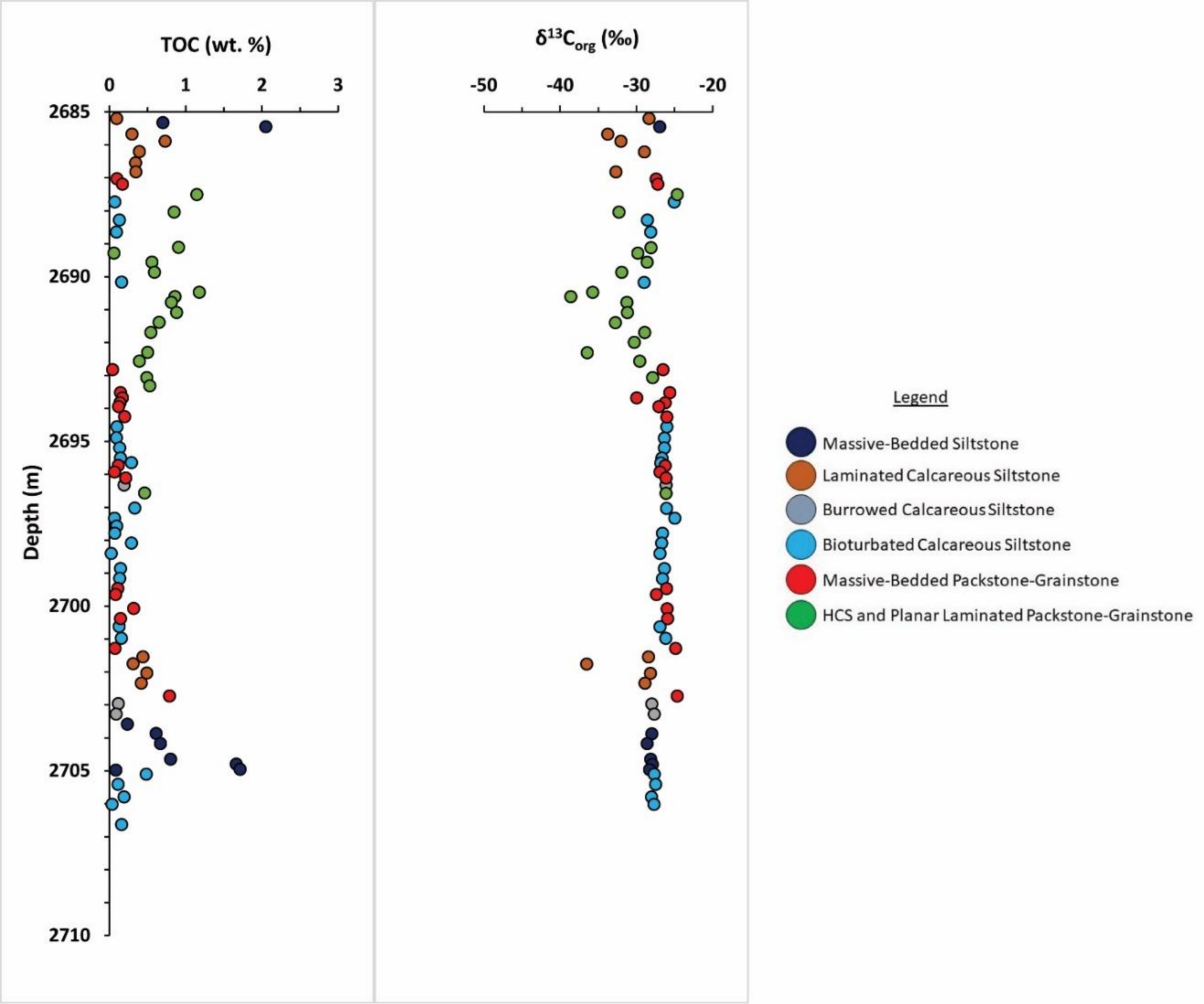


Figure 3.2: Downcore variation in TOC and $\delta^{13}C_{org}$ in the studied core interval.

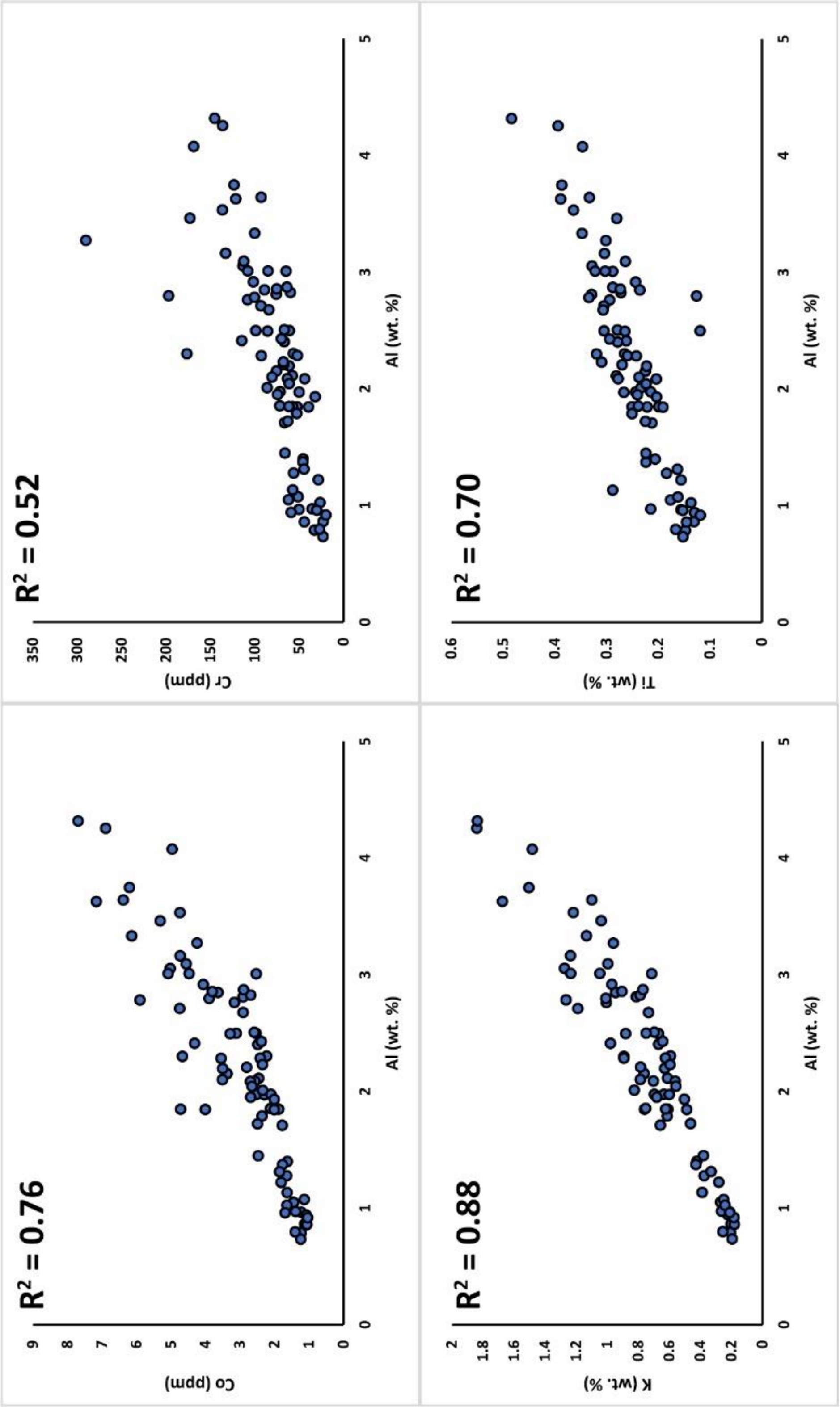


Figure 3.3: Plots of detrital input proxy contents vs. Al showing generally positive trends and the utility of these elements as proxies of detrital input.

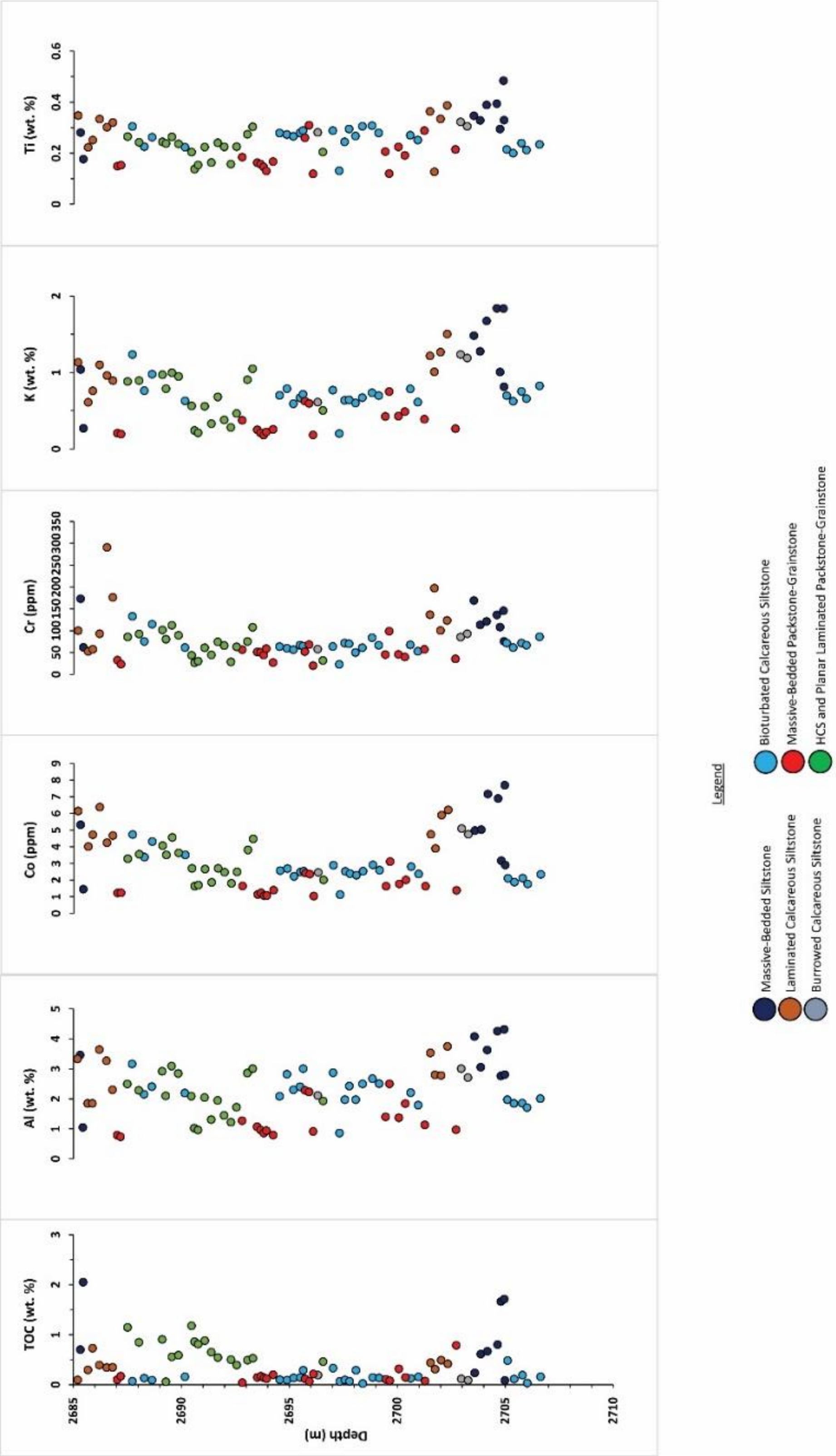


Figure 3.4: TOC and elemental proxies of detrital input and their variation with depth in the studied core.

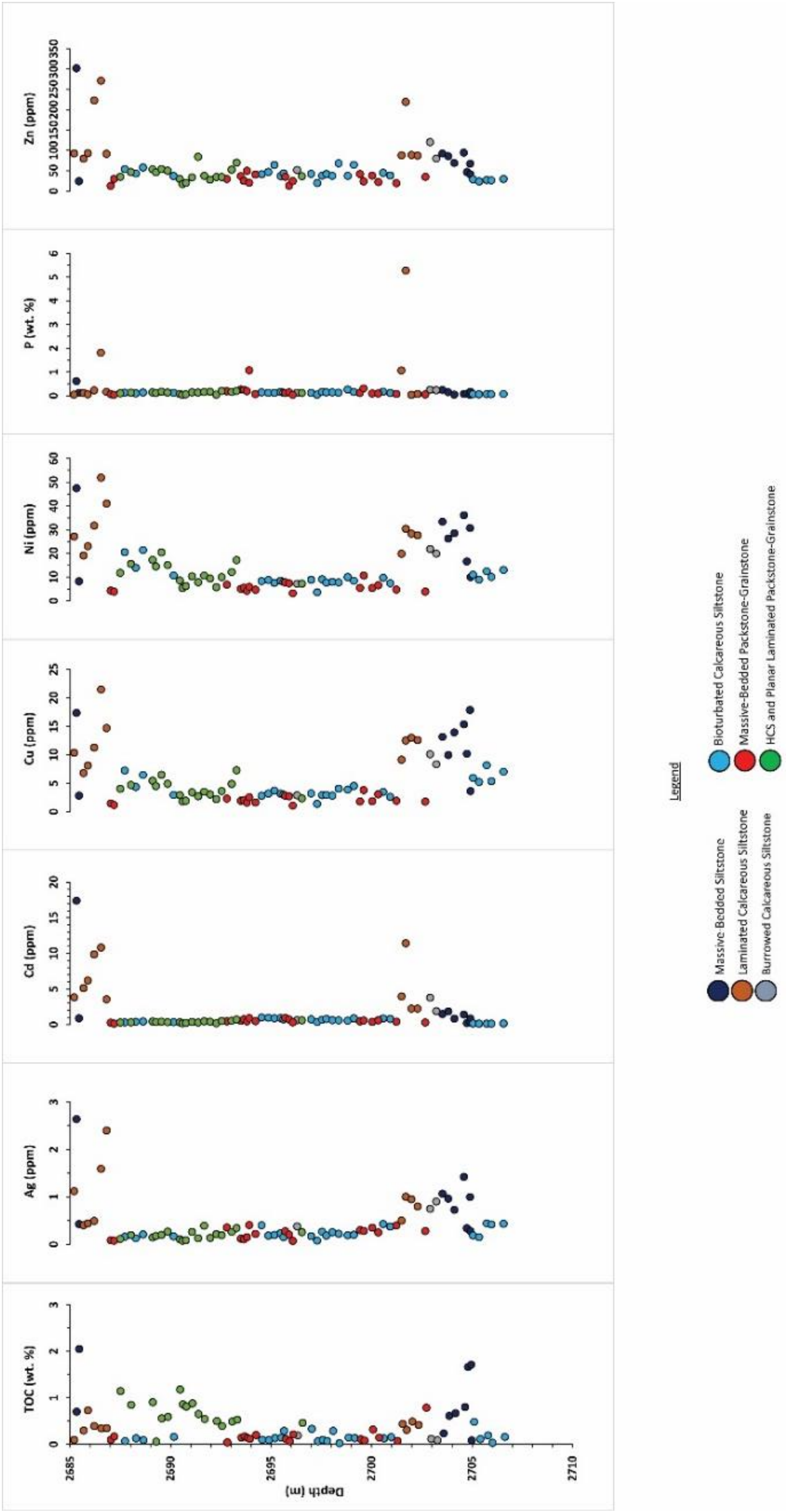


Figure 3.5: TOC and elemental proxies of productivity and their variation with depth in the studied core.

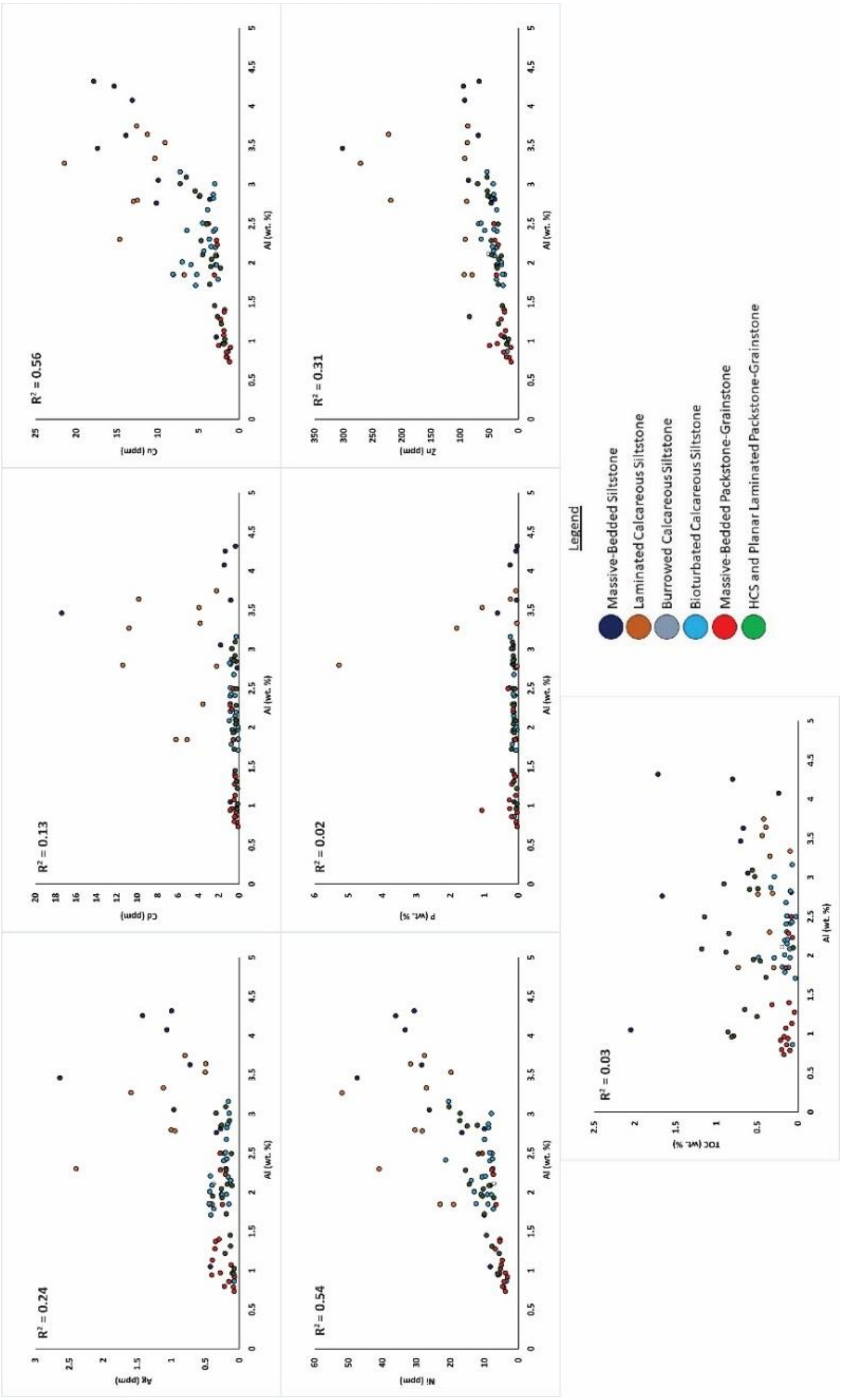


Figure 3.6: Plots of concentrations of elemental paleoproductivity proxies and TOC content vs. Al concentration respectively. Lack of correlation in all plots supports allochthonous nature of organic matter.

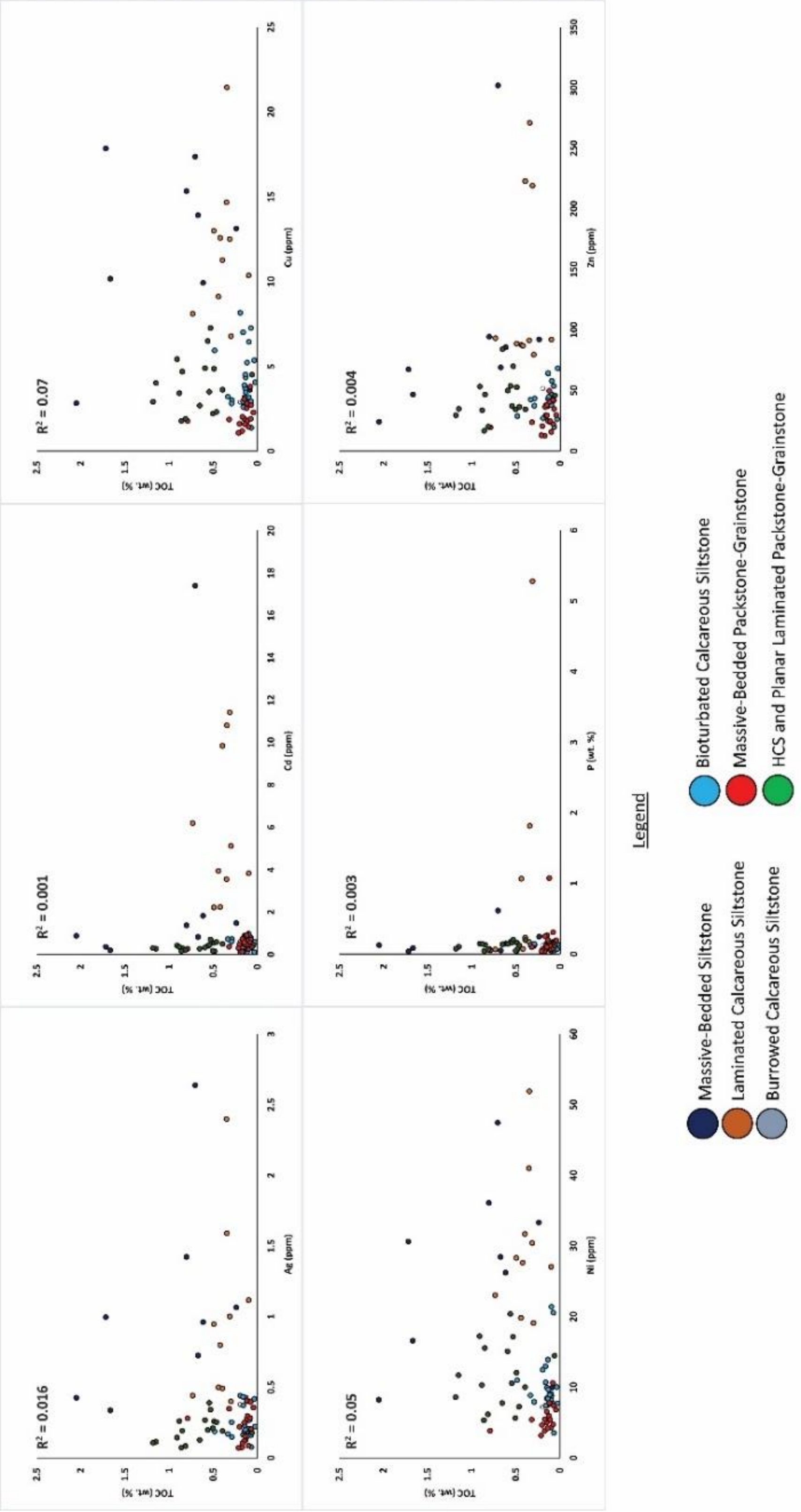


Figure 3.7: Plots of TOC vs. elemental proxies of productivity showing lack of correlation between productivity proxies and organic matter.

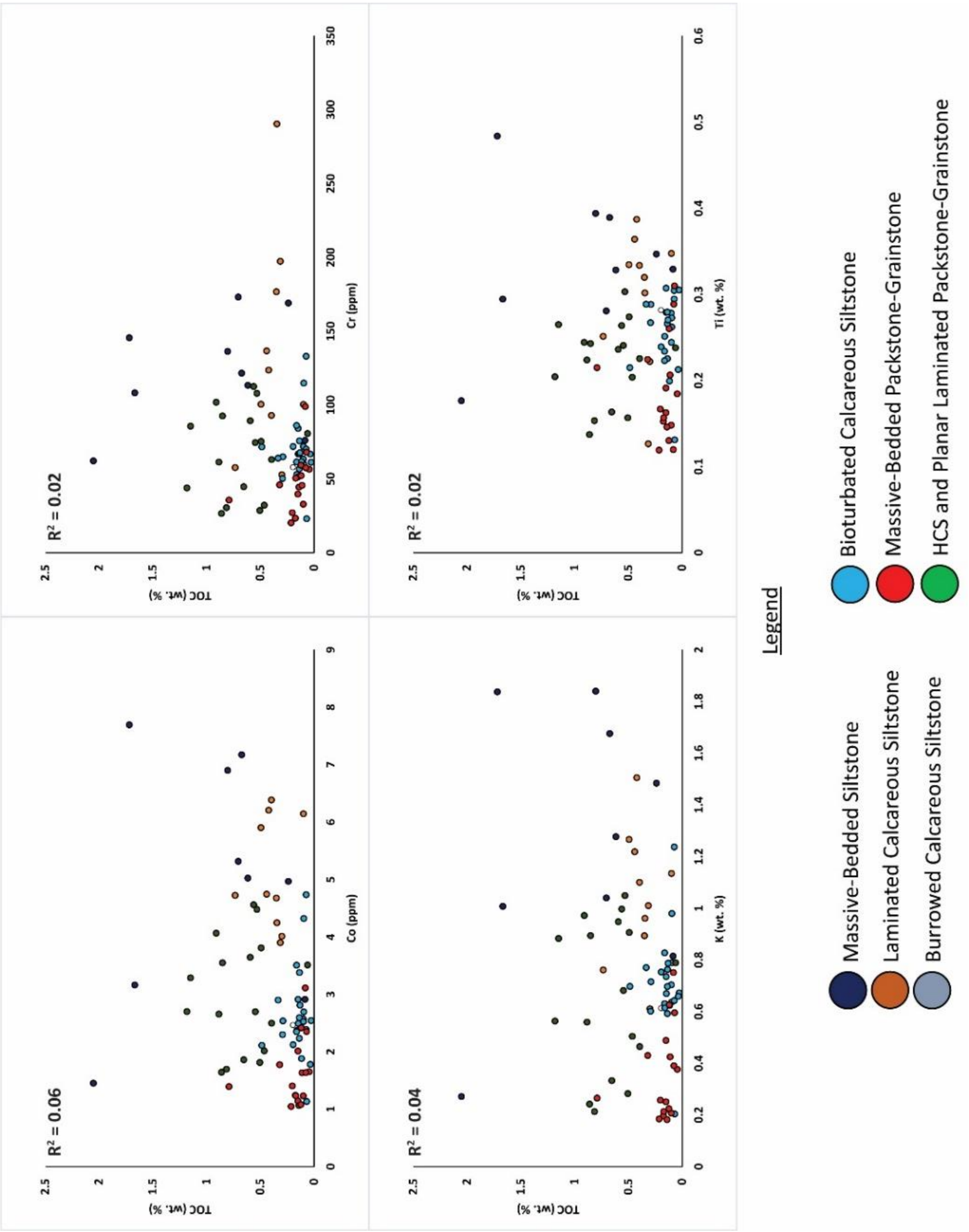


Figure 3.8: Plots of TOC vs. proxies of detrital input showing lack of correlation between detrital input proxies and organic matter.

Tables

Table 3.1: Total organic carbon (TOC) content and organic carbon isotope ($\delta^{13}C_{org}$) values of Mississippian Limestone samples. Samples for which analyses were not run are denoted by “nd”.

Sample Depth (m)	TOC (wt. %)	$\delta^{13}C_{org}$ (‰)
2685.20	0.1	-28.4
2685.32	0.7	nd
2685.44	2.1	-27.0
2685.67	0.3	-33.8
2685.88	0.7	-32.0
2686.20	0.4	-29.0
2686.54	0.3	nd
2686.81	0.4	-32.7
2687.03	0.1	-27.4
2687.19	0.2	-27.2
2687.50	1.1	-24.7
2687.73	0.1	-25.1
2688.03	0.9	-32.3
2688.28	0.1	-28.6
2688.64	0.1	-28.1
2689.11	0.9	-28.1
2689.28	0.1	-29.8
2689.56	0.6	-28.6
2689.86	0.6	-32.0
2690.16	0.2	-29.0
2690.47	1.2	-35.7
2690.60	0.9	-38.6
2690.77	0.8	-31.3
2691.08	0.9	-31.2
2691.38	0.7	-32.8
2691.69	0.5	-28.9
2691.99	nd	-30.3
2692.30	0.5	-36.4
2692.56	0.4	-29.6
2692.82	0.0	-26.5
2693.06	0.5	-27.9
2693.30	0.5	nd
2693.52	0.1	-25.6
2693.67	0.2	-30.0
2693.82	0.1	-26.2
2693.94	0.1	-27.1
2694.25	0.2	-26.0
2694.55	0.1	-26.0

Sample Depth (m)	TOC (wt. %)	$\delta^{13}C_{org}$ (‰)
2694.89	0.1	-26.3
2695.19	0.1	-26.3
2695.50	0.1	-26.7
2695.65	0.3	-26.8
2695.73	0.1	-26.2
2695.93	0.1	-26.9
2696.11	0.2	-26.1
2696.32	0.2	-26.1
2696.57	0.5	-26.1
2697.02	0.3	-26.0
2697.33	0.1	-25.0
2697.57	0.1	nd
2697.78	0.1	-26.6
2698.08	0.3	-26.7
2698.39	0.0	-26.9
2698.85	0.1	-26.4
2699.16	0.1	-26.6
2699.46	0.1	-26.1
2699.64	0.1	-27.4
2700.07	0.3	-26.0
2700.38	0.1	-25.9
2700.62	0.1	-26.9
2700.97	0.2	-26.1
2701.28	0.1	-24.9
2701.53	0.4	-28.4
2701.75	0.3	-36.5
2702.03	0.5	-28.2
2702.34	0.4	-28.9
2702.72	0.8	-24.7
2702.96	0.1	-28.0
2703.27	0.1	-27.7
2703.58	0.2	nd
2703.87	0.6	-28.0
2704.17	0.7	-28.6
2704.64	0.8	-28.1
2704.80	1.7	-27.9
2704.95	1.7	-28.3
2704.98	0.1	nd
2705.10	0.5	-27.7
2705.40	0.1	-27.5
2705.79	0.2	-28.0
2706.01	0.0	-27.7
2706.62	0.2	nd

Table 3.2: Total contents (carbonate fraction + non-carbonate fraction contents) of detrital input elemental proxies of Mississippian Limestone samples.

Sample Depth (m)	Al (wt. %)	K (wt. %)	Ti (wt. %)	Co (ppm)	Cr (ppm)
2685.20	3.33	1.13	0.35	6.15	100.42
2685.32	3.46	1.04	0.28	5.32	173.24
2685.44	1.05	0.27	0.18	1.45	62.23
2685.67	1.85	0.61	0.22	4.01	52.79
2685.88	1.85	0.76	0.25	4.73	57.66
2686.20	3.64	1.10	0.33	6.39	93.09
2686.54	3.27	0.96	0.30	4.25	290.49
2686.81	2.30	0.89	0.32	4.68	176.76
2687.03	0.79	0.21	0.15	1.23	32.94
2687.19	0.73	0.20	0.15	1.24	23.40
2687.50	2.50	0.88	0.27	3.29	85.78
2687.73	3.16	1.24	0.30	4.74	133.16
2688.03	2.28	0.89	0.24	3.55	92.72
2688.28	2.15	0.76	0.23	3.38	75.77
2688.64	2.41	0.98	0.26	4.32	115.00
2689.11	2.92	0.97	0.24	4.07	101.95
2689.28	2.10	0.79	0.24	3.51	80.72
2689.56	3.09	1.00	0.26	4.56	112.66
2689.86	2.85	0.95	0.24	3.65	89.43
2690.16	2.20	0.63	0.22	3.51	61.57
2690.47	2.09	0.56	0.20	2.70	43.98
2690.60	1.02	0.24	0.14	1.64	26.61
2690.77	0.96	0.21	0.15	1.70	30.54
2691.08	2.05	0.56	0.22	2.66	61.43
2691.38	1.31	0.33	0.16	1.86	44.78
2691.69	1.95	0.68	0.24	2.70	74.65
2691.99	1.45	0.38	0.22	2.48	66.26
2692.30	1.22	0.28	0.16	1.81	28.65
2692.56	1.72	0.46	0.23	2.50	63.10
2692.82	1.28	0.38	0.18	1.65	56.55
2693.06	2.86	0.91	0.27	3.81	75.47
2693.30	3.01	1.05	0.30	4.48	108.04
2693.52	1.07	0.25	0.16	1.14	51.38
2693.67	0.97	0.21	0.16	1.24	50.52
2693.82	0.86	0.18	0.15	1.07	44.53
2693.94	0.94	0.22	0.13	1.08	59.37
2694.25	0.80	0.26	0.17	1.41	27.11
2694.55	2.09	0.70	0.28	2.57	63.52

Sample Depth (m)	Al (wt. %)	K (wt. %)	Ti (wt. %)	Co (ppm)	Cr (ppm)
2694.89	2.83	0.79	0.27	2.70	60.04
2695.19	2.30	0.59	0.27	2.23	56.77
2695.50	2.40	0.67	0.28	2.49	67.01
2695.65	3.01	0.72	0.29	2.54	64.96
2695.73	2.29	0.63	0.26	2.42	52.24
2695.93	2.23	0.60	0.31	2.35	68.15
2696.11	0.92	0.19	0.12	1.05	20.24
2696.32	2.11	0.61	0.28	2.47	57.96
2696.57	1.93	0.50	0.20	2.02	32.26
2697.02	2.87	0.77	0.29	2.90	64.13
2697.33	0.86	0.20	0.13	1.13	23.12
2697.57	1.97	0.64	0.24	2.53	71.97
2697.78	2.43	0.64	0.29	2.39	70.18
2698.08	1.97	0.60	0.27	2.30	50.33
2698.39	2.50	0.67	0.31	2.54	61.29
2698.85	2.68	0.74	0.31	2.91	84.27
2699.16	2.51	0.70	0.28	2.60	66.92
2699.46	1.40	0.42	0.21	1.64	45.71
2699.64	2.50	0.75	0.12	3.11	99.08
2700.07	1.37	0.43	0.22	1.78	46.00
2700.38	1.84	0.49	0.19	2.02	39.71
2700.62	2.21	0.79	0.27	2.81	67.76
2700.97	1.79	0.61	0.25	2.37	53.09
2701.28	1.13	0.39	0.29	1.64	57.61
2701.53	3.53	1.22	0.36	4.75	136.69
2701.75	2.80	1.01	0.13	3.90	197.41
2702.03	2.78	1.27	0.33	5.91	100.56
2702.34	3.75	1.51	0.39	6.21	123.74
2702.72	0.97	0.27	0.21	1.39	35.66
2702.96	3.01	1.24	0.32	5.09	85.42
2703.27	2.71	1.19	0.31	4.75	93.45
2703.58	4.08	1.48	0.35	4.97	169.11
2703.87	3.06	1.28	0.33	5.03	113.49
2704.17	3.63	1.68	0.39	7.17	121.63
2704.64	4.26	1.84	0.39	6.90	136.43
2704.80	2.76	1.01	0.29	3.17	108.40
2704.95	4.32	1.84	0.48	7.70	145.60
2704.98	2.81	0.81	0.33	2.91	76.08
2705.10	1.98	0.70	0.21	2.11	71.72
2705.40	1.85	0.62	0.20	1.88	61.82
2705.79	1.85	0.75	0.24	2.13	71.95

Sample Depth (m)	Al (wt. %)	K (wt. %)	Ti (wt. %)	Co (ppm)	Cr (ppm)
2706.01	1.71	0.66	0.21	1.78	66.83
2706.62	2.01	0.83	0.23	2.35	86.21

Table 3.3: Total contents (carbonate fraction + non-carbonate fraction contents) of elemental proxies of paleoproductivity of Mississippian Limestone samples.

Sample Depth (m)	P (wt. %)	Ag (ppm)	Cd (ppm)	Cu (ppm)	Ni (ppm)	Zn (ppm)
2685.20	0.05	1.12	3.83	10.36	27.08	92.17
2685.32	0.62	2.64	17.41	17.37	47.47	301.99
2685.44	0.13	0.43	0.88	2.82	8.25	24.26
2685.67	0.12	0.40	5.12	6.77	19.10	79.65
2685.88	0.07	0.44	6.20	8.11	23.04	93.23
2686.20	0.23	0.49	9.85	11.26	31.72	222.97
2686.54	1.82	1.59	10.81	21.45	51.92	271.16
2686.81	0.17	2.40	3.55	14.68	41.01	91.44
2687.03	0.07	0.09	0.25	1.43	4.30	15.81
2687.19	0.04	0.08	0.13	1.19	3.86	12.63
2687.50	0.10	0.11	0.27	4.02	11.73	34.92
2687.73	0.13	0.16	0.31	7.25	20.55	53.81
2688.03	0.13	0.19	0.31	4.69	15.57	46.72
2688.28	0.11	0.13	0.37	4.34	13.92	42.96
2688.64	0.14	0.21	0.43	6.44	21.42	57.93
2689.11	0.15	0.14	0.43	5.42	17.24	53.25
2689.28	0.12	0.18	0.35	4.50	14.49	45.98
2689.56	0.17	0.20	0.40	6.49	20.41	53.84
2689.86	0.14	0.27	0.33	4.90	15.09	49.93
2690.16	0.12	0.16	0.32	2.93	10.71	36.95
2690.47	0.08	0.11	0.30	2.91	8.61	29.51
2690.60	0.04	0.07	0.16	1.78	5.34	16.74
2690.77	0.06	0.08	0.22	1.90	6.18	20.12
2691.08	0.14	0.26	0.35	3.41	10.34	33.70
2691.38	0.14	0.13	0.27	2.69	7.78	84.17
2691.69	0.16	0.39	0.44	3.49	10.59	37.32
2691.99	0.18	0.13	0.41	3.02	9.42	27.76
2692.30	0.05	0.21	0.17	2.21	5.67	34.37
2692.56	0.20	0.19	0.50	3.62	10.03	34.55
2692.82	0.19	0.36	0.45	2.28	6.81	29.65
2693.06	0.16	0.26	0.55	4.86	12.09	52.73
2693.30	0.20	0.34	0.71	7.26	17.17	69.95
2693.52	0.27	0.12	0.52	1.91	5.03	29.44
2693.67	0.25	0.10	0.74	2.02	5.46	36.51
2693.82	0.20	0.15	0.45	1.57	4.21	25.00
2693.94	1.08	0.41	0.89	2.52	5.93	49.66
2694.25	0.07	0.22	0.48	1.62	4.68	20.62
2694.55	0.15	0.40	0.98	2.80	8.31	41.33
2694.89	0.12	0.18	0.94	3.17	8.82	46.68
2695.19	0.13	0.20	0.87	3.68	7.52	63.94

Sample Depth (m)	P (wt. %)	Ag (ppm)	Cd (ppm)	Cu (ppm)	Ni (ppm)	Zn (ppm)
2695.50	0.16	0.23	0.89	3.17	8.43	36.81
2695.65	0.13	0.15	0.73	3.00	7.95	43.41
2695.73	0.12	0.28	0.91	2.81	7.80	40.46
2695.93	0.15	0.20	0.71	2.71	7.41	34.85
2696.11	0.04	0.07	0.30	1.07	3.19	13.09
2696.32	0.13	0.38	0.62	2.88	7.20	51.65
2696.57	0.12	0.25	0.59	2.31	7.25	36.46
2697.02	0.13	0.17	0.73	3.20	8.86	42.50
2697.33	0.05	0.08	0.35	1.38	3.56	19.81
2697.57	0.16	0.27	0.68	2.91	9.09	37.80
2697.78	0.15	0.18	0.78	2.93	7.66	41.78
2698.08	0.15	0.25	0.62	2.80	7.95	37.40
2698.39	0.13	0.22	0.59	4.05	7.73	68.30
2698.85	0.27	0.19	0.53	3.89	9.98	37.36
2699.16	0.16	0.20	0.86	4.51	8.42	64.44
2699.46	0.12	0.30	0.44	1.80	5.43	24.71
2699.64	0.31	0.28	0.56	3.80	10.63	42.08
2700.07	0.10	0.35	0.37	1.86	5.43	23.77
2700.38	0.10	0.25	0.58	3.06	6.57	37.84
2700.62	0.18	0.43	0.86	3.47	9.71	44.75
2700.97	0.12	0.37	0.77	2.60	7.40	38.05
2701.28	0.08	0.40	0.41	1.89	4.75	22.12
2701.53	1.07	0.50	3.95	9.11	19.84	87.81
2701.75	5.28	1.00	11.43	12.50	30.42	219.21
2702.03	0.04	0.95	2.23	12.99	28.32	88.74
2702.34	0.07	0.80	2.24	12.58	27.66	86.99
2702.72	0.05	0.28	0.27	1.77	3.86	19.49
2702.96	0.25	0.75	3.76	10.08	21.79	120.26
2703.27	0.24	0.90	1.88	8.32	19.89	80.13
2703.58	0.25	1.07	1.48	13.12	33.34	92.21
2703.87	0.15	0.96	1.83	9.93	26.25	85.80
2704.17	0.05	0.73	0.83	13.91	28.47	69.03
2704.64	0.07	1.42	1.38	15.34	36.12	94.44
2704.80	0.09	0.34	0.20	10.17	16.61	46.72
2704.95	0.04	1.00	0.37	17.85	30.65	67.47
2704.98	0.17	0.27	0.85	3.62	10.02	40.96
2705.10	0.07	0.19	0.15	5.93	11.01	28.81
2705.40	0.06	0.15	0.11	5.22	8.93	23.97
2705.79	0.07	0.44	0.12	8.16	12.48	27.09
2706.01	0.07	0.42	0.11	5.36	10.04	26.30
2706.62	0.08	0.43	0.15	7.00	12.99	29.53

Table 3.4: Calculated enrichment factors for detrital input elemental proxies vs. “average carbonates” (Turekian and Wedepohl, 1961) calculated on the basis of total element content.

Sample Depth (m)	EF_{Co}	EF_{Cr}	EF_{K}	EF_{Th}	EF_{Ti}
2685.20	7.74	1.15	0.53	0.56	1.09
2685.32	6.45	1.91	0.47	0.51	0.85
2685.44	5.81	2.26	0.40	1.06	1.77
2685.67	9.13	1.09	0.51	0.81	1.26
2685.88	10.74	1.19	0.64	0.71	1.43
2686.20	7.36	0.98	0.47	0.46	0.96
2686.54	5.45	3.39	0.46	0.70	0.97
2686.81	8.54	2.93	0.60	0.76	1.46
2687.03	6.56	1.59	0.41	0.81	1.97
2687.19	7.11	1.22	0.42	0.54	2.18
2687.50	5.54	1.31	0.55	0.45	1.12
2687.73	6.29	1.61	0.61	0.35	1.01
2688.03	6.53	1.55	0.61	0.46	1.12
2688.28	6.60	1.34	0.55	0.62	1.10
2688.64	7.52	1.82	0.63	0.64	1.14
2689.11	5.86	1.33	0.52	0.59	0.88
2689.28	7.02	1.47	0.58	0.55	1.19
2689.56	6.19	1.39	0.50	0.70	0.90
2689.86	5.38	1.20	0.52	0.39	0.87
2690.16	6.71	1.07	0.45	0.53	1.07
2690.47	5.44	0.80	0.42	0.62	1.03
2690.60	6.74	0.99	0.37	0.58	1.41
2690.77	7.42	1.21	0.34	0.97	1.67
2691.08	5.46	1.15	0.43	0.66	1.15
2691.38	5.96	1.30	0.39	0.57	1.31
2691.69	5.81	1.46	0.54	0.82	1.30
2691.99	7.18	1.74	0.41	1.70	1.63
2692.30	6.24	0.90	0.36	0.57	1.35
2692.56	6.09	1.40	0.42	1.05	1.37
2692.82	5.43	1.69	0.46	1.22	1.52
2693.06	5.60	1.01	0.49	0.71	1.01
2693.30	6.25	1.37	0.54	0.65	1.06
2693.52	4.48	1.83	0.36	0.70	1.59
2693.67	5.37	2.00	0.34	1.27	1.70
2693.82	5.22	1.98	0.33	0.95	1.78
2693.94	4.82	2.41	0.37	1.07	1.45
2694.25	7.41	1.30	0.50	0.75	2.20
2694.55	5.17	1.16	0.52	0.85	1.40

Sample Depth (m)	EF_{Co}	EF_{Cr}	EF_{K}	EF_{Th}	EF_{Ti}
2694.89	4.01	0.81	0.43	0.63	1.01
2695.19	4.07	0.94	0.40	0.80	1.21
2695.50	4.35	1.06	0.43	0.89	1.22
2695.65	3.54	0.82	0.37	0.62	1.01
2695.73	4.44	0.87	0.43	0.78	1.20
2695.93	4.43	1.17	0.42	0.66	1.46
2696.11	4.79	0.84	0.31	0.49	1.36
2696.32	4.90	1.05	0.45	0.66	1.40
2696.57	4.38	0.64	0.41	0.46	1.11
2697.02	4.24	0.85	0.42	0.51	1.05
2697.33	5.51	1.02	0.37	0.59	1.59
2697.57	5.38	1.39	0.50	0.54	1.30
2697.78	4.13	1.10	0.41	0.62	1.27
2698.08	4.90	0.97	0.48	0.71	1.42
2698.39	4.28	0.94	0.42	0.98	1.28
2698.85	4.57	1.20	0.43	0.72	1.20
2699.16	4.35	1.02	0.43	0.72	1.17
2699.46	4.91	1.25	0.47	0.87	1.55
2699.64	5.23	1.51	0.47	0.64	0.50
2700.07	5.43	1.28	0.49	0.72	1.72
2700.38	4.59	0.82	0.41	0.44	1.09
2700.62	5.35	1.17	0.55	0.86	1.29
2700.97	5.57	1.13	0.53	0.94	1.47
2701.28	6.08	1.94	0.54	2.09	2.67
2701.53	5.64	1.48	0.54	0.54	1.08
2701.75	5.86	2.69	0.56	0.68	0.48
2702.03	8.91	1.38	0.71	0.47	1.26
2702.34	6.96	1.26	0.62	0.65	1.08
2702.72	6.02	1.40	0.42	0.89	2.32
2702.96	7.10	1.08	0.64	0.63	1.12
2703.27	7.36	1.32	0.68	0.74	1.18
2703.58	5.12	1.58	0.57	0.52	0.89
2703.87	6.91	1.42	0.65	0.78	1.13
2704.17	8.30	1.28	0.72	0.40	1.13
2704.64	6.81	1.22	0.67	0.37	0.97
2704.80	4.81	1.50	0.57	0.49	1.12
2704.95	7.48	1.29	0.66	0.59	1.18
2704.98	4.35	1.03	0.45	0.90	1.23
2705.10	4.49	1.39	0.55	0.43	1.14
2705.40	4.28	1.28	0.53	0.45	1.13
2705.79	4.81	1.48	0.63	0.87	1.35

Sample Depth (m)	EF_{Co}	EF_{Cr}	EF_{K}	EF_{Th}	EF_{Ti}
2706.01	4.38	1.49	0.60	0.58	1.31
2706.62	4.91	1.64	0.64	0.77	1.22

Table 3.5: Calculated enrichment factors for paleoproductivity elemental proxies vs. “average carbonates” (Turekian and Wedepohl, 1961) calculated on the basis of total element content.

Sample Depth (m)	EF Ag	EF Cd	EF Cu	EF Ni	EF P	EF Zn
2685.20	2.01	13.79	0.33	0.17	0.15	0.58
2685.32	4.57	60.31	0.53	0.29	1.87	1.83
2685.44	2.43	10.04	0.28	0.16	1.25	0.49
2685.67	1.30	33.28	0.39	0.22	0.65	0.91
2685.88	1.43	40.28	0.46	0.26	0.37	1.06
2686.20	0.81	32.45	0.32	0.18	0.67	1.29
2686.54	2.92	39.64	0.69	0.33	5.83	1.74
2686.81	6.26	18.54	0.67	0.37	0.78	0.83
2687.03	0.66	3.82	0.19	0.11	0.90	0.42
2687.19	0.61	2.06	0.17	0.11	0.55	0.36
2687.50	0.28	1.32	0.17	0.10	0.44	0.29
2687.73	0.30	1.19	0.24	0.14	0.45	0.36
2688.03	0.51	1.60	0.22	0.14	0.62	0.43
2688.28	0.35	2.07	0.21	0.14	0.52	0.42
2688.64	0.52	2.15	0.28	0.19	0.60	0.50
2689.11	0.30	1.75	0.20	0.12	0.53	0.38
2689.28	0.51	2.00	0.22	0.14	0.59	0.46
2689.56	0.38	1.55	0.22	0.14	0.59	0.37
2689.86	0.57	1.41	0.18	0.11	0.52	0.37
2690.16	0.45	1.75	0.14	0.10	0.59	0.35
2690.47	0.31	1.71	0.15	0.09	0.38	0.30
2690.60	0.43	1.92	0.18	0.11	0.45	0.34
2690.77	0.53	2.70	0.21	0.14	0.69	0.44
2691.08	0.77	2.06	0.18	0.11	0.74	0.35
2691.38	0.58	2.48	0.21	0.12	1.10	1.35
2691.69	1.20	2.73	0.19	0.11	0.88	0.40
2691.99	0.55	3.36	0.22	0.14	1.28	0.40
2692.30	1.03	1.69	0.19	0.10	0.42	0.59
2692.56	0.66	3.47	0.22	0.12	1.21	0.42
2692.82	1.68	4.26	0.19	0.11	1.60	0.49
2693.06	0.55	2.30	0.18	0.09	0.60	0.39
2693.30	0.68	2.84	0.25	0.12	0.71	0.49
2693.52	0.67	5.78	0.19	0.10	2.61	0.58
2693.67	0.64	9.14	0.22	0.12	2.76	0.79
2693.82	1.07	6.34	0.19	0.10	2.42	0.61
2693.94	2.58	11.33	0.28	0.13	12.01	1.11
2694.25	1.65	7.17	0.21	0.12	0.87	0.54
2694.55	1.15	5.61	0.14	0.08	0.74	0.42

Sample Depth (m)	EF Ag	EF Cd	EF Cu	EF Ni	EF P	EF Zn
2694.89	0.39	4.00	0.12	0.07	0.46	0.35
2695.19	0.51	4.52	0.17	0.07	0.58	0.58
2695.50	0.58	4.43	0.14	0.07	0.70	0.32
2695.65	0.30	2.91	0.10	0.06	0.46	0.30
2695.73	0.72	4.80	0.13	0.07	0.55	0.37
2695.93	0.55	3.81	0.13	0.07	0.70	0.33
2696.11	0.46	3.92	0.12	0.07	0.46	0.30
2696.32	1.07	3.50	0.14	0.07	0.64	0.51
2696.57	0.79	3.65	0.13	0.08	0.66	0.40
2697.02	0.36	3.04	0.12	0.06	0.46	0.31
2697.33	0.54	4.81	0.17	0.09	0.60	0.48
2697.57	0.81	4.14	0.15	0.10	0.85	0.40
2697.78	0.45	3.84	0.13	0.07	0.63	0.36
2698.08	0.77	3.77	0.15	0.08	0.77	0.40
2698.39	0.53	2.83	0.17	0.06	0.56	0.57
2698.85	0.43	2.39	0.15	0.08	1.04	0.29
2699.16	0.48	4.10	0.19	0.07	0.67	0.54
2699.46	1.28	3.79	0.13	0.08	0.86	0.37
2699.64	0.68	2.71	0.16	0.09	1.30	0.35
2700.07	1.53	3.27	0.14	0.08	0.74	0.36
2700.38	0.81	3.75	0.17	0.07	0.56	0.43
2700.62	1.16	4.65	0.16	0.09	0.84	0.43
2700.97	1.25	5.18	0.15	0.09	0.70	0.45
2701.28	2.10	4.32	0.18	0.09	0.73	0.41
2701.53	0.85	13.40	0.27	0.12	3.17	0.52
2701.75	2.15	49.02	0.47	0.23	19.81	1.65
2702.03	2.04	9.59	0.49	0.21	0.17	0.67
2702.34	1.28	7.16	0.35	0.15	0.21	0.49
2702.72	1.73	3.39	0.19	0.08	0.57	0.42
2702.96	1.49	14.97	0.35	0.15	0.88	0.84
2703.27	1.99	8.31	0.32	0.15	0.91	0.62
2703.58	1.57	4.37	0.34	0.17	0.64	0.47
2703.87	1.89	7.18	0.34	0.18	0.52	0.59
2704.17	1.20	2.74	0.40	0.16	0.15	0.40
2704.64	2.01	3.88	0.38	0.18	0.18	0.47
2704.80	0.73	0.86	0.39	0.13	0.33	0.36
2704.95	1.39	1.02	0.43	0.15	0.09	0.33
2704.98	0.58	3.63	0.14	0.07	0.64	0.31
2705.10	0.57	0.93	0.32	0.12	0.37	0.31
2705.40	0.49	0.70	0.30	0.10	0.36	0.27
2705.79	1.43	0.77	0.46	0.14	0.41	0.31

Sample Depth (m)	EF Ag	EF Cd	EF Cu	EF Ni	EF P	EF Zn
2706.01	1.47	0.78	0.33	0.12	0.42	0.32
2706.62	1.29	0.89	0.37	0.14	0.40	0.31

CHAPTER IV

ORGANIC GEOCHEMISTRY OF THE MISSISSIPPIAN LIMESTONE ON THE ANADARKO SHELF

4.1 Abstract

An evaluation of source rock characteristics of the Mississippian Limestone interval is warranted due to recent discovery of hydrocarbons contained in low permeability reservoirs. Hydrocarbon exploration and exploitation efforts have focused on applying modern completion techniques to various proven and potential source rocks, including heterogeneous lithologies such as the Mississippian Limestone. Over the years, Mississippian-aged reservoirs of the Anadarko Shelf and Basin, including the Mississippian Limestone interval, have produced significant volumes of hydrocarbons, therefore understanding petroleum generation within the Mississippian Limestone interval is important for evaluating future hydrocarbon production potential. Several previous studies have suggested that the Mississippian Limestone interval of the Anadarko Shelf and Basin of Oklahoma is a viable source rock which not only hosts oils sourced from the regionally extensive and prolific Woodford shale, but also hosts oils generated from the Mississippian Limestone interval. Variation in source rock lateral extent and quality are typically observed in the Mississippian Limestone due to inherent depositional heterogeneity during Mississippian time across central Oklahoma. This study investigates source rock quality and depositional settings of the Mississippian Limestone interval using samples retrieved from a core drilled in Kingfisher County within the STACK resource play area of the Anadarko Shelf of Oklahoma. Rock samples were investigated for their petroleum generation potential using Rock-Eval pyrolysis, and molecular geochemistry via gas chromatography and mass spectrometry techniques. Results of Rock-Eval pyrolysis suggest poor source rock quality, with a maximum TOC value of 1.86 wt. % and maximum hydrogen index (HI) value of 271. Thermal maturity based on pyrolysis and biomarker parameters suggest thermal maturity level of Mississippian Limestone rocks are within the oil window. Likewise, insights from biomarkers indicated the presence of mixed type II-III organic matter and supported previous studies which reported oxic-suboxic depositional redox conditions for the Mississippian Limestone interval in the STACK resource play area. The Mississippian diagnostic extended tricyclic terpane biomarkers are observed in higher abundance relative to hopane biomarkers suggesting that perhaps observed Mississippian biomarker fingerprints represents fluid migration from nearby Mississippian sections with good source rock quality. More extensive investigations of the Mississippian Limestone interval within the STACK on the Anadarko Shelf will be required to conclusively resolve this question of the viability of the Mississippian Limestone interval as a source rock within the STACK.

4.2 Introduction

There is a very long history of petroleum production from the Anadarko Shelf and Basin of Oklahoma dating from the early 1900s (Koch et al., 2014) with cumulative production to date of more than 900 million barrels of oil and 6.4 tcf of gas from the Anadarko Basin and Shelf (Higley, 2014). Despite this long production history, the USGS estimates that there may still be up to 31 million barrels of oil, 99 billion cubic feet of gas and 4 million barrels of natural gas liquids of potential resources yet to be discovered in this world class petroliferous region (Higley, 2014). In recent times, the STACK and SCOOP resource play (Fig. 4.1) has become an epicentre of hydrocarbon exploration and exploitation within the Anadarko Shelf and Basin due to the application of modern completion techniques which combine horizontal drilling and hydraulic fracturing (Koch et al., 2014).

Several studies have investigated the geochemistry of Mississippian Limestone rocks and associated fluids across Oklahoma, with several of these studies confirming the petroleum generation capability of some Mississippian intervals by identifying a number of diagnostic Mississippian biomarkers in produced hydrocarbons and from Mississippian Limestone extracts (e.g., Wang and Philp, 1997; Kim and Philp, 2001; Atwah etal., 2019; Atwah et al., 2020). Furthermore, some recent studies in the STACK play area within the Anadarko Shelf have relied on a combination of stable isotope geochemistry and various elemental proxies to reconstruct environmental conditions during deposition and to speculate on source rock properties of the Mississippian Limestone interval (Adeboye et al., 2020; Adeboye et al., manuscript in preparation). Other recent geochemical studies of the Mississippian Limestone interval within the STACK and SCOOP resource play have primarily employed organic geochemical techniques carried out on oil samples which were collected from the greater Anadarko Basin, but not specifically from within the Anadarko Shelf. Furthermore, these organic geochemical studies have not explicitly studied the Mississippian Limestone interval specifically for its source rock properties using rock samples of the interval (e.g., Atwah et al., 2019; Symcox and Philp, 2019). Various previous studies suggest that the hydrocarbon resources produced from the Mississippian Limestone interval are a mixture of hydrocarbons which were generated by the regionally extensive, underlying Woodford Shale and those which were self-sourced from sediments of the Mississippian Limestone interval itself (Kim and Philp, 2001; Symcox and Philp, 2019; Wang and Philp, 2019).

Organic matter amount, type and maturity are parameters of paramount importance when evaluating hydrocarbon production potential of self-sourced hydrocarbon resource plays (Wust et al., 2013), such as the Mississippian Limestone within the STACK resource play area. Although various studies have confirmed the presence of petroleum source rock intervals within the Mississippian Limestone interval (e.g., Wang and Philp, 1997; Atwah et al., 2020), lateral variation in source rock quality within the Mississippian Limestone interval remains unexplained and underexplored. In this study, we investigated the hydrocarbon generation potential and depositional setting of the Mississippian

Limestone interval within the STACK resource play area of the Anadarko Shelf by combining Rock-Eval pyrolysis screening and biomarker geochemistry. We thus shed light on factors controlling lateral variation observed in petroleum source rock potential within the Mississippian Limestone interval. Such variations are particularly significant to account for when identifying sweet-spots for well placement within the unconventional STACK resource play. This study also provides a better understanding of paleodepositional environmental conditions (e.g., redox) source rock properties of the Mississippian Limestone interval within the STACK resource play area in Kingfisher County, Oklahoma by employing insights from biomarker geochemistry.

4.3 Study Area, Samples and Methods

4.3.1 Geological and Paleogeographic Setting

The Mississippian Limestone interval in the Mid-Continent region of the U.S.A. is considered to be part of the 2nd order Kaskaskia supersequence as defined by Sloss (1963). Sediments making up the Mississippian Limestone interval were deposited close to the equator (Gutschick and Sandberg, 1983), along a distally steepened ramp (LeBlanc, 2014), in an ancient epeiric sea (Gutschick and Sandberg, 1983) during a period of climate transition (Haq and Schutter, 2008). The changing climate during Mississippian time would have impacted paleoproductivity and detrital input, factors that would both influence the genesis and fate of sedimentary organic matter preserved in the Mississippian Limestone interval. The Mississippian Limestone interval is underlain by the Woodford Shale, Devonian petroleum source rock in the US Mid-Continent region, and overlain by rocks of the Pennsylvanian Springer Formation (Wang and Philp, 1997).

There is poor age constraint on rocks of the Mississippian Limestone interval in our study area due to the lack of conodonts within the interval, although Hunt (2017) reports ages of ~ 346.7 to 330.9 Ma (Middle Osagean to Late Chesterian, Uppermost Tournaisian to Latest Visean) for Mississippian Limestone samples obtained to the east of our study site.

In our study area, the Mississippian Limestone interval is of heterogeneous lithology, and is comprised of calcareous, siliciclastic siltstones and carbonate packstones-grainstones. Wang et al. (2019) identified a total of 7 distinct lithofacies within the Mississippian Limestone on the core examined for the current study as follows: (1) glauconitic siltstone-fine sandstone (2) massive-bedded siltstone (3) laminated calcareous siltstone (4) burrowed calcareous siltstone (5) bioturbated calcareous siltstone (6) massive-bedded packstone-grainstone (7) hummocky cross stratified and planar laminated packstone-grainstone. Except for the glauconitic siltstone-fine sandstone, all lithofacies are present in the samples employed for the current study. Although only enumerated here, Wang et al. (2019) and Adeboye et al. (2020) provide greater details about the geology and paleogeography of the Mississippian Limestone interval, as well as the facies classification of the Mississippian Limestone interval which is employed in the current study.

4.3.2 Sample selection

Ten samples were collected across an interval of a cored petroleum exploration well drilled in Kingfisher County, Oklahoma. Sampling was conducted based on the core descriptions of Wang et al. (2019) and the geochemical study of Adeboye et al. (manuscript in preparation), with sample selection done to ensure a plurality in TOC content and lithofacies. Organic carbon stable isotope results and elemental proxy contents for the 10 samples selected for biomarker analyses are reported in Adeboye et al. (manuscript in preparation).

4.3.3 Pyrolysis and hydrocarbon extraction

Rock samples were powdered and about 60mg of each sample was screened pyrolytically using a Vincent Technology Rock-Eval 6 instrument. The pyrolysis program was operated on source rock mode to evaluate hydrocarbon generation potential and total organic content (TOC) as described by Espitalie et al. (1977) and Bordenave et al. (1993). Samples from organic-rich intervals were further extracted to recover hydrocarbons. About 30g of rock powder sample was extracted using a Dionex™ ASE™ 350 Accelerated Solvent Extractor System. Rock powder samples were placed in stainless steel 22ml extraction cells and tightly sealed. The ASE extraction program was set at 100°C and 200 psi with dichloromethane as an extraction solvent. Extraction was performed in 3 cycles per sample to ensure complete extraction of hydrocarbons from the rock samples. Afterword, extracted hydrocarbon fluids were reduced in volume to approximately 1 ml under a gentle stream of nitrogen at ambient temperature. Two aliquots of extracted hydrocarbons were prepared for n-alkane and biomarker analyses.

For n-alkanes and isoprenoids, whole hydrocarbon extract was injected on a gas chromatograph equipped with a flame ionization detector (GC-FID). For biomarkers, extracted fluid samples were then spiked with a b-cholane standard (Chiron) for quantitative biomarker analysis. Next, spiked hydrocarbon fluids were treated with silica-gel columns to fractionate the sample into saturate and aromatic hydrocarbons. For high resolution biomarker detection, the saturate fraction was passed through a zeolite column to remove n-alkanes. Both saturate (n-alkane–free) and aromatic fractions were then analyzed using gas chromatography–mass spectrometry (GC-MS).

4.3.4 Gas Chromatography and Mass Spectrometry

Gas chromatography and mass spectrometry analyses were conducted using facilities at the Geochemical and Environmental Research Group (GERG), Texas A&M University, College Station. The first aliquot of extracted hydrocarbons (that is, whole hydrocarbon extracts from crushed rocks) were analyzed on an Agilent 7890 gas chromatograph equipped with a flame ionization detector (GC-FID). The GC is equipped with J&W DB-1 GC Column, 60m x 0.25 mm x 0.25 µm. Helium was used as a carrier gas with the column flow set at 1.3 ml/min. The GC oven temperature was programmed from 35°C to 320°C at a temperature ramp of 3°C/min and held at 320 for 10 minutes. The analysis was performed under a spitless injection mode with a solvent delay set at 6 minutes. The second aliquot (that is, the rock extracts that have been separated into saturate and aromatic fractions following silica-gel column chromatography) of the saturate hydrocarbon was analyzed on an Agilent 7890 gas chromatograph interfaced to an Agilent 5977 mass selective detector (GC-MS). The GC-MS is equipped with J&W DB-1 GC Column, 60m x 0.25 mm x 0.25 µm with helium carrier gas at a flow rate of 1.2 ml/min, pressure of 19.93 psi, and an average velocity of 20.538 cm/sec. The GC-MS is operated on splitless injection, with the oven programmed at an initial temperature of 35°C for 2 minutes and increased at a rate of 2°C/minute to 80°C, then 3°C/minute from 80°C to 320°C, followed by 15 minutes at 320°C. The analysis was carried out using 70 eV ionization potential. GC-MS data were acquired in single ion monitoring (SIM) mode with 50–100 msec dwell times for ions of interest. Compound ratios were calculated directly from peak areas or peak heights of targeted markers and compared with b-cholane standard.

4.4 Results and Discussion

4.4.1 Source Rock Potential

Rock-Eval results are summarised in Table 4.1 and are expounded upon in this section. TOC estimated from Rock-Eval pyrolysis ranged from 0.09 wt. % to 1.86 wt. %, showing a wide range of TOC contents in the samples analysed for this study. The carbonate content of samples was up to 8.36 wt. %. Rock-Eval T_{max} ranged from 400°C to 451°C while calculated R_o (Jarvie et al., 2001), an indication of thermal maturity, ranged from 0.04 % to 0.96 %. The calculated R_o values spanning such a large range, are likely an artefact of calculating R_o from T_{max} measurements because R_o estimated based on organic petrology in the area where the examined core was drilled is reported to be between 0.8 to 0.9 R_o (Cardott, 2012) hence, the samples are within the oil window (Hunt, 2002). S1 values > 0.5 mg HC/g of rock coupled with S2 values > 2.5 mg HC/g may be indicative of source rocks with good hydrocarbon generative potential (Peters, 1986). The Mississippian Limestone samples from the Anadarko Shelf examined in this study have S1 values which are between 0.13 mg HC/g and 2.50 mg HC/g and S2 values which range from 0.11 mg HC/g to 4.05 mg HC/g although only 2 of the samples studied have S2 values greater than 2.5 mg HC/g (Table 4.1). Overall, these S1 and S2 values suggest that these Mississippian Limestone samples have poor source rock potential for oil. Similarly, oil prone source rocks tend to have TOC values of at least 1 wt. % or higher (Palacas, 1984; Peters and Cassa, 1994; Sorkhabi, 2016), a property which is not present in these Mississippian Limestone interval samples.

Although it has been reported that carbonate source rocks tend to have lower TOC contents than shales (e.g., Palacas, 1984), the fact that these Mississippian Limestone interval samples have low TOC values in addition to low S1 and S2 values suggest that the Mississippian Limestone interval, at least in our study area, would be a poor source rock interval. Hydrogen index (HI) values were between 120 and 271 for the samples examined while oxygen index values were between 8 and 233. Oil prone source rocks typically have HI values of $\geq$ 300 (Peters et al., 2006; McCarthy et al., 2011) and none of the samples of the Mississippian Limestone examined our Anadarko Shelf study site have hydrogen index values that are that high (Table 4.1).

Production index (PI) was no greater than 0.66, with a minimum PI value of 0.35 been calculated from the 10 samples examined for this study. Large production index values could indicate the existence of a petroleum accumulation. Furthermore, a production index value of 0.1 (corresponding to R_o values of around 0.6%) represents the top of the oil window while a production index of 0.4 corresponds to the bottom of the oil window, which is equivalent to R_o values of about 1.4% (Peters, 1986). Similarly, T_{max} temperatures in the range of 435°C to 460°C are representative of organic matter that is in the oil window (Espitalie et al., 1977) and based on this parameter, most of the samples of the Mississippian Limestone examined for this study are within the oil window for thermal maturation (Table 4.1). Regardless, it is unlikely that the Mississippian Limestone interval from our Anadarko Shelf study site, at least judging from the PI of the samples examined in this study, will generate significant amounts of oil due to the relatively high values of PI, which suggests maturity beyond the oil window, and the observed low HI and OI values of these samples.

The findings from Rock-Eval pyrolysis analysis of these Mississippian Limestone interval samples could be a consequence of two scenarios; first, observed low Rock-Eval parameters (e.g., TOC, S1, S2, HI, etc.) are due to depletion arising from the thermal maturation of (carbonate) source rocks which had fair petroleum generation potential and which have in fact generated hydrocarbons due to being in within the oil window. The second scenario for the observed low Rock-Eval parameters obtained from these samples is that pyrolysis results are controlled by initial paleoredox conditions at time of Mississippian Limestone sediment deposition on the Anadarko Shelf. Unfavourable depositional conditions, such as oxic redox state, would have resulted in poor preservation of Mississippian organic matter. Although the first scenario cannot be ruled out, the second scenario could be more plausible due to findings from other studies on paleodepositional redox conditions of the Mississippian Limestone interval within the STACK resource play on the Anadarko Shelf (e.g., Adeboye et al., 2020) and suggests that there is significant lateral variation in source rock quality, and hence hydrocarbon generation potential, within the Mississippian Limestone interval.

4.4.2 Molecular Geochemistry

Gas chromatography results are summarised in Table 4.2. Pristane/phytane ratios range in value from 0.79 to 1.63, while carbon preference index (CPI) values were between 0.34 to 1.39. Similarly, odd-to-even predominance (OEP) values were between 0.44 to 1.06. The ratio of pristine/phytane has been used to interpret paleodepositional conditions (e.g., Brooks et al., 1969; Powell and McKirdy, 1973; Didyk et al., 1978; Sofer, 1988; Hughes et al., 1995; Patranabis-Deb et al., 2016). Pristane/phytane ratios < 2 are interpreted as indicating deposition under marine anoxic conditions, while values of the pristine/phytane ratio > 3 indicate deposition in oxic settings or are interpreted as indicating detrital sources of organic matter (e.g, Powell and McKirdy, 1973; Hughes et al., 1995). Furthermore, it has been suggested that organic matter deposited under alternating oxic-anoxic conditions yield pristane/phytane ratios of around 1 (Didyk et al., 1978). These authors also reported that organic matter deposited under wholly oxic conditions produce values of pristane/phytane which are much greater than 1 while organic matter deposited under wholly anoxic conditions yield values of pristane/phytane that are less than 1.

The values of pristane/phytane ratio calculated for all the samples examined in this study are all less than 2 and are mostly around 1, thus the ratio suggests that environmental redox conditions during deposition of the Mississippian Limestone within the Anadarko Shelf fluctuated between oxic-anoxic conditions (or, depositional redox conditions were suboxic, cf. Adeboye et al., 2020). The ratio of pristane/phytane consequently does not conclusively elucidate paleodepositional environmental conditions for our samples, and by extension for our study site. Thus, in order to clarify what environmental conditions were like on the Anadarko Shelf at the time of deposition of the samples examined in this study, a plot of Pr/nC_{17} vs. Ph/nC_{18} was made (Fig. 4.2). This plot has been shown to be useful for deciphering paleodepositional environmental conditions (Shanmugam, 1985). Our samples plot in the mixed zone, where there is an overlap between oxidixing and reducing conditions (perhaps suboxic conditions as proposed by Adeboye et al., 2020 from independent evidence encompassing isotope geochemistry and trace element geochemistry). Furthermore, our results also show that the organic matter type present in the Mississippian Limestone interval samples examined for this study is of mixed type II-III, which might explain the lack of significant oil source rock capacity of these samples and perhaps, of the lack of significant oil source rock potential within the wider Mississippian Limestone interval within the Anadarko Shelf (Fig. 4.2, Table 4.1).

CPI values ≤ 1 are suggestive of deposition under highly anoxic environments or, indicate carbonate source rocks whereas CPI values ≥ 1 indicate deposition under more oxic conditions or could indicate shaley source rocks (Moldowan et al., 1985). It has also been reported that extant vascular plants have CPI values which are > 3 (van Dongen et al., 2006) and contribution of organic matter input predominantly from land plants results in CPI values which are > 1 (Ficken et al., 2000; Eglinton et al., 2006). The CPI values (Table 4.2) for the Mississippian Limestone interval samples examined in this study are all ≥ 1, except for the sample from 8828 ft (2690.77 m), suggesting that deposition of organic matter associated with these samples occurred in an oxic environment or, organic matter input stemmed predominantly from land plants or terrestrial sources, or both. Consequently, these samples are unlikely to have sourced any oil. Although, complications could arise from interpretations relying solely on CPI values (cf. Bray and Evans, 1961), we have drawn from a variety of different biomarker and organic geochemical parameters to arrive at our interpretation in this study. Oxic paleodepositional redox conditions inferred for sediments of the Mississippian Limestone interval within the Anadarko Shelf support the interpretation that observed Mississippian biomarker fingerprints represent fluid migration from nearby Mississippian section with good source rock quality, which would further confirm the lateral heterogeneity within the Mississippian Limestone interval. The CPI values could however, also be a consequence of Mississippian Limestone sediments with fair initial source rock quality, having generated hydrocarbons in-situ and these hydrocarbons having some carbonate contribution.

It has been reported that OEP values of Mississippian Limestone extracts and oils are generally < 1, in contrast to OEP values of Woodford Shale sourced oils and source rock extracts which tend to be > 1, although there could be some overlap in OEP values between Woodford Shale and Mississippian Limestone interval oils and source rock extracts (Al Atwah et al., 2019). Furthermore, OEP values close to 1 are suggestive of mature oils and source rocks (Peters et al., 2007). The OEP values of the Mississippian Limestone samples examined for this study (Table 4.2) are broadly similar to those reported for Mississippian Limestone oils and source rock extracts by Al Atwah et al. (2019), who reported OEP values between 0.94 to 1.04 for Mississippian Limestone interval source rock extracts and oils. The calculated OEP values for the source extract from the Mississippian Limestone interval from the STACK in the Anadarko Shelf area of Oklahoma also indicate that these samples are mature since the OEP values are close to 1.

4.4.3 Thermal Maturity Parameters

Computed Ts/(Ts+Tm) ratios for the Anadarko Shelf Mississippian Limestone samples examined in this study ranged from 0.55 to 0.81 (Table 4.3). These values are relatively high, and indicate that these samples are mature, because Tm is converted to Ts as maturity increases (Waples and Machihara, 1990; Bennett and Olsen, 2007). The Ts/(Ts+Tm) ratio, a qualitative indicator of maturity, is in agreement with calculated R_o, which suggests that most of these samples are within the oil window (Table 4.1). It has also been suggested that low Ts/(Ts+Tm) ratios may be due to presence of carbonates (Bennett and Olsen, 2007 and references therein), thus the relatively high Ts/(Ts+Tm) ratios encountered in the examined samples could be influenced by the mixed carbonate-clastic lithology of the Mississippian Limestone interval.

The extremely low (almost zero) values for the gammacerane/hopane ratio also strongly support the fact that the organic matter from the Anadarko Shelf Mississippian Limestone samples studied for the current work were deposited in oxygenated settings (cf. Adeboye et al., 2020) because an abundance of gammacerane is indicative of a strongly stratified water column, perhaps due to unusually high salinities (e.g., Waples and Machihara, 1990). The high preponderance of tricyclic terpanes within the Mississippian Limestone samples studied here are also indicative of the oxic and less saline conditions during deposition of these samples within the Anadarko Shelf since precursors of tricyclic terpanes are thought to be more abundant in oxygenated settings (Dahl et al., 1993; Bennett and Olsen, 2007 and references therein).

4.4.4 Comparison with Woodford Shale Organic Matter

Mississippian Limestone interval organic matter possess a series of extended tricyclic terpanes up to C_{44} (Figs. 4.3 and 4.4). Furthermore, Organic matter extracts from the Mississippian Limestone intervals investigated in this study display enrichments of C_{27} sterane biomarkers relative to C_{28} and C_{29} sterane biomarkers (Fig. 4.3). While the representative mass-to-charge chromatogram shown for 191 and 217 respectively in figures 4 A and B are from one of the ten samples examined in this study, both representative chromatograms are similar to those of the other nine samples not shown in that all ten samples have similar compounds within them. Equally, the chromatograms from all ten samples indicate that the Mississippian Limestone interval organic matter extracts possess a series of tricyclic terpanes up to C_{40} in abundance, similar to reports published by previous investigations conducted on the Mississippian Limestone interval and, a situation which these previous authors describe as not been widely observed in extracts from Woodford shale organic matter (e.g., Al Atwah et al., 2019; Wang and Philp, 2019; Atwah et al., 2020). It has however been argued by Symcox and Philp (2019) that the diagnostic nature of extended tricyclic terpanes up to C_{44} as being indicative of Mississippian Limestone sourced organic matter, or hydrocarbons, within the Anadarko Basin and Shelf is questionable since immature Woodford shale intervals are rarely targeted for liquids production. These researchers explain that in the higher maturity intervals from which Woodford shale sourced liquid hydrocarbons are produced, the terpenoid biomarkers are too degraded to be detectable. These authors further go on to report the presence of extended tricyclic terpanes in oils from Woodford shale producing wells from Kingfisher and Canadian counties suggesting that the Devonian-Mississippian interval is a single petroleum system which is solely sourced by the regionally extensive and prolific Woodford shale. The arguments and supporting evidence put forward by Symcox and Philp (2019) stating that the Devonian-Mississippian interval within the Anadarko Shelf and Basin is a single petroleum system, solely sourced by the regionally extensive and prolific Woodford shale, has been previously suggested by Kim and Philp (2001) who noted that the organic matter in the Mississippian Limestone interval is type II to type III, and who reported that there appears to be a strong relationship between terrigenous detritus and an abundance of tricyclic terpanes. Results from the current study and the study by Atwah et al. (2020) which show Mississippian Limestone interval samples possessing type II-III organic matter, and an abundance of tricyclic terpanes, does not support the conclusions of Symcox and Philp (2019). Extracts of immature Woodford Shale and Mississippian Limestone interval source rocks show different terpenoid signatures (Atwah et al., 2020). Furthermore, Mississippian Limestone oils contain higher proportions of tricyclic terpanes whereas, Woodford Shale oil contains higher proportions of hopanes (Atwah et al., 2020). Although we did not examine Woodford Shale oil or source rock extracts in this study, our Mississippian Limestone rock extracts also had an abundance of extended tricyclic terpanes, similar to what was reported in the literature by Atwah et al. (2020). Finally, the study by Symcox and Philp (2019) only examined oil samples without looking at any source rock extracts thus, due to the fact that fluids do migrate in the subsurface, it could be the case that some of their results are due to fluids which migrated from other areas and intermingled with Woodford Shale sourced fluids hence their results indicating a Woodford source for oils within the Mississippian Limestone interval. Our current study, which uses rock extracts solely, would not have this problem of fluid migration and coupled with the other diagnostic

Mississippian Limestone biomarker signatures, indicate that Woodford Shale sourced oils are geochemically distinct from Mississippian Limestone sourced oils, even if the Mississippian Limestone sourced oil was generated from a nearby Mississippian source within the STACK and not in the 10 samples examined for this study.

The relative enrichment of C_{27} sterane found in the chromatograms of all ten samples (Fig. 4.3) differentiates Mississippian Limestone organic matter extract from Woodford shale extracts since Woodford shale organic matter extracts tend to exhibit enrichment in C_{29} sterane (cf. Miceli Romero and Philp, 2012; Al Atwah et al., 2019). Unlike the relatively high ratios of bisnorhopane to hopane that was reported by Al Atwah et al. (2019) in their study of the Mississippian Limestone interval away from the STACK play area, ratios of bisnorhopane to hopane in our Mississippian Limestone interval samples are zero (Table 4.3) thereby ruling out algal sourced organic matter input, at least into the STACK play area of the Anadarko Shelf, where our samples are sourced from. Bisnorhopane to hopane ratios of zero also serve to differentiate Mississippian Limestone samples from this study to Woodford shale samples, which have low (but non-zero) bisnorhopane to hopane ratios (Al Atwah et al., 2019).

4.5 Summary and Conclusions

Source rock potential within the Mississippian Limestone interval has been observed and documented by many studies, however, lateral variation within the Mississippian Limestone interval remains unexplained, particularly within the STACK resource play area of the Anadarko Shelf. Examined Mississippian Limestone samples exhibit low petroleum generation potential with TOC less than 2 wt. % and maximum hydrogen index of 271. Pyrolysis and biomarker maturity indicators suggest that samples have reached the oil window with calculated R_o values up to 0.96% and T_{max} values up to 451°C. Biomarkers diagnostic of Mississippian Limestone sediments are observed in all samples, including the abundance of extended tricyclic terpanes relative to hopanes, as well as abundance of C_{27} sterane biomarkers relative to C_{28} and C_{29} steranes. Based on the pyrolysis results and molecular geochemistry data of the examined samples, two possible explanations are proposed for explaining the variation in source rock quality within the Mississippian Limestone: the first explanation is that perhaps, the samples examined in the current study are spent source rocks which have already generated and expelled oil. Thus, Rock-Eval pyrolysis results and TOC data in the examined samples are indicative of a poor source rock interval, and the Mississippian biomarker signatures represent retained, in-situ generated hydrocarbons. The second explanation is that inferred oxic paleoredox conditions during deposition of Mississippian Limestone sediments in our Anadarko Shelf study site is responsible for poor source rock signatures suggested by Rock-Eval parameters (TOC, HI, etc), and the observed Mississippian biomarker fingerprints represent migrated fluids from nearby Mississippian Limestone intervals with better source rock potential. Further studies of the Mississippian Limestone interval, which examine samples obtained from multiple locations within the Anadarko Shelf will help to clarify which of the two explanations presented here is true.

4.6 Acknowledgements

We would like to acknowledge Newfield Exploration (since purchased by the former Encana Corporation, which currently trades under the Ovintiv Inc. name) for providing access to the core from which we obtained the samples examined in this study. We are also grateful to the Geochemical and Environmental Research Group (GERG) at Texas A&M University for carrying out the biomarker analysis. Discussions with several researchers on how to improve the ideas presented in the paper are gratefully acknowledged. OOA is grateful to the Oklahoma Geological Foundation (OGF) for the Herbert G. and Shirley A. Davis Geology Fellowship, the National Association of Black Geoscientists (NABG) for the Mack Gipson Scholarships and the American Association of Petroleum Geologists (AAPG) for the Grants-in-Aid awards without which this work, and the overall PhD project which it is a part of, would have been impossible. We would also like to place on the record our appreciation to the Oklahoma State University Mississippian Consortium, as well as the Boone Pickens School of Geology, for providing additional funding which enabled us to undertake this study. This is Oklahoma State University – Boone Pickens School of Geology contribution # XXXX-XXX.

Figures

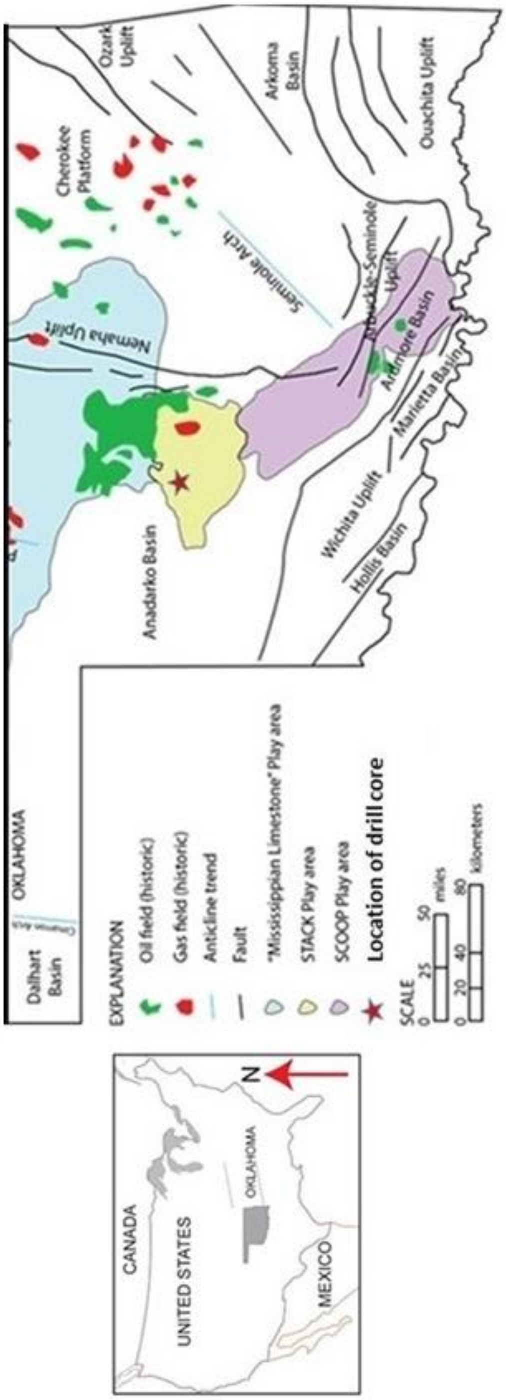


Figure 4.1: Outline of the STACK resource play area in Oklahoma, red star shows the core location from which samples were obtained for this study. Inset map shows the position of the State of Oklahoma within the contiguous USA. (After Hunt, 2017).

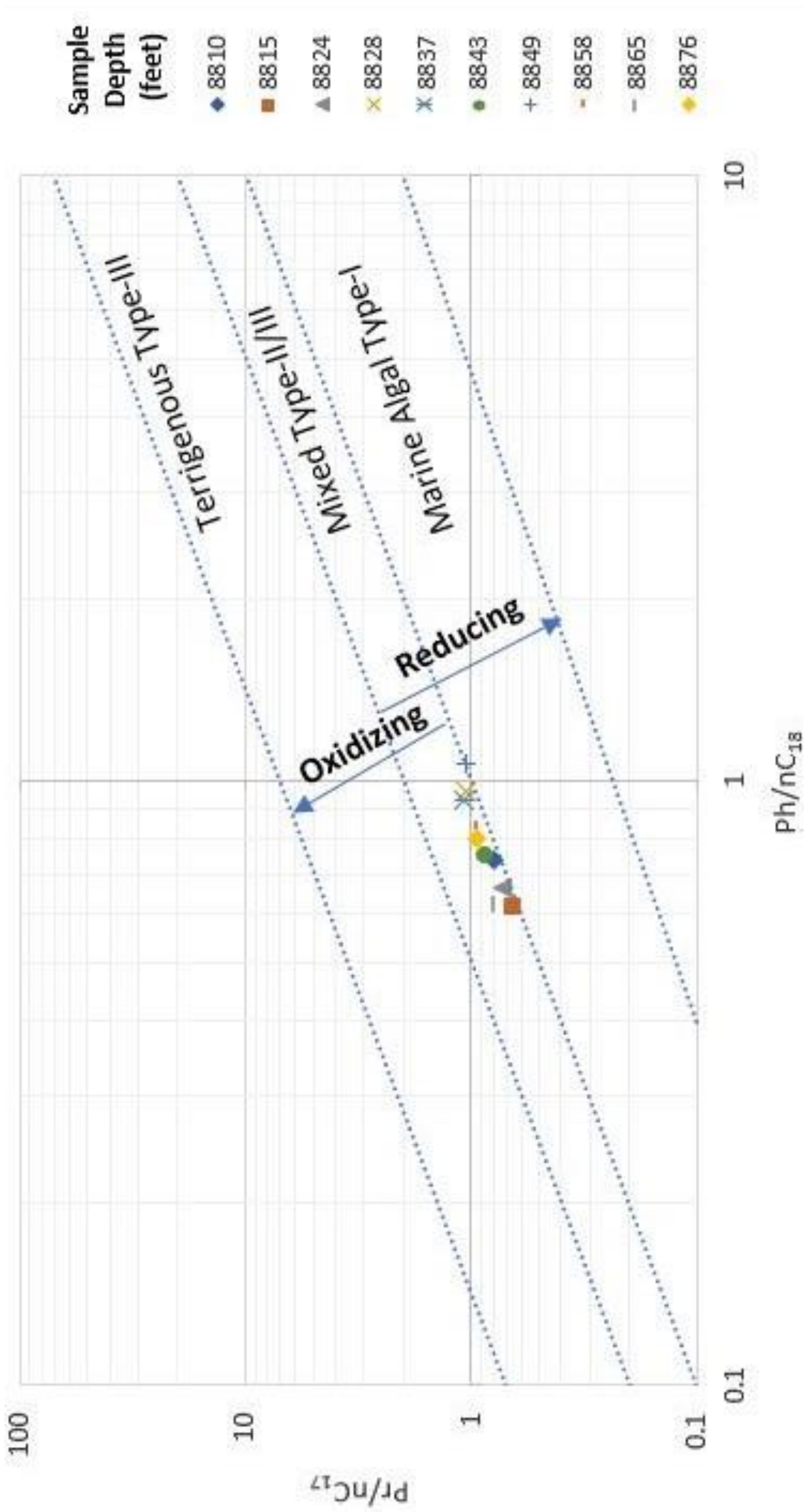


Figure 4.2: Pr/nC_{17} vs. Ph/nC_{18} plot showing environmental conditions at time of deposition of Mississippian Limestone interval samples examined in this study (after Shanmugam, 1985).

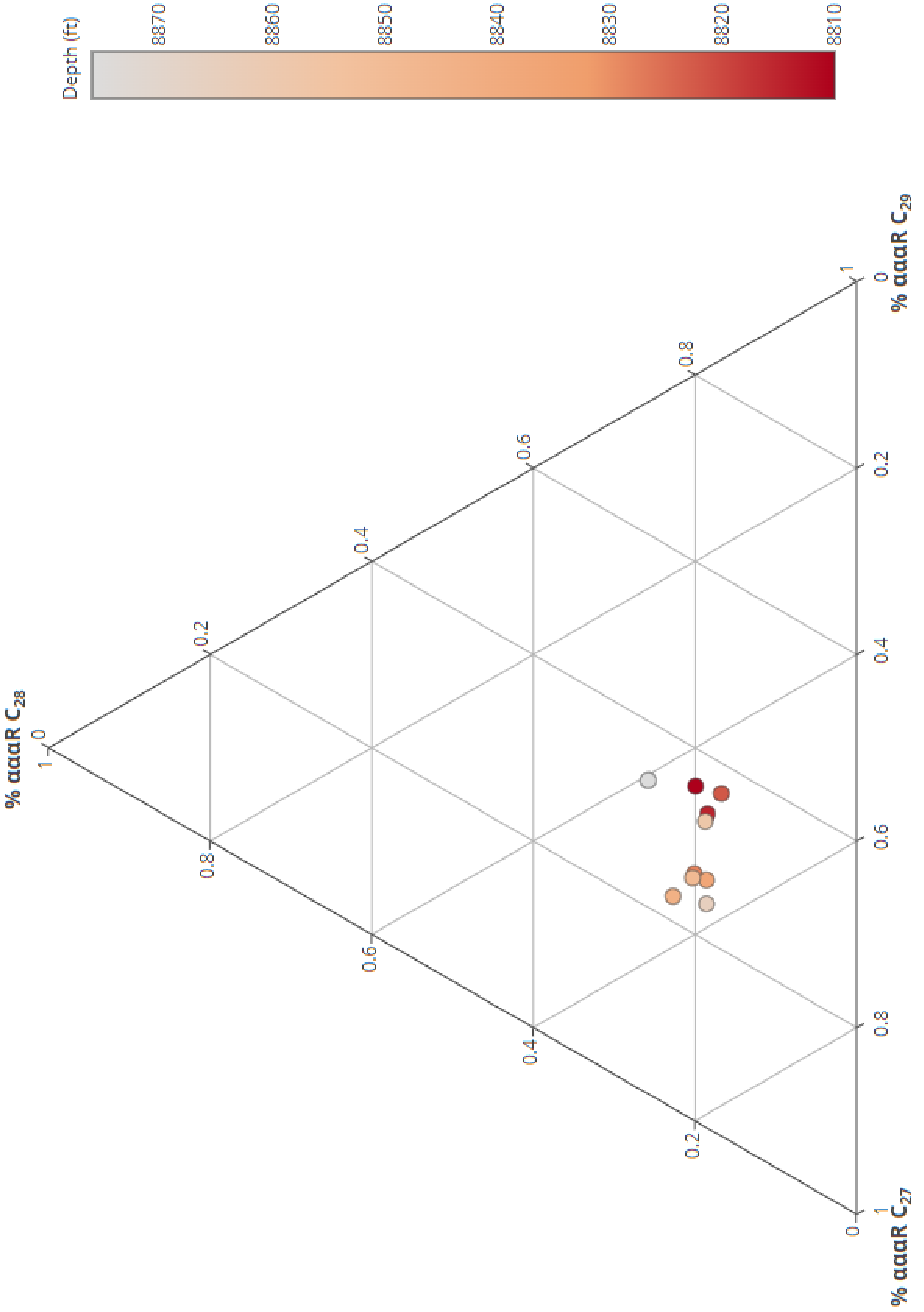
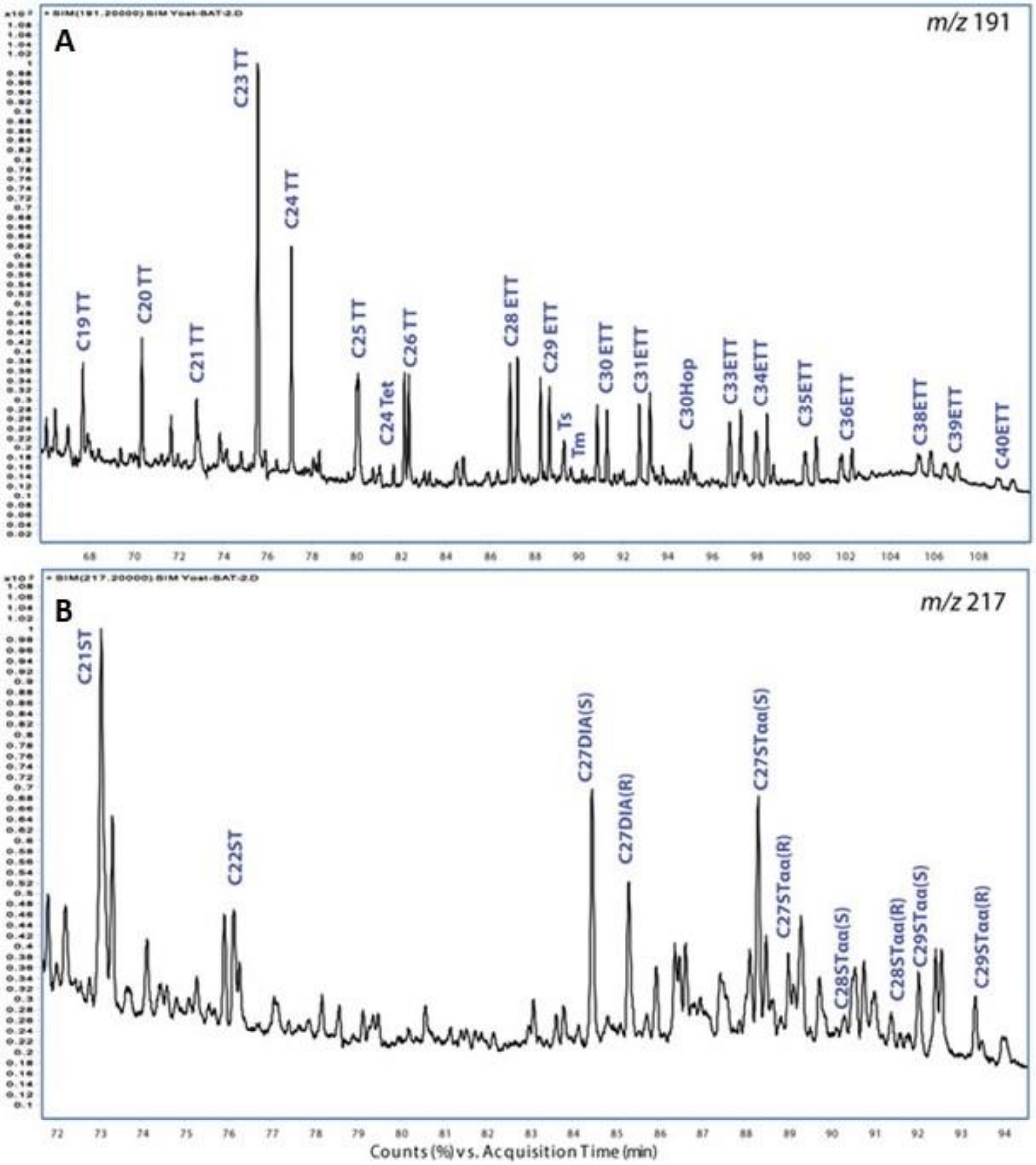


Figure 4.3: Ternary diagram showing enrichment of C_{27} sterane biomarkers relative to C_{28} and C_{29} sterane biomarkers in the Mississippian Limestone interval samples investigated in this study.



Peak Identification Key

m/z 191 Terpane Biomarkers	
Label	**Compound**
C19 TT	C19 tricyclic diterpane
C20 TT	C20 tricyclic diterpane
C21 TT	C21 tricyclic diterpane
C23 TT	C23 tricyclic terpane
C24 TT	C24 tricyclic terpane
C25 TT	C25 tricyclic terpane (S+R)
C24 Tet	C24 tetracyclic terpane (TET)
C26 TT	C26 tricyclic terpane (S+R)
C28 ETT	C28 extended tricyclic terpane (S+R)
C29 ETT	C29 extended tricyclic terpane (S+R)
Ts	Ts 18a(H)-trisnorhopane
Tm	Tm 17a(H)-trisnorhopane
C30 ETT	C30 extended tricyclic terpane (S+R)
C31 ETT	C31 extended tricyclic terpane (S+R)
C29 Hop	C29 Tm 17a(H)21b(H)-norhopane
C30 Hop	C30 17a(H)-hopane
C33 ETT	C33 extended tricyclic terpane (S+R)
C31 Hop	C31 22S+R 17a(H) homohopane
C34 ETT	C34 extended tricyclic terpane (S+R)
C32 Hop	C32 22S+R 17a(H) bishomohopane
C35 ETT	C35 extended tricyclic terpane (S+R)
C33 Hop	C33 22S+R 17a(H) trishomohopane
C36 ETT	C36 extended tricyclic terpane (S+R)
C34 Hop	C34 22S+R 17a(H) extended hopane
C35 Hop	C35 22S+R 17a(H) extended hopane
C38 ETT	C38 extended tricyclic terpane (S+R)
C39 ETT	C39 extended tricyclic terpane (S+R)
C40 ETT	C40 extended tricyclic terpane (S+R)
m/z 217 Sterane Biomarkers	
Label	**Compound**
C21 ST	C21 sterane
C22 ST	C22 sterane
C27 DIA(S)	C27 ba 20S diacholestane
C27 DIA(R)	C27 ba 20R diacholestane
C27 STαα(S)	C27 αα 20S cholestane
C27 STαα(R)	C27 αα 20R cholestane
C28 STαα(S)	C28 αα 20S cholestane
C28 STαα(R)	C28 αα 20R cholestane
C29 STαα(S)	C29 αα 20S cholestane
C29 STαα(R)	C29 αα 20R cholestane

Figure 4.4: (A): Representative mass-to-charge (m/z) 191 chromatograms showing extended tricyclic terpanes up to C44 which are characteristic of Mississippian Limestone interval organic matter in the Anadarko Shelf and Basin, Oklahoma. (B): Representative mass-to-charge (m/z) 217 chromatograms showing sterane biomarkers characteristic of the Mississippian Limestone interval organic matter.

Tables

Table 4.1: Rock-Eval pyrolysis results and calculations.

Sample depth, ft (m)	Carbonate (wt. %)	Rock-Eval TOC (wt. %)	S_1 mg HC/g	S_2 mg HC/g	S_3 mg CO_2/g	T_{max} (°C)	Calculated % R_o[1]	HI[2]	OI[3]	PI[4]
8810.10 (2685.32)	1.67	1.86	2.50	4.05	0.23	446	0.87	218	12	0.38
8815.00 (2686.81)	2.82	1.70	1.83	3.40	0.15	451	0.96	200	9	0.35
8822.54 (2689.11)	4.10	0.34	0.29	0.53	0.21	444	0.83	156	62	0.35
8828.00 (2690.77)	8.36	0.06	0.13	0.09	0.14	416	0.33	150	233	0.59
8837.00 (2693.52)	5.91	0.10	0.23	0.12	0.20	400	0.04	120	200	0.66
8843.50 (2695.50)	3.11	0.23	0.87	0.60	0.16	434	0.65	261	70	0.59
8849.50 (2697.33)	8.26	0.09	0.15	0.11	0.15	420	0.40	122	167	0.58
8858.50 (2700.07)	3.93	0.14	0.49	0.38	0.17	431	0.60	271	121	0.56
8865.93 (2702.34)	1.83	0.74	1.03	1.29	0.16	440	0.76	174	22	0.44
8876.00 (2705.40)	3.48	0.46	1.33	1.23	0.13	441	0.78	267	28	0.52

[1]Calculated vitrinite reflectance equivalent = $((0.018 \cdot T_{max}) - 7.16)$ [2]Hydrogen index (HI) = $(S_2 \cdot 100/TOC)$ [3]Oxygen index (OI) = $(S_3 \cdot 100/TOC)$ [4]Production index (PI) = $(S_1/(S_1+S_2))$

Table 4.2: Gas chromatography results.

Sample Depth, ft (m)	Pr/Ph	Pr/n-C_{17}	Ph/n-C_{18}	CPI	OEP
8810.10 (2685.32)	1.29	0.80	0.74	1.05	0.95
8815.00 (2686.81)	1.26	0.65	0.62	1.39	0.96
8822.54 (2689.11)	1.06	0.74	0.67	1.16	1.02
8828.00 (2690.77)	0.85	1.06	0.96	0.34	0.44
8837.00 (2693.52)	1.02	1.09	0.93	1.15	1.04
8843.50 (2695.50)	1.25	0.87	0.76	1.05	0.90
8849.50 (2697.33)	0.79	1.07	1.06	1.27	1.06
8858.50 (2700.07)	1.04	0.94	0.84	1.00	0.96
8865.93 (2702.34)	1.63	0.80	0.63	1.36	0.96
8876.00 (2705.40)	0.91	0.94	0.80	1.02	0.99

Pr/Ph = pristane/phytane ratio; Pr/n-C_{17} = pristane/n-C_{17} ratio; Ph/n-C_{18} = phytane/n-C_{18} ratio; CPI = carbon preference index (calculated using the equation of Marzi et al., 1993); OEP = odd-to-even predominance (calculated using the equation of Scalan and Smith, 1970)

Table 4.3: Selected biomarker ratios.

Sample Depth, ft (m)	Bisnorhop/Hop[1]	Ts/(Ts+Tm)[2]	Gam/Hop[3]	Mor/Hop[4]	C_{29}/C_{30}[5] Hop	Dia/Reg[6]
8810.10 (2685.32)	0.00	0.81	0.003	0.003	0.09	0.50
8815.00 (2686.81)	0.00	0.71	0.000	0.000	0.11	0.43
8822.54 (2689.11)	0.00	0.72	0.001	0.001	0.01	0.50
8828.00 (2690.77)	0.00	0.64	0.000	0.000	0.01	0.44
8837.00 (2693.52)	0.00	0.55	0.000	0.000	0.01	0.42
8843.50 (2695.50)	0.00	0.57	0.005	0.005	0.89	0.42
8849.50 (2697.33)	0.00	0.66	0.001	0.001	0.01	0.40
8858.50 (2700.07)	0.00	0.55	0.002	0.002	0.47	0.38
8865.93 (2702.34)	0.00	0.64	0.000	0.000	0.03	0.41
8876.00 (2705.40)	0.00	0.64	0.000	0.000	0.08	0.37

[1] Bisnorhopane/Hopane [2] Trisnorhopane Stable/Trisnorhopane maturable [3] Gammacerane/Hopane [4] Moretane/Hopane [5] C_{29}/C_{30} hopane [6] Diasterane/Regular sterane

CHAPTER V

CONCLUSIONS AND FUTURE DIRECTIONS

5.1 Conclusions

Based on the totality of evidence arising from multiple geochemical assessments conducted in the course of this project, including stable isotope analysis of nitrogen and organic carbon, analysis of chemical elements and saturate biomarker investigations, the following conclusions can be made about the Mississippian Limestone interval within the STACK resource play on the Anadarko Shelf of Oklahoma:

1) Redox conditions were oxic to suboxic when sediments of the Mississippian Limestone interval were deposited on the Anadarko Shelf of Oklahoma.
2) There is a lack of evidence for enhanced organic matter paleoproductivity at time of deposition of sediments of the Mississippian Limestone interval within the Anadarko Shelf.
3) Results from this study do not signify heightened detrital input into the Anadarko Shelf during deposition of sediments of the Mississippian Limestone.
4) The Mississippian Limestone interval is laterally very heterogeneous and while the few samples we examined for source rock characteristics for this project displayed poor source rock quality, we are unable to conclusively rule out the fact that sediments of the Mississippian Limestone interval are capable of generating

hydrocarbons in other, more favourable locations within the STACK resource play of the Anadarko Shelf.

5.2 Future Directions

It has been reported from previous studies of heterogeneous lithologies that saturate fraction biomarkers give equivocal source input and organic matter provenance results (e.g., Jiang et al., 2001). Consequently, future studies on the Mississippian Limestone interval within the STACK resource play area of the Anadarko Shelf should include the evaluation of various aromatic biomarker compounds, since these have been shown to provide unambiguous organic matter provenance and source input results in settings with mixed systems (see Jiang et al., 2001), such as the Mississippian Limestone interval of the Anadarko Shelf. Finally, any future study of the Mississippian Limestone interval within the greater Anadarko Shelf and Basin should account for and include samples that span the geographic extent of the interval, as well as the lithological heterogeneity of the Mississippian Limestone interval in order to get a better handle on lateral variations in the properties of this very heterogeneous sedimentary interval.

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