

ANALYSIS OF THE URANIUM TO ORGANIC CARBON
RELATIONSHIP IN THE ORGANIC-RICH OHIO SHALE
OF EASTERN KENTUCKY

By

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Abstract: Organic-rich shales have become increasingly important to unconventional petroleum reservoirs, and tools such as the gamma-ray have been used to locate them due to the radioactivity of elements such as uranium, potassium, and thorium present within shales. Complex sedimentary processes of organic-rich black shales are responsible for highly variable geochemical signals. Generally, there is a strong correlation between gamma-ray signature, as a result of radioactive uranium (U), and total organic carbon (TOC) in many Devonian black shales due to similar depositional processes of U and TOC. However, this strong correlation between U and TOC does not seem to be present within the Cleveland Shale interval based on gamma-ray data.

In order to interpret ancient ocean conditions, trace metal uranium and molybdenum (Mo), and total organic carbon inventory of the Cleveland Shale and Lower Huron members of the Devonian Ohio Shale Group of eastern Kentucky were evaluated in order to determine the degree of basin restriction and paleoredox state of the Appalachian Basin at the time of deposition. The Ohio Shale Group provides a remarkable study area for this investigation along the basin margin of the Appalachian Basin, as trace metal U and Mo data give insight on the opening and closing of the basin throughout the Devonian Period. The Cleveland member of the Ohio Shale Group displays a weak to moderate correlation between TOC and trace metal U and Mo. In contrast, the two subdivisions that are defined in this study of the Lower Huron of the same stratigraphic group has a much stronger correlation between TOC and trace metal U and Mo. In fact, many sections throughout the lower and uppermost Cleveland Shale interval have greater organic carbon contents (up to 6.0 wt.%) than that of sections in the Lower Huron that have more radioactivity as a result of higher U contents. This discrepancy between U, Mo, and organic carbon accumulation along the basin margin setting is a result of trace metal availability in the water column, basin geometry, location within the basin, and a fluctuating sea level that impacted the degree of restriction and sill depth dividing the water masses surrounding the Appalachian Basin.

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CHAPTER I

INTRODUCTION

The gamma-ray tool is a non-destructive method used on core or outcrop samples that involves reading the radioactivity of certain trace metals that have been incorporated into the sediment. Typically, the gamma-ray tool has a relatively high response in black shales due to the natural radioactivity of uranium that is present within black shales (Schmoker, 1981; Lüning and Kolonic, 2003). Black shales are defined as dark gray or brown to black mudrocks containing organic matter and silt- and clay-sized particles that accumulated together (Swanson, 1961; Tourtelot, 1979; Schmoker, 1981; Wignall and Myers, 1988; Lüning and Kolonic, 2003). These organic-rich black shales form where large quantities of organic matter accumulated as a result of high productivity and where oxygen-depleted water conditions are present (Schmoker, 1981; Spirakis, 1996; Lüning and Kolonic, 2003). Due to the accumulation of organic matter (OM) and uranium under anoxic conditions, the gamma-ray log response is typically high in black shales with high TOC (Schmoker, 1981; Wignall and Myers, 1988; Spirakis, 1996; Lüning and Kolonic, 2003). Reduction of uranium occurs under anoxic conditions and is intensified under euxinic conditions when free sulfides are present (Klinkhammer and Palmer, 1991; Lovely et al., 1991; Lovely, 1993; Spirakis, 1996; Algeo and Maynard, 2004). High organic carbon preservation in sediments can occur due to processes such as high particle sinking velocities,

aggregational processes in the water column, rapid burial, or during periods of intense productivity (Hedges et al., 2001; Calvert and Pedersen, 1992).

Gamma-ray techniques have been reliable for finding economically profitable, high TOC zones in ancient basins by reading high radioactivity as an indicator for high organic content due to the assumed linear relationship between U and TOC (e.g. Bell et al., 1940). Uranium concentration is important to the petroleum industry due to this association between uranium and organic carbon, and thus gamma-ray and organic carbon. Gamma-ray based isopach mapping is a technique used by researchers to predict the extent of source rocks within ancient basins (Schmoker 1980, 1981; Fertl and Rieke, 1980; Herron, 1991; Lüning and Kolonic, 2003). For example, the Upper Devonian Woodford Shale of Oklahoma displays a strong correlation between gamma-ray and TOC (e.g. Lüning and Kolonic, 2003), while the similar-aged members of the Ohio Shale Group of Eastern Kentucky exhibits a decoupling between gamma-ray response and TOC. Although there are similar depositional environments within these shale groups, U as an indicator of organic-richness through gamma-ray response cannot always be used reliably as some black shales do not have a strong correlation between TOC and U content (Lüning and Kolonic, 2003). The decoupling of a stable U/TOC relationship may be due to oxidation of reduced U during oxic periods or in the presence of phosphate (Lüning and Kolonic, 2003).

1.1 Trace Metal Geochemistry

Seawater is a major geochemical reservoir that has a variety trace metals that can be used as geochemical proxies. The analysis of trace metal data can be reliably used to identify ocean current and redox conditions (Brumsack, 1980; Calvert and Pederson, 1993; Algeo and Maynard, 2004; Algeo and Rowe, 2012) and to determine the variation in redox conditions in organic-rich black shales (Vine and Tourtelot, 1970; Pratt and Davis, 1992; Algeo and Maynard, 2004; Brumsack, 2006). Trace elements exhibit considerable enrichment in organic-rich black shales (Calvert and Pedersen, 1993; Algeo and Maynard, 2004).

Variability in trace metal concentrations within a vertical section of rock indicate evolution of watermass geochemistry as a result of differential rates of trace metal uptake by the sediment. High productivity and oxygen depleted environmental conditions are required in order to create an environment in which large quantities of organic matter and U can be preserved in black shales (Swanson, 1961, Tourtelet, 1979; Schmoker, 1981; Lüning and Kolonic, 2003; Piper and Calvert, 2009). Basin geometry has a significant influence on trace metal accumulation. For example, a large basin with a shallow sill such as the Black Sea will be renewed in trace metals less readily than a smaller basin with deeper sills such as the Saanich Inlet (Figure 1) (Algeo and Lyons, 2006; Algeo and Rowe, 2012). Within a restricted basin environment, such as the Michigan Basin, the basin margin and deeper basin settings have drastically different geochemical signatures as a result of a shifting pycnocline, or layer in which water density rapidly increases with depth, that fluctuated during the rise and fall of sea level (Formolo et al., 2014). Sea level fluctuated throughout the Devonian, and the Ohio Shale Group has varied trace metal concentrations as a result of restriction and sill variability (Algeo and Rowe, 2012). At times when eustatic levels are high, the silled margins of basins are deep sills,

allowing for more trace metals to be delivered into the system, however during eustatic falls marginal sills are more shallow and restricts circulation of trace metals into the system (Figure 1) (e.g., Algeo and Lyons, 2006; Algeo and Rowe, 2012). Under basinal geometries that are considered restricted or silled basins, large amounts of organic matter in the sediment and poor circulation of oxygenated waters allows for oxygen-depleted bottom water conditions (Algeo and Rowe, 2012).

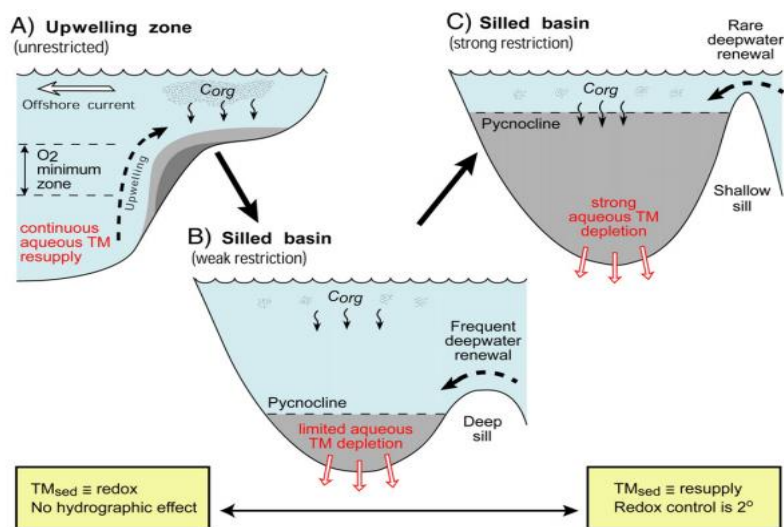


Figure 1. Models of different basin geometries that influence trace metal accumulation. A) continental shelf upwelling zone. B) anoxic basin with deep sill. C) anoxic basin with shallow sill (Algeo and Rowe, 2012).

1.2 Uranium Geochemistry

Uranium content has been a useful indicator for bottom water anoxia in ancient sediments (Wignall and Myers, 1988; Anderson et al., 1989; Jones and Manning, 1994; Tribouillard et al., 2006). Uranium is present as either soluble U(VI) or as insoluble U(IV) oxidation states (Langmuir, 1978; Klinkhammer and Palmer, 1991; Calvert and Pedersen, 1993). The incorporation of U into the rock record can occur under a variety of conditions/mechanisms:

active biological uptake of U by organisms that eventually become part of the rock record in organic-rich sediments; chemically dissolved state of U(VI) that is incorporated in sediments on the ocean floor is preserved; chemical reduction in anoxic water columns of soluble U(VI) to insoluble U(IV); or diffusion of dissolved U(VI) into anoxic sediments where it is reduced and then precipitated (Anderson et al., 1989; Lovley et al., 1991).

The primary source of uranium that is concentrated in marine black shales is attributed to the availability of uranium present within the water column at the time of deposition (Swanson, 1961; Spirakis, 1996). The uranium/ TOC ratio in black shales is influenced by many factors such as the primary uranium content of the water body, carbonate content, and the sedimentation rate at the time of deposition (Lüning and Kolonic, 2003). Uranium (U) is removed from sea water by diffusion across the sediment-water interface of organic-rich sediments and is the largest single sink of U in the global U budget (Schmoker, 1981; Klinkhammer and Palmer, 1991; Lüning and Kolonic, 2003). This process is more intense during euxinic conditions, when the water column is fully depleted in oxygen, and has the presence of free hydrogen sulfide (Anderson et al., 1989; Algeo and Maynard, 2004; Brumsack, 2006; Tribovillard et al., 2006). Since U is enriched in anoxic/euxinic sediments, it is therefore used as a proxy indicator of sediment deposition under such conditions (Figure 2) (Algeo and Maynard, 2004; Tribovillard et al., 2006).

Uranium has been a useful proxy for determining the organic-richness in shales through the use of the gamma-ray tool due to the response to the radioactivity given off from U and the relationship with highly organic sections of shale that tend to contain an abundance of U, however this approach would be problematic for zones that have a depleted amount of uranium, despite having high organic content, such as the Ohio Shale Group of Eastern Kentucky.

1.3 Molybdenum Geochemistry

Sedimentary Mo has been used in studies as a proxy for benthic redox potential. Molybdenum generally has a strong correlation to organic-richness in marine black shale facies that are deposited during oxygen-depleted conditions and is affected by the areal extent of bottom water anoxia (Emerson and Huested, 1991; Jones and Manning, 1994; Algeo and Lyons, 2006; Algeo, 2007). Under reducing conditions, the stable oxidation state of molybdenum is Mo (IV), while in the presence of H₂S, insoluble molybdenum sulfide complexes form, leading to an enrichment of Mo under euxinic conditions (Emerson and Huested, 1991; Tribovillard et al., 2006). Restricted basins generally exhibit lower concentrations due to rates of Mo uptake by the sediment surpassing the resupply rate of Mo by deepwater renewal (Emerson and Huested, 1991; Algeo et al., 2007; Algeo and Maynard, 2008). Deepwater Mo concentrations and renewal times are ultimately reflected by the rate of deepwater exchange relative to basin volume, which is strongly influenced by basin and sill geometry (Algeo et al., 2007).

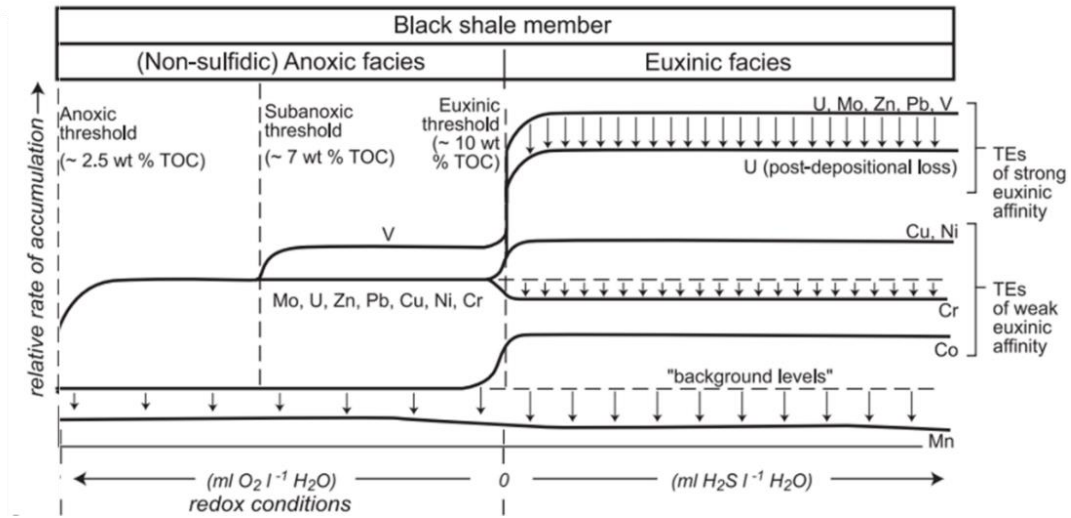


Figure 2. Redox threshold scale for trace metal enrichment, divided between anoxic (non-sulfidic) and euxinic (sulfidic) facies. Both U and Mo experience increased enrichment and preservation under euxinic conditions (Modified from Algeo and Maynard, 2004)

CHAPTER II

BACKGROUND

2.1 Acadian Orogeny

The Acadian Orogeny (411-315 Ma) developed as a product of oblique convergence along a large strike-slip fault zone between the Laurussian and Avalon terrane (Ettensohn, 1987). Throughout the Devonian, widespread deposition of thick intervals of black and gray shales were deposited across many parts of present-day North America. Throughout the Late Devonian (Famennian), the regionally extensive Huron and Cleveland Shale Members of the Ohio Shale Group were deposited within the Appalachian Basin (Ettensohn, 1987). The Ohio Shale is age-equivalent to other Upper Devonian shales such as the New Albany (Illinois Basin), the Antrim (Michigan Basin), Chattanooga (Tennessee), and the Woodford (Oklahoma). During the time of deposition, Kentucky was divided between the Illinois Basin, Cincinnati Arch, and the Appalachian Basin and roughly two thirds of Kentucky is underlain by Devonian strata (Nuttall, 2005). Five major tectonic depositional cycles of fine- to course-grained sediment occurred throughout the Devonian Acadian tectophase, each cycle beginning with rapid subsidence within the basin (Ettensohn, 1987).

2.2 Eustatic influences and basinal restriction

Eustasy plays a significant role in restricted or silled marine basins; an overall fall of eustatic level would result in further restriction of the basin setting due to lowered water depths over a basin's marginal sills, while on the other hand a rise in eustatic levels would increase water depths of a basin's marginal sills thus increasing inflow and outflow of surface waters (Algeo and Lyons, 2006; Algeo and Rowe, 2012). Sill variability impacts organic carbon and deepwater redox conditions by limiting the inflow of nutrient-rich waters into a basin setting. As an example, in the Cariaco Basin during a glaciation event (~16 - 6 kyr B.P.), the marginal sills of the basin were deepened and an influx of nutrient-rich intermediate waters stimulated primary productivity and deepwater anoxia ensued (Haug et al., 1998; Yarincik et al., 2000). The Devonian Ohio Shale group provides a case study of the relationship of eustasy to basinal restriction and trace metal accumulation patterns. Throughout the Devonian, the Appalachian Basin was in communication between the Michigan and Illinois basins as well as the Rheic Ocean across shallow marginal sills (Figure 4) (Algeo and Maynard, 2008; Algeo and Rowe, 2012). Overall, eustatic elevations were rising through the Middle and Late Devonian, followed by a significant short-term eustatic falls at the Frasnian/Famennian boundary and the Devonian-Carboniferous boundary (Figure 3) (Johnson et al., 1985; Pashin and Ettensohn, 1995). These eustatic falls are linked to an episode of continental glaciation in South America (Isaacson et al., 2008) and a piedmont glaciation in Laurussia (Pashin and Ettensohn, 1995; Brezinski et al., 2008; Ettensohn et al., 2020). Glaciation in Cleveland seas was made evident by a large granitoid boulder that was embedded in the upper section of the Cleveland Shale in northeastern Kentucky (Lierman and Mason, 2007; Ettensohn et al., 2007; Ettensohn et al., 2020).

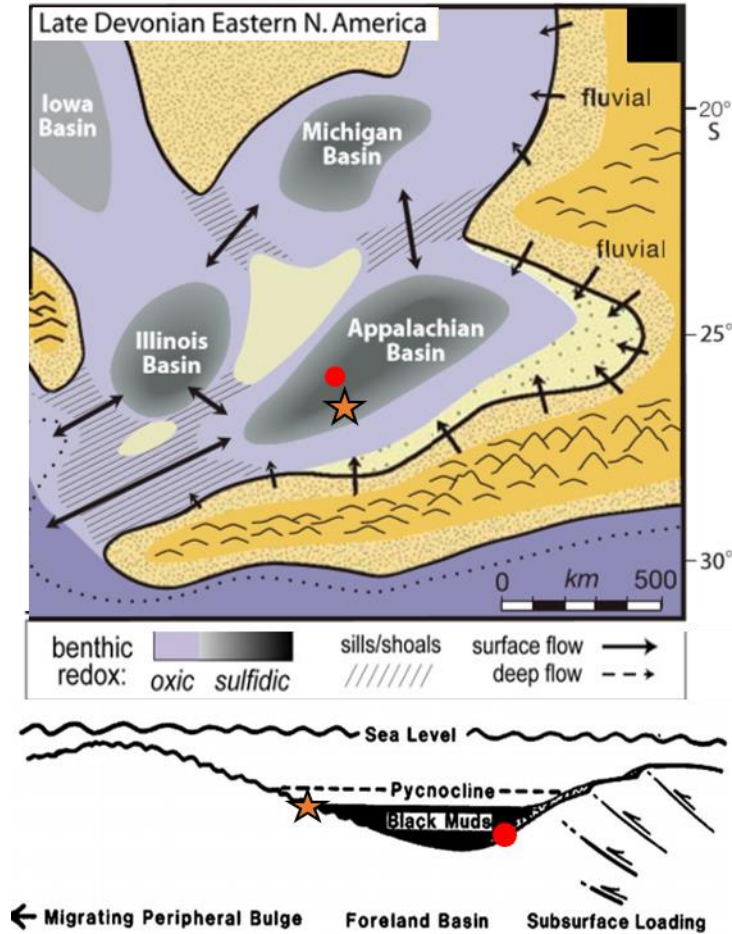


Figure 3. Paleogeography of eastern North America in the Late Devonian (~360 Ma) showing marginal sills and Appalachian Basin in relation to surrounding basins and the Rheic Ocean. Location designated with the orange star illustrates an estimated location of the well for this study: Well 566765 Letcher County, KY. Location designated by a red circle indicates a deeper basin setting from previous studies such as Algeo and Maynard, 2008. (modified from Ettensohn, 1997; Algeo and Maynard, 2008).

2.3 Study Area

This study is focused on the Late Devonian Ohio Shale of eastern Kentucky within the central Appalachian Basin. The Devonian Ohio Shale Group of the western Appalachian Basin has been an economic gas resource for Kentucky due to the group's organic richness. The early division of the Ohio Shale was originally based off outcrop samples, well cuttings, and gamma-ray logs (Lewis and Schwietering, 1971; Provo et al., 1978). In eastern Kentucky, the Cleveland

and Huron members are black to dark gray shales that are divided by the gray to greenish gray silty-shale Three Lick Bed and overlain by the Berea Sandstone and Bedford shale.

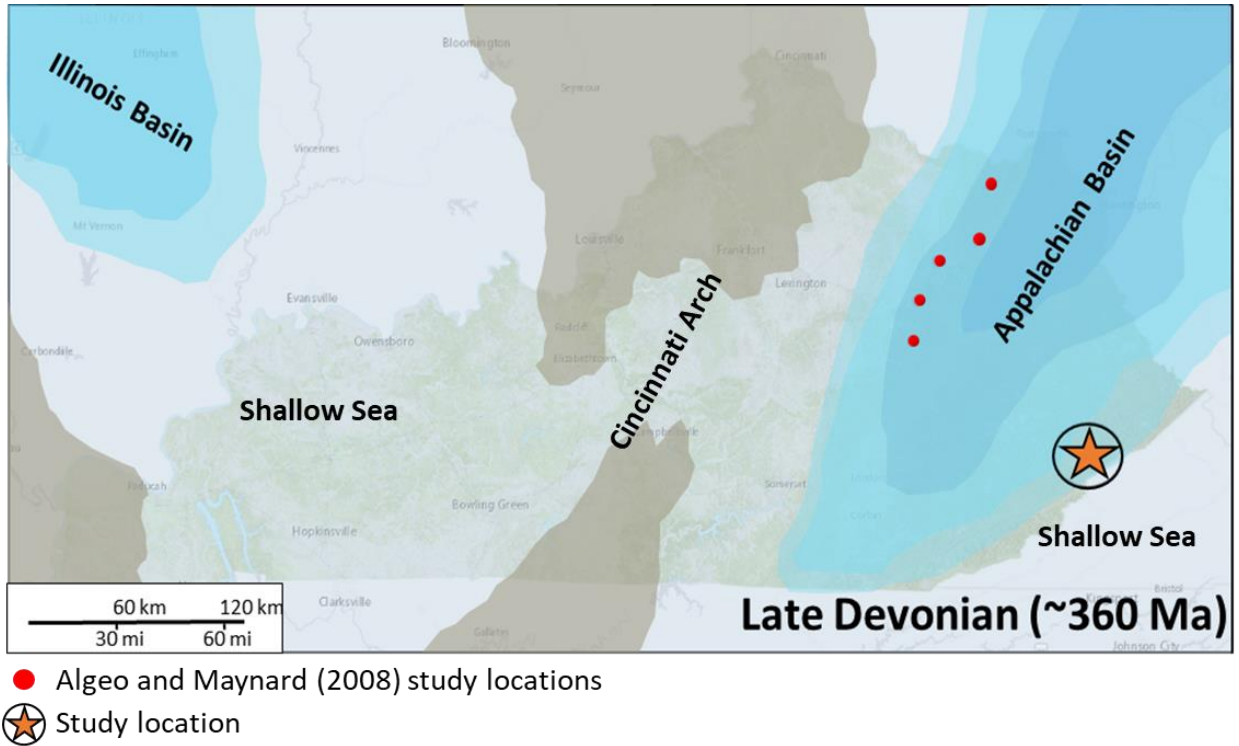


Figure 4. Paleogeography of Kentucky displaying the location of Well 566765 (orange star and circled in black) in Letcher County, KY, the well used for this study. Displayed in red are the estimated locations of the study locations used in Algeo and Maynard (2008) study. Paleoreconstruction based off Blakey (2013).

2.4 Stratigraphic Framework

In eastern Kentucky, the Famennian Ohio Shale is the stratigraphic interval that resides above the marine Olentangy Shale, and below the fluvial Bedford Formation and the Berea Sandstone sequence (Figure 5). The Ohio Shale Group has two carbonaceous black shale sequences, the Huron and Cleveland Shale members that are separated by a westward thinning tongue of gray-to dark gray silty-shale of the Chagrin Member (Lewis and Schwietering, 1971;

Schwietering, 1979; Hohn et al., 1980; Roen, 1980; Roen, 1984). Due to the extensiveness of Late Devonian black shale deposition, these units have been used as a regional stratigraphic reference.

The Cleveland Shale Member is the uppermost unit of the Ohio Shale Group. Based off of a well log from Well 566765 from Letcher County, KY, the average gamma ray across the 23 m (75 ft) thick Cleveland Shale interval is ~220 API. According to a thesis by Otto (2015), the average TOC of the Cleveland Shale in eastern Kentucky is 6.1 wt. %; this average includes the lower portion of the Cleveland that has significantly lower TOC levels, reaching a TOC of 9.4 wt.% (Otto, 2015). The Cleveland Member of the Ohio Shale Group has been correlated from eastern Kentucky into West Virginia and to the north into Ohio and has equivalent age and nomenclature across the Appalachian Basin. The Cleveland Member was deposited parallel to strike of the paleo-slope of the Appalachian Basin in a north-south direction from Ohio, through eastern parts of Kentucky, and into Tennessee (Schmoker, 1981; Pashin and Ettensohn, 1995).

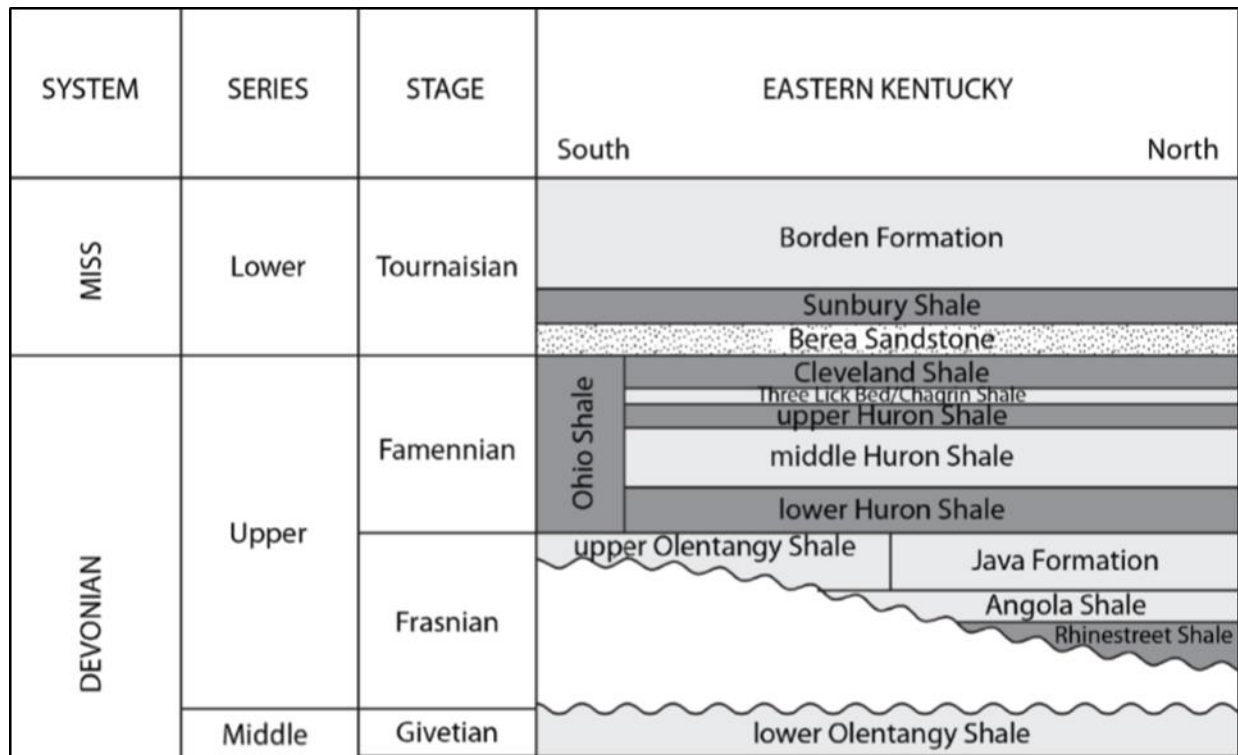


Figure 5. Stratigraphic column for Eastern Kentucky Devonian and Mississippian system tracts (From Repetski et al., 2008).

The Three Lick Bed consists of three greenish-gray shale beds separated by fissile, brownish to black shale units and is correlated to the Chagrin Shale Member and has been used as a widespread marker bed via gamma-ray log across states of Ohio, Tennessee, and into Indiana through correlative beds (Provo et al., 1977). Characteristics of the Three Lick Bed include burrows that are both horizontal and vertical, some that are filled with pyrite (Provo et al., 1977). Due to the presence of pyrite-filled burrows within the unit, the Three Lick Bed was likely deposited during a period of oxygen-rich bottom waters that allowed for the presence of oxygen-dependent organisms. The Three Lick Bed in Letcher County, KY displays a gamma ray response of 200-250 API and is 17.4 meters (57 ft) thick. According to Otto (2015) from a study on a nearby well, the Chagrin of his investigation has TOC averages at 0.8 wt.%.

The Huron Members exist as two black shale intervals of the Upper and Lower Huron, and are divided by a gray silty-shale facies of the Middle Huron. The Huron Member within the Ohio Shale Group is one of the thickest, most extensive, and most prolific black shale hydrocarbon reservoirs in the Appalachian Basin, spanning from western New York, through eastern Kentucky, and into Tennessee (Roen, 1984). The Huron Members range from low to moderate to high TOC. The Upper Huron is a black to dark gray organic rich shale. In Well 566765, the Upper Huron displays an average gamma ray of 280 API and is 44 feet thick. According to Otto (2015), the average TOC for the Upper Huron is 3.1 wt.%. The Middle Huron is a light to dark gray siltstone. In Well 566765, the Middle Huron has an average gamma ray response of 225 API and is 67.7 m (222 ft) thick. The average TOC across this interval is 1.5 wt.% (Otto, 2015).

In comparison to the Cleveland interval, the Lower Huron Member of the Ohio Shale Group has significantly higher gamma-ray signatures and displays the characteristic linear relationship between uranium and TOC preservation (Figure 5). Based off well logs for well 566765, the Lower Huron interval is 37.8 m (124 ft) thick and the average gamma ray across the interval is 400 API. The average TOC of the Lower Huron according to the Otto study of a nearby well is 5.7 wt.%, which is similar to the TOC of the Cleveland interval, despite the depletion of U and thus lower gamma ray response (Otto, 2015).

The Cleveland Shale in Ohio and parts of Kentucky displays a much lower gamma response in comparison to the Lower Huron, yet has a relatively high total organic carbon content. The particular well that was sampled is in Letcher County, Kentucky. This study site is southwest of the well used in Otto (2015), and south-southeast of the wells used in Algeo and Maynard (2008). Samples were gathered from the overlying Lower Mississippian-age Berea

Sandstone as well as the Devonian-age Cleveland, Three Lick Bed, and Lower Huron Members in order to assess the climatic differences during this period of time. Based off of previous core descriptions and with respect to the other members of the Ohio Shale Group, the uppermost member, the Cleveland Shale, exhibits high organic carbon content despite the suppressed gamma response.

CHAPTER III

METHODOLOGY

3.1 Sampling

The research analyzes well core samples from Letcher County, Kentucky (well record number 566765) (Carter Coordinates: 8-I-82 1125N, 1170E). Well 566765 has a completed drilling date of December 10th, 2007 with a vertical depth of 1380 m (4,526 ft). The cored interval of this well is from 1134-1354 m (3720-4441 ft), which is 220 m (721 ft) of core. The cored unit contains the Ohio Shale Group which is subdivided into the Lower Huron, Middle Huron, Upper Huron, Three Lick Bed, and Cleveland shale members.

Sixty rock core samples were collected at a sampling rate of 1 sample per 5 feet (1.5 meters) from the Berea Sandstone, Cleveland, the Three Lick Bed, and Lower Huron members of the Ohio Shale group (Figure 6) in order to assess the differences in trace metal accumulation during the Devonian and into the beginning of the Mississippian. This rock core provided 3 samples for the Berea Sandstone, 17 samples for the Cleveland Shale, 6 samples for the Three Lick Bed, and then 34 samples were taken from the Lower Huron Shale unit. The sampled well is located southwest of the study site discussed by Otto (2015) and southeast of the study areas

investigated by Algeo and Maynard (2008) (Figure 4). The cored well for this investigation had portions of missing core, specifically in the Upper and Middle Huron Shale units of the Ohio Shale Group, which allowed for higher resolution sampling of the intervals of interest. The intervals of interest were primarily the Cleveland and Lower Huron shales. A significant amount of pyrite was observed throughout the Lower Huron Unit I and II, however pyrite was not included in sampling. Writing and markings were present on the outside of the core, thus samples were taken from the inner portion of the core to avoid potential contamination.

3.2 Geochemical Analyses

Samples were crushed and homogenized with a ball mill using a tungsten carbide vial and then divided into two splits and stored in Teflon vials. One split was used to measure total carbon (TC) and total inorganic carbon (TIC) content with a Carbon Sulfur Analyzer (Eltra CS-2000) at Oklahoma State University in order to calculate total organic carbon (TOC). Samples that were used to measure TC were weighed on ceramic boats and then transferred into a horizontal resistance furnace for combustion within the analyzer. Typical analysis time for total carbon (TC) is 60 to 180 seconds depending on the sampling material. Corresponding samples that were used to measure total inorganic carbon (TIC) were measured in the induction furnace of the carbon sulfur analyzer. During the measurements of total carbon and total inorganic carbon, several samples were duplicated in order to maintain confidence in data and to detect any potential drift in data within the analyzer.

The measurement for TOC was estimated using the calculation:

$$\text{Total Carbon (TC)} - \text{Total Inorganic Carbon (TIC)} = \text{Total Organic Carbon (TOC)}$$

The second sample split was ashed at 900°C for 8-10 hours in order to remove all organic material followed by a three-acid heat and pressure digestion using trace metal grade acids: 3 mL nitric (HNO₃), 2 mL hydrochloric (HCl) and 2 mL hydrofluoric (HF) using a pressure and temperature digestion system (PicoTrace) until fully digested. This digestion process consisted of a five phase heating program from 70°C up to 190°C, heating up no faster than 50°C/hour, and then maintained that maximum temperature of 190°C for 5 hours in order to assure complete digestion. Samples were then placed back on the heat plate and evaporated until dry. The evaporation process consists of a six phase program starting at 20°C up to 170°C and then maintaining that maximum temperature for 2.5 hours. The evaporated samples within the Teflon canisters were then removed from the heat plate, and checked for complete sample evaporation. The dried samples were treated with 5% trace metal grade nitric and returned back to the heat plate for approximately 60 minutes to fully dissolve. The dissolving process consisted of a program ranging from 40°C up to 60°C. Each dissolved sample was subjected to 1 mL of 50% nitric and 9 mL of Mili-Q reference water. Samples then underwent a 30-fold dilution with 2% trace metal grade nitric acid.

The diluted samples were analyzed using a ThermoScientific iCapQc inductively coupled plasma-mass spectrometer (ICP-MS) at Oklahoma State University in order to measure trace metal concentrations such as uranium (U), molybdenum (Mo), vanadium (V), nickel (Ni).

Standard reference material USGS SDO-1 was measured alongside the investigation samples in order to establish analytical accuracy in the assessment of organic-rich Ohio Shale Group.

Analytical accuracy from the standard reference material USGS SDO-1 has a margin of error of 3.47% for U and 5.30% for Mo, which are well within the USGS accepted margins of error.

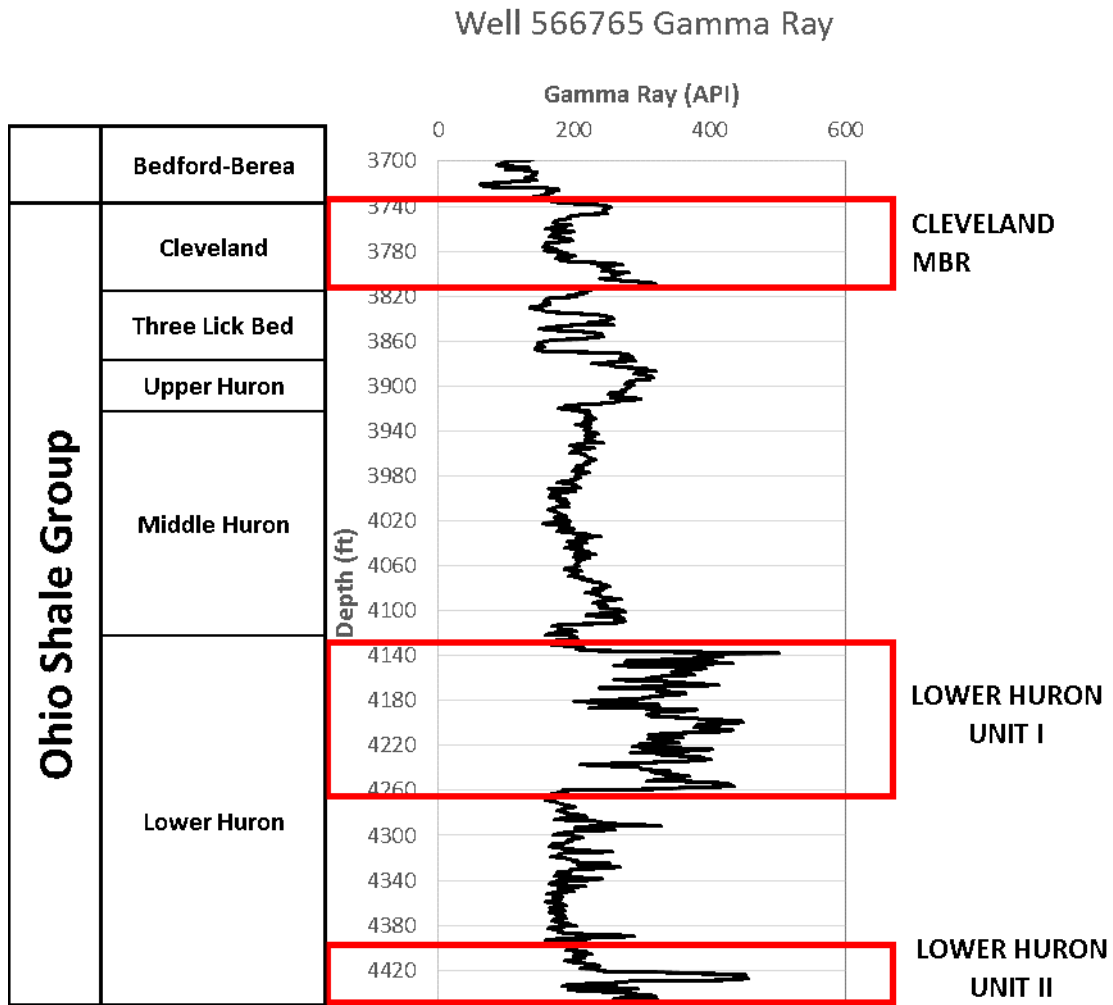


Figure 6. Gamma-ray log for Well 566765, Letcher County, Kentucky. Intervals that are boxed in red are the Cleveland, and Lower Huron Units I and II in which trace element (TE) data and total organic carbon (TOC) data were recorded.

CHAPTER IV

RESULTS

Results of elemental concentrations for molybdenum (Mo), uranium (U), as well as total organic carbon (TOC) were measured and shown below along with general core descriptions. A table with averages of data used in this study for each stratigraphic unit is available in Table 1. Tables with all other geochemical data and core descriptions are located in the Appendix section (Tables A1 and A2).

4.1 Geochemical Results and Core Description: Lower Huron Shale Unit II

The Lower Huron Shale Unit II is characterized as a dark gray to black shale with frequent pyritization. Pyrite frequency and thickness of pyrite bedding increased towards the base of the observed interval. At the base of the observed section, a significant burrow (~2.5 cm thick) occurs in black shale. This burrow pyritized.

Uranium values range from 1.3 ppm to 37.3 ppm. The average U values for this interval is 8.9 ppm. Molybdenum values for the Lower Huron Shale Unit II range from 1.7 ppm to 190.4 ppm. The average Mo value for this interval is 36.6 ppm. Total organic carbon values range for the Lower Huron range from 0.1 wt.% to 8.5 wt.%, and average to 2.1 wt.%. The average value for the U/TOC ratio across the Lower Huron Shale Unit II interval is 9.1. The Mo/TOC ratio of the Unit II interval is 18.2. The Lower Huron Unit II interval is low in U and TOC.

4.2 Geochemical Results and Core Description: Lower Huron Shale Unit I

The Lower Huron Shale Unit I is characterized as a dark gray to black shale occasional interbedding of gray shale, with sparse sections of pyrite laminae. Pyrite nodules and laminae were noted throughout the whole Unit I interval, as well as pyrite-filled fractures. During geochemical analysis, pyrite was not included in sampling. No marine fossils or evidence of burrowing were observed in the Lower Huron Unit I interval.

Uranium values range from 5.8 ppm to 34.1 ppm. The average U values for this interval is 20.5 ppm. Molybdenum values for the Lower Huron Shale Unit I range from 16.9 ppm to 144.8 ppm. The average Mo value for this interval is 83.3 ppm. Total organic carbon values range for the Lower Huron Shale Unit I range from 0.7 wt.% to 8.5 wt.%, and average to 4.8 wt.%. The average value for the U/TOC ratio across the Lower Huron Shale Unit I interval is 5.2, and the average Mo/TOC ratio is 18.4. The Lower Huron Shale Unit I is very high in U and TOC relative to the other observed units.

4.3 Geochemical Results and Core Description: Three Lick Bed

The Three Lick Bed interval is observed to consist of green to brown shales with interbedded thin gray siltstones. No shelly marine fossils or evidence of burrowing were observed in the cored interval. The presence of the Three Lick Bed provided a useful marker bed in between the Cleveland and Lower Huron units.

Moving into the Three Lick Bed interval, there is a large decrease in uranium concentration. Uranium for this interval ranges from 1.3 ppm to 8.7 ppm and averages at 3.8 ppm. Molybdenum values for the Three Lick Bed interval ranges from 0.5 ppm to 19.8 ppm and averages at 18 ppm. Total organic carbon values for the Three Lick Bed range from 0.5 wt.% to 4.8 wt.% with an average of 1.5 wt.%. The average value for the U/TOC ratio across the Three Lick Bed interval is 3, and the average Mo/TOC ratio is 20.3. The Three Lick Bed interval is low in U and TOC.

4.4 Geochemical Results and Core Description: Cleveland Shale Member

The Cleveland Shale is characterized as a dark brown to black clay shale with thin interbedding of thin dark gray to light gray siltstones. Gray interbedding ranged from a 1-2 cm

to as large as approximately 10 cm, with an increasing frequency and thickness of interbedding at the base of the Cleveland interval. Increasing thin pyrite laminae occurs at the base of the Cleveland interval, along with the presence of a small pyrite nodule within the last meter of the Cleveland interval. Marine invertebrate fossils were not apparent in hand sample and burrowing or post-depositional alterations were not observed.

Uranium values range from 4.6 ppm to 22.9 ppm. Throughout the sampled interval, the average value for U is 12.3 ppm. Molybdenum (Mo) values range from 2.9 ppm to 84.8 ppm. The average Mo values for the Cleveland Shale interval is 52.5 ppm. Total organic carbon values for the Cleveland Shale interval ranges from 1.5 wt.% to 5.4 wt.%. Average TOC for this interval is 3.8 wt.%. The average value for the U/TOC ratio across the Cleveland Shale interval is 3.3, and the average Mo/TOC ratio is 13.51. Throughout the Cleveland interval, the concentration of U is relatively stable. The Cleveland Shale interval is moderately high in U and TOC relative to the other observed intervals of the Ohio Shale Group.

4.5 Geochemical Results and Core Description: Berea Sandstone

The Berea Sandstone is dominantly dark gray to brown siltstone with interbedded fine- to medium-grained sandstone with possible pyrite. Sampled sections were found to be unfossiliferous and did not have the presence of any burrowing.

Uranium (U) values for this interval range from 3.8 ppm to 7.0 ppm. The average U values for the Berea Sandstone is 5.1 ppm. Molybdenum (Mo) values for the Berea Sandstone range from 14.5 ppm to 41.8 ppm with an average value of 24.1 ppm. Total organic carbon (TOC) values range from 2.4 wt.% to 7.9 wt.% and average at 4.5 wt.%. The average value for the U/TOC ratio across the Berea Sandstone interval is 1.33, and the average Mo/TOC ratio is 5.51. The Berea Sandstone interval is relatively high U and TOC.

Table 1. Comparison of the average TOC, U, Mo, U/TOC and Mo/TOC for Berea Sandstone, Cleveland Shale, Three Lick Bed, and Lower Huron Shale Units I and II.

Stratigraphic Unit	TOC Avg.	U Avg.	Mo Avg.	U/TOC	Mo/TOC
	wt. %	ppm	ppm		
Berea Sandstone	4.5	5.1	24.1	1.33	5.51
Cleveland Shale	3.8	12.3	52.5	3.30	13.51
Three Lick Bed	1.5	3.8	18.0	3.00	20.30
Lower Huron Shale Unit I	4.8	20.5	83.3	5.20	18.37
Lower Huron Shale Unit II	2.1	8.9	36.6	9.07	18.19

CHAPTER V

DISCUSSION

In many typical Devonian black shales across North America, such as the Woodford and Antrim shales, there is a general understanding that gamma-ray response to the radioactivity of uranium has a strong correlation to organic richness within shales (Schmoker, 1981; Lüning and Kolonic, 2003). However, throughout the Cleveland Shale and parts of the Lower Huron interval there exists a decoupling of U and TOC (Figure 8). Within the Lower Huron Unit II, U and TOC have a positive correlation of $r=0.91$, and the Lower Huron Unit I has a relatively strong positive correlation of $r=0.75$ (Figure 8). However, the Cleveland Shale interval exhibits a positive but moderate correlation of $r=0.50$. Within the upper portion of the Cleveland Shale interval is a decoupling of U and TOC between 1150-1140 m. Throughout this interval, U concentration is low for a black shale and remains relatively stable until the end of the interval where there is an increase in concentrations of U and Mo, implying greater drawdown of these trace metals. Throughout the middle stages of the Cleveland, TOC gradually increases and does not have a strong correlation with the U profile (Figure 7). This disconnect could be tied to

increased deepwater restriction due to a lowering of sea level during climatic cooling and ice sheet formation in the Southern Hemisphere (Streel et al., 2000), resulting in the shallowing of silled margins and a restricted supply of trace metals from the open Rheic Ocean to the Appalachian Basin, which would also affect the resupply rate of nutrients that provide for the production of organic matter (Johnson et al., 1985; Pashin and Ettonsohn, 1995; Algeo et al., 2007; Algeo and Maynard, 2008).

Location within a basin, such as deep within the basin or on the basin margin, plays a significant role in the accumulation of trace elements due to potential variation in the location of the pycnocline (Algeo and Rowe, 2012; Formolo et al., 2014). In cored locations that are thought to be within the basin margin setting, such as the study well, it is more likely that this environment would be more susceptible to geochemical alterations due to a shifting pycnocline than that of a core that is located in a deeper, more stable setting (e.g. Lyons et al., 1993; Formolo et al., 2014). In a deeper basin setting, redox conditions are likely to be more stable, whereas the basin margin may experience fluctuations in redox conditions based on the location of the pycnocline. The result of fluctuations in pycnocline location on the basin margin trace metal profiles has been observed in shifting trace metal signatures in other locations (Figures 7, 8) (e.g. Lyons et al., 1993; Formolo et al., 2014). The high variability of U in shale is evident in the Cleveland Member, where U content ranges from 4.64 ppm up to 22.87 ppm (Figure 9). Similar variability within data is also shown in the Lower Huron Unit I ranging from 5.77 ppm to 34.07 ppm; and Unit II ranging from as low as 1.30 ppm to 37.27 ppm. This high trace metal U variability on the basin margin is influenced by sea level fluctuating throughout the Famennian stage during the deposition of the Ohio Shale Group, impacting location of the pycnocline and degree of sill between the Appalachian Basin and surrounding basins and the Rheic Ocean

(Johnson et al., 1985; Algeo and Maynard, 2008; Algeo and Rowe, 2012). Due to the redox-sensitivity of U and other trace metals, post-depositional alteration due to changes in bottom water redox conditions may change the oxidation state of metals like U and result in the release of U back into the water column (Abshire et al., 2020). Post-depositional oxidation may result in sediments in the geologic record that are enriched in organic carbon without the enrichments of redox-sensitive trace metals such as U and Mo (Abshire et al., 2020). Unlike other studies that have looked into the Cleveland Shale of Kentucky (e.g. Algeo and Rowe, 2012), Well 566765 provides four general trends present within the Cleveland member. Overall, the variability within U and TOC along the marginal setting of the Appalachian Basin is not only limited to the Cleveland. For example, within the Lower Huron Unit I and II are six major trends that have been established for this study (Figure 7). These U concentration variations during the Late Devonian signify long periods of restriction that resulted in extended periods of deepwater residence times (Algeo et al., 2007; Algeo and Tribovillard, 2009).

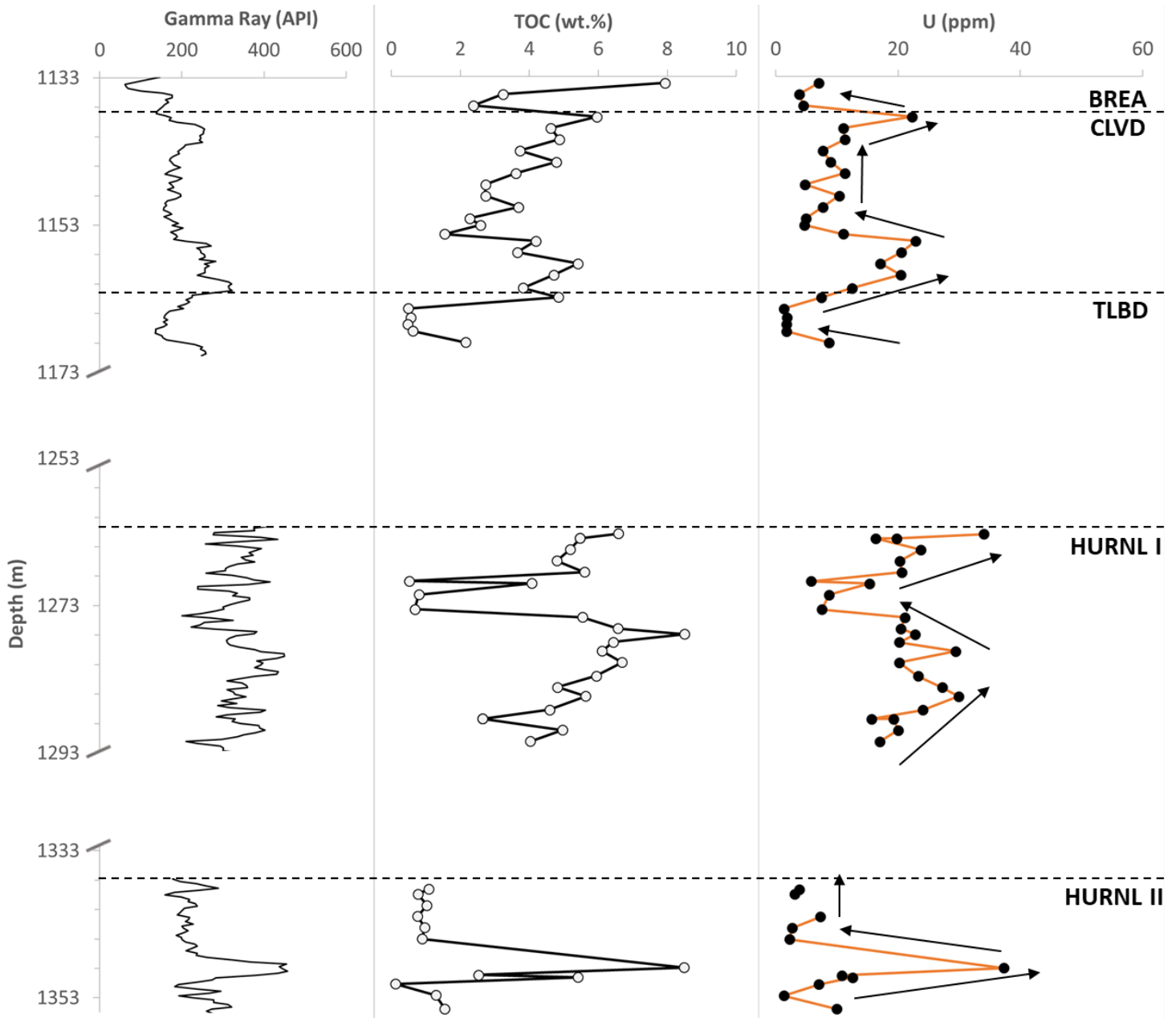


Figure 7. Gamma-ray, total organic carbon (TOC), and trace metal content uranium (U) data from cored Well 566765 from Letcher County, Kentucky. Trace metal measurement U are represented by the orange line with general data trends labeled by black arrows. Dotted Lines divide conventional stratigraphic units. BREA = Berea Sandstone, CLVD = Cleveland Shale, TLBD = Three Lick Bed, HURNL I = Lower Huron Unit I, HURNL II = Lower Huron Unit II. Diagonal line with blank along y-axis indicates a significant jump in depth. Gamma-ray data courtesy of the Kentucky Geological Survey.

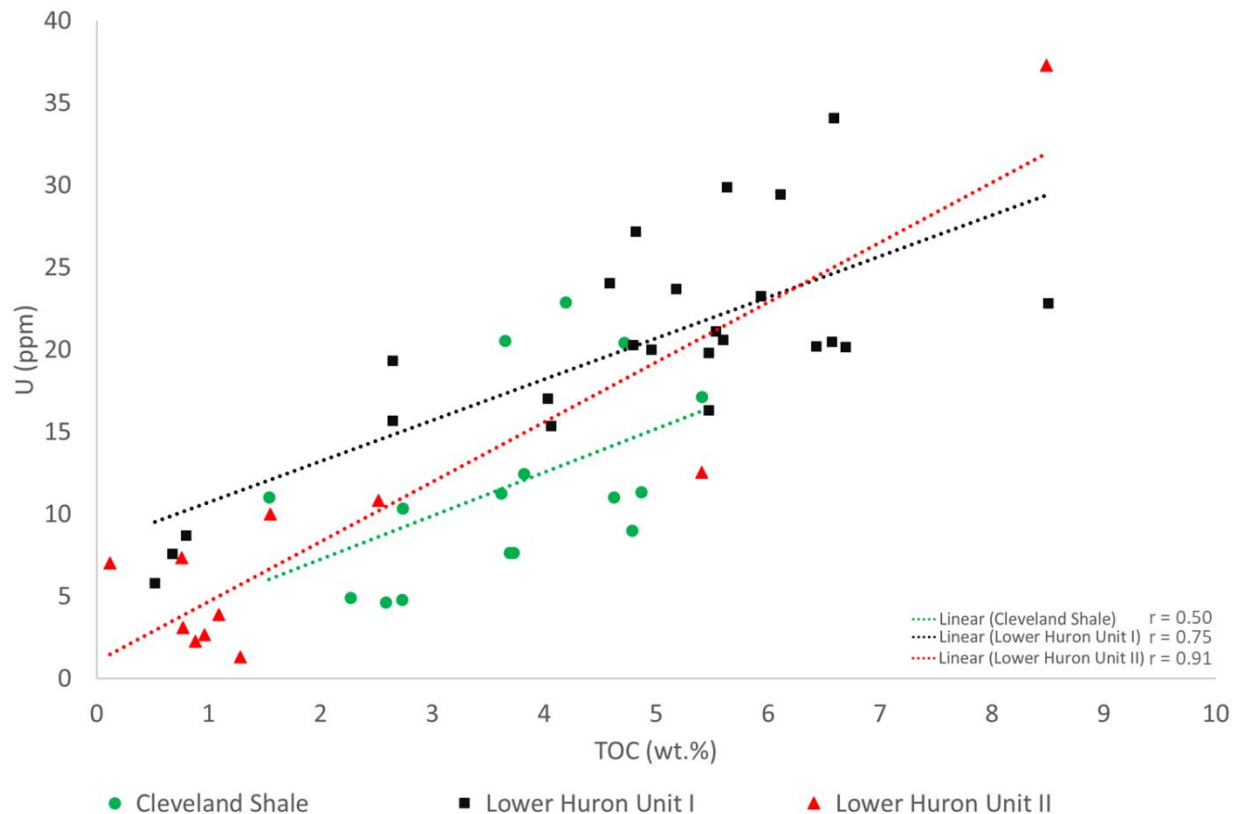


Figure 8. Trace metal content uranium (U) plotted against total organic carbon (TOC) for the major study intervals for this study: the Cleveland Shale, and Lower Huron Units I and II. Trend lines for the study intervals shown to distinguish trends in data. Pearson correlation coefficient (r) values displayed to show the difference between selected shale units, with a typical, organic-rich Devonian black shale having a strong correlation value close to $r = 1.0$.

Based on the molybdenum (Mo) content of the Ohio Shale Group, general trends throughout the entire dataset have similar shifts in U and Mo, although shifts in Mo concentration are much more drastic than the shifts in U content (Figure 9). This similarity between U and Mo is not unexpected, as both U and Mo are enriched under anoxic-euxinic conditions. Molybdenum in the sediment reflects the availability of trace metal Mo in the watermass, so when bottom waters are well connected during less restrictive conditions, the concentration of Mo will be high (Algeo and Lyons, 2006; Algeo and Maynard, 2008). The Mo

proxy data shows that at the time of the Lower Huron Unit II deposition, the Appalachian Basin ranged from a semi-restricted to restricted basin with non-static bottom water conditions, with a majority of concentrations for this interval not exceeding 50 ppm, while some samples show extraordinarily high Mo enrichment values that are also supported by enrichments in TOC and U, indicating that basin geometry fluctuated between semi-restrictive to restrictive (Figure 9) (Robl et al., 1983; Algeo et al., 2007). This contrast in trace metal concentration in the upper and lower sections compared to the middle section of the Lower Huron Unit II is likely due to post-depositional re-oxygenation, which would drastically decrease the concentration of trace metal Mo and U seen in the upper and lower sections (e.g. Abshire et al., 2020). The introduction of oxygen can be attributed to burrowing organisms based on the observed bioturbation in the lower portions, and increased frequency of interbedded gray siltstones in the upper sections of the Lower Huron Unit II interval (Figure 9). Molybdenum content of the Lower Huron Unit II suggests that the Appalachian Basin became increasingly restricted and anoxic-euxinic throughout the beginning of the Famennian stage, as indicated by a majority of concentrations not exceeding 50 ppm, with a brief interval of high concentrations that signify a period of increased circulation of bottom waters (Figure 9). Molybdenum content of the Lower Huron Unit I interval indicates that the Appalachian Basin developed into a mostly semi-restricted basin, shown by an overall enrichment of Mo as a result of increased circulation between nearby basins and the open ocean in comparison to the Lower Huron Unit II interval (Figure 9) (Robl et al., 1983; Algeo et al., 2007). Our Mo proxy data show that deepwater conditions along the Appalachian Basin margin during the lower Cleveland Shale interval were anoxic-euxinic, as concentrations exceed 50 ppm and up to 104 ppm (Figure 9). Depositional settings became increasingly restrictive and anoxic/euxinic conditions continued throughout the

middle and upper Cleveland deposition, as Mo values are decreased to below 50 ppm and remain low until the end of the Cleveland interval (Figure 9). Molybdenum data suggest that there was a brief resupply of trace metals into the basin at the end of the Cleveland, with a large input of Mo to ~105 ppm at the Cleveland-Berea Sandstone boundary (Figure 9).

Before and during the deposition of the Lower Huron at the Frasnian/Famennian boundary, eustatic fall occurred, resulting in further restriction of the Appalachian Basin (Johnson et al., 1985; Pashin and Ettensohn, 1995; Algeo et al., 2007; Algeo and Rowe, 2012). Within anoxic silled basins, such as the Late Devonian Appalachian Basin, large-scale deepwater renewal tends to have an initial rapid increase in sedimentary Mo concentrations that are later followed by a trend toward lower Mo and high TOC values (Figure 9, Figure 10) (Algeo and Lyons, 2006). The ratio of Mo/TOC in the sediment reflects the availability of trace metal Mo in the watermass; when bottom waters are well connected to an open system of water, the Mo/TOC ratios are high (Algeo and Lyons, 2006). Mo/TOC ratio data for this study suggests that the Lower Huron Units I and II were not strongly restricted at the time of deposition, with a ratio between 10 and 25 for a majority of the sampled intervals, indicating a semi-restricted environment throughout the Lower Huron (Figure 9) (Robl et al., 1983; Algeo and Lyons, 2006; Algeo et al., 2007). The Mo/TOC ratios suggest that the eustatic fall decreased the degree of sill on the basin, further restricting it resulting in lowered Mo/TOC ratios to ~10, but slowly rebounded to values of ~16-19 throughout the middle Lower Huron as sea level continued to rise (Figure 9) (Johnson et al., 1985; Algeo et al., 2007; Algeo and Rowe, 2012). The Appalachian Basin continued to be semi-restricted with surrounding basins and the open Rheic Ocean as sea levels continued to rise, increasing cyclicity of deepwater renewal, thus increasing Mo/TOC ratios to ~20-25 in the upper Lower Huron Unit I interval (Figure 9). A large eustatic fall at the

Devonian/Carboniferous boundary occurred during the deposition of the upper Cleveland Shale (Pashin and Ettensohn, 1995; Algeo et al., 2007; Algeo and Rowe, 2012). This eustatic fall during the upper Cleveland Shale lowered the Mo/TOC ratio to values to below 11, indicating further but not complete restriction and slowing the renewal of trace metals into the watermass in the Appalachian Basin (Figure 9, Figure 10). This restriction of the Appalachian Basin during Cleveland time was fairly stable, as most Mo/TOC ratios at this interval do not fluctuate above ~11. During the deposition of the Cleveland Shale, the Appalachian Basin became further restricted as sea level continued to fall, with a momentary shift in U, Mo, and TOC values at the boundary between the upper Cleveland Shale and the Bedford-Berea Sandstone boundary (Figure 9).

The eustatic fall during the Cleveland Shale interval increased the degree of restriction of the Appalachian Basin, however according to the U, Mo, and TOC data, conditions along the basin margin where the study site for this investigation is located was not completely restricted. Uranium and molybdenum data suggest that bottom water conditions and the availability of these trace metals in the water column remained fairly consistent throughout the middle to upper Cleveland interval (Figure 9). However, this was not evident in the TOC data. After the initial eustatic event at the beginning of the Cleveland interval, the amount of organic carbon gradually increased from less than 2 wt. % up to a maximum of 6 wt. % at the end of the Cleveland interval (Figure 9). The conundrum between TOC and trace metal U and Mo in the Cleveland interval is impacted by a fluctuating location of the pycnocline as a result of sea level change, as well as the remobilization of trace metals as a result of post-depositional oxidation due to dissolved oxygen (e.g. Jaminski, 1997; Jaminski et al., 1998). This discrepancy could also be linked to a global decrease of U and Mo that coincides with a trend toward generally more

reducing conditions, resulting in the drawdown of these dissolved trace metals during the Late Devonian and a weaker correlation to TOC (Algeo, 2004; Algeo and Maynard, 2008). It is also possible that glacial dilution in the Cleveland seas could result in the observed conundrum between TOC and trace metal accumulations. Recent work suggests that glaciers may be major resources of terrestrial nutrients and dissolved organic matter through glacier meltwater, stimulating organic productivity (Syvitski et al., 1990; Hood et al., 2009, Martínez-García et al., 2014; Ettensohn et al., 2020). The introduced meltwater would likely cause a dilution of, or mixing with, the seawater trace metal composition, especially near the basin margins, thus strongly impacting the redox-sensitive metals (e.g., Herbert et al., 2020). Furthermore, increasing watermass restriction due to eustatic fall during Cleveland deposition resulted in the shallowing of silled margins and limited the circulation of deep waters from surrounding water masses into the Appalachian Basin, further limiting the availability of Mo and U and potentially exposing previously anoxic sediments to oxygenated waters (Jaminski, 1997; Jaminski et al., 1998; Algeo and Maynard, 2008; Abshire et al., 2020).

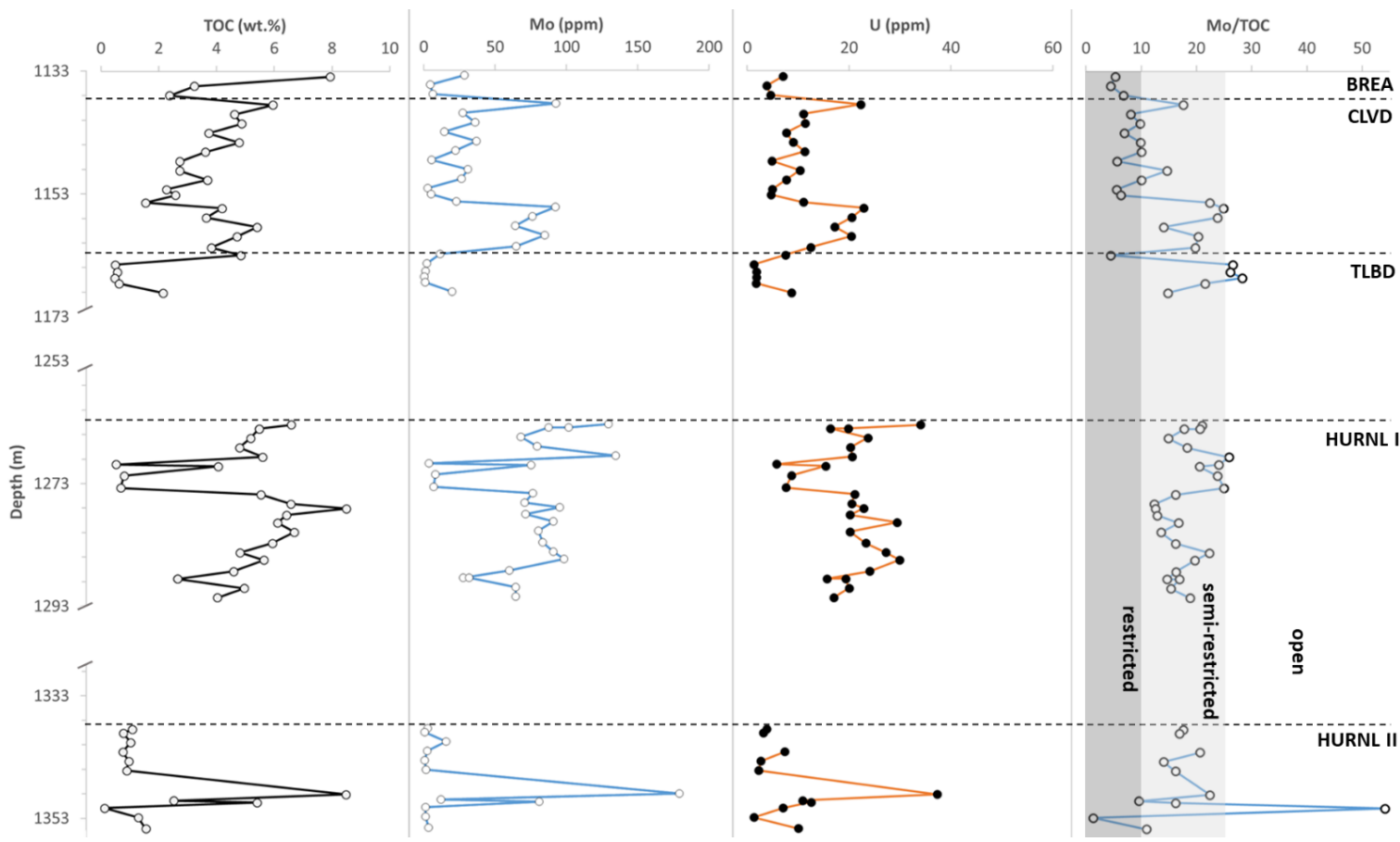


Figure 9. Total organic carbon (TOC) and trace metal molybdenum (Mo) and uranium (U) concentration and Mo/TOC ratio profiles from Well 566765. Dotted line divides conventional stratigraphic units. BREA = Berea Sandstone, CLVD = Cleveland Shale, TLBD = Three Lick Bed, HURNL I = Lower Huron Unit I, HURNL II = Lower Huron Unit II. Diagonal line with blanks along y-axis indicates a significant jump in depth. Shaded regions indicate general basin restriction conditions of restricted, semi-restricted, and open (adapted from Robl et al., 1983; Algeo et al., 2007)

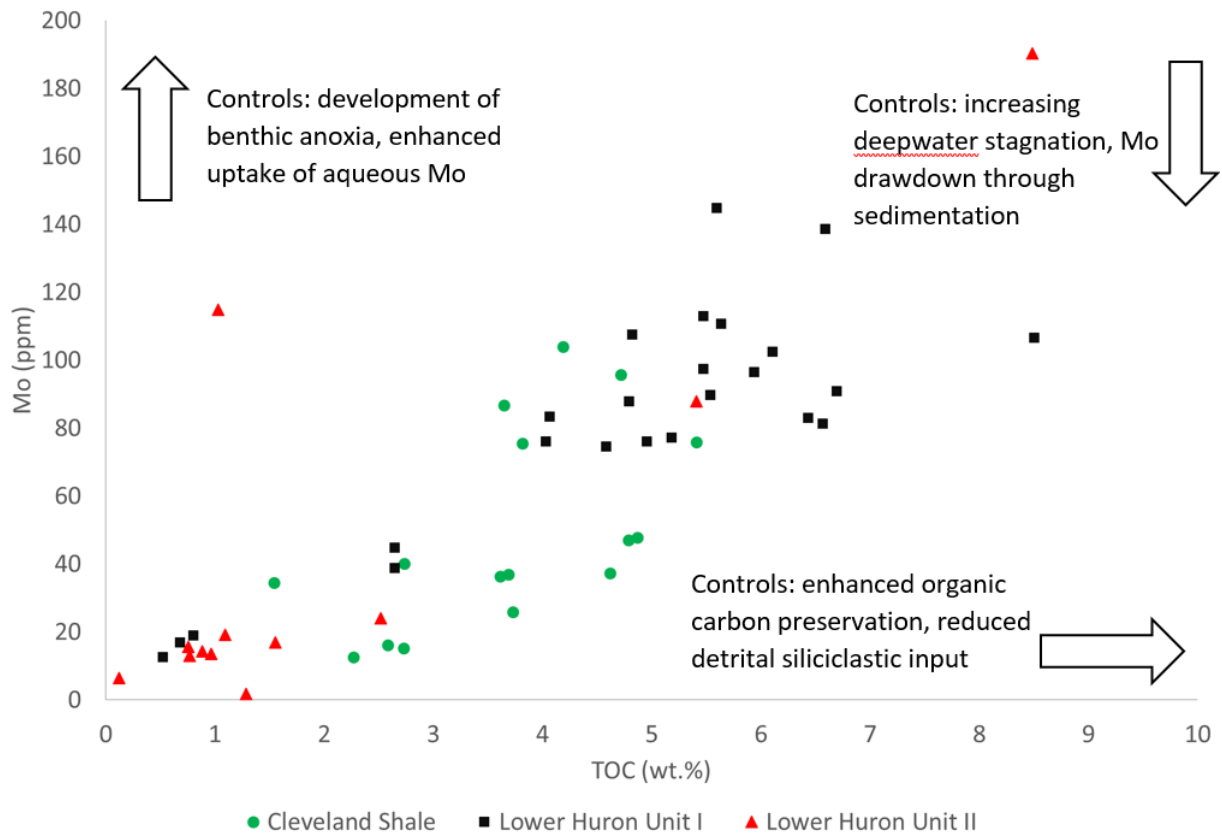


Figure 10. Trace metal content molybdenum (Mo) plotted against total organic carbon (TOC) for the major study intervals: the Cleveland Shale, and Lower Huron Units I and II. Generalized patterns of sedimentary Mo-TOC covariation that is associated with deepwater renewal in silled anoxic basins (adapted from Algeo and Lyons, 2006).

CHAPTER VI

CONCLUSION

The uranium (U) content in black shales has been historically used as a proxy for organic-richness, however there are some exceptions in which the correlation between U and TOC is not always dependable as an indicator for economically-productive sedimentary rocks. Our Ohio Shale data show that lower concentrations of U does not equate to low amounts of TOC. In fact, many sections throughout the Cleveland Shale interval have higher TOC despite having much lower concentrations of U than that of the more radioactive, higher U content Lower Huron that resides several hundred meters below within the same stratigraphic group. Both subdivisions of the Lower Huron that were evaluated exhibit a strong positive correlation between U/TOC, while the Cleveland Shale has a moderate relationship. This differentiation between the two Devonian shales is tied to water conditions that were influenced by basin geometry, sea level change at the time of deposition, and location within the basin setting. This is captured in the different U and Mo concentrations, as well the ratio between Mo/TOC. The Cleveland Shale interval is a snapshot in time that likely shows the closing of the Appalachian Basin during the Devonian. At the onset of the Cleveland deposition, the basin was semi-restricted and allowed for deepwater renewal of trace elemental U and Mo. Proxy data showing large differences in trace metal concentration in both studied subdivisions of the Lower Huron

and the Cleveland Shale interval likely suggests that throughout the Lower Huron deposition, the degree of sill and restriction varied, due to basin settings. In addition, glaciation also impacted the local to regional tectonic settings and thus the basin morphology, and caused meltwater pulses. The introduced freshwater, high in nutrients and low in transition metals, potentially enhanced the observed differences in the redox-metal proxies to organic matter content, especially along the basin margins. Our results show that the trace metal to organic carbon correlation in the Appalachian Basin was linked to multiple mechanisms including tectonic basin settings and glaciation, and concurrent water level changes strongly impacting the basin margin with a shifting pycnocline and local changes in water composition. In contrast, the deeper basin setting was likely less impacted with changes in trace metal composition and organic carbon burial at much slower rates.

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APPENDICES

Table A1. Total organic content (TOC), U, Mo, Mo/TOC from the Ohio Shale Group

Sample ID	Depth	Stratigraphic Interval	TOC	U	Mo	U/TOC	Mo/TOC
	m	Name	wt %	ppm	ppm		
1	1133.9	Berea Sandstone	7.9	7.0	41.8	0.89	5.27
2	1135.4	Berea Sandstone	3.2	3.8	14.5	1.18	4.48
3	1136.9	Berea Sandstone	2.4	4.6	16.1	1.92	6.77
4	1138.4	Cleveland Shale	6.0	22.3	104.9	3.74	17.60
5	1140.0	Cleveland Shale	4.6	11.0	37.2	2.39	8.06
6	1141.5	Cleveland Shale	4.9	11.3	47.7	2.33	9.81
7	1143.0	Cleveland Shale	3.7	7.7	25.9	2.06	6.95
8	1144.5	Cleveland Shale	4.8	9.0	47.1	1.88	9.85
9	1146.0	Cleveland Shale	3.6	11.3	36.3	3.12	10.05
10	1147.6	Cleveland Shale	2.7	4.8	15.3	1.76	5.60
11	1149.1	Cleveland Shale	2.7	10.4	40.1	3.79	14.68
12	1150.6	Cleveland Shale	3.7	7.7	37.0	2.08	10.02
13	1152.1	Cleveland Shale	2.3	4.9	12.6	2.18	5.56
14	1153.1	Cleveland Shale	2.6	4.6	16.2	1.80	6.29
15	1154.3	Cleveland Shale	1.5	11.0	34.5	7.14	22.37
16	1155.2	Cleveland Shale	4.2	22.9	104.0	5.46	24.84
17	1156.7	Cleveland Shale	3.6	20.5	86.8	5.63	23.80
18	1158.2	Cleveland Shale	5.4	17.1	75.9	3.17	14.04
19	1159.8	Cleveland Shale	4.7	20.4	95.8	4.33	20.32
20	1161.6	Cleveland Shale	3.8	12.4	75.5	3.26	19.79
21	1162.8	Three Lick Bed	4.8	7.5	21.5	1.55	4.44
22	1164.3	Three Lick Bed	0.5	1.3	12.9	2.72	26.57
23	1165.6	Three Lick Bed	0.6	1.8	14.7	3.26	26.13
24	1166.5	Three Lick Bed	0.5	1.8	13.5	3.71	28.28
25	1167.4	Three Lick Bed	0.6	1.7	13.5	2.74	21.56
26	1168.9	Three Lick Bed	2.1	8.7	31.8	4.04	14.82

* Horizontal line separates stratigraphic intervals

Table A1 (continued) Total organic content (TOC), U, Mo, Mo/TOC from the Ohio Shale Group

Sample ID	Depth	Stratigraphic Interval	TOC	U	Mo	U/TOC	Mo/TOC
	m	Name	wt %	ppm	ppm		
27	1262.8	Lower Huron Shale	6.6	34.1	138.6	5.17	21.03
28	1263.4	Lower Huron Shale	5.5	19.8	113.0	3.62	20.65
29	1264.9	Lower Huron Shale	5.2	23.7	77.1	4.57	14.89
30	1266.4	Lower Huron Shale	4.8	20.3	87.8	4.23	18.32
31	1268.0	Lower Huron Shale	5.6	20.6	144.8	3.68	25.87
58	1269.2	Lower Huron Shale	0.5	5.8	12.5	11.10	24.05
32	1269.5	Lower Huron Shale	4.1	15.4	83.4	3.78	20.54
33	1271.0	Lower Huron Shale	0.8	8.7	19.0	10.86	23.81
34	1273.0	Lower Huron Shale	0.7	7.6	16.9	11.16	24.96
35	1274.1	Lower Huron Shale	5.5	21.1	89.8	3.81	16.22
36	1275.6	Lower Huron Shale	6.6	20.5	81.3	3.12	12.38
60	1276.4	Lower Huron Shale	8.5	22.8	106.6	2.68	12.54
37	1277.4	Lower Huron Shale	6.4	20.2	82.9	3.14	12.90
38	1278.6	Lower Huron Shale	6.1	29.4	102.5	4.81	16.77
39	1280.2	Lower Huron Shale	6.7	20.2	90.9	3.01	13.58
40	1282.0	Lower Huron Shale	5.9	23.3	96.4	3.92	16.24
41	1283.5	Lower Huron Shale	4.8	27.2	107.6	5.64	22.33
42	1284.7	Lower Huron Shale	5.6	29.9	110.8	5.30	19.67
43	1286.6	Lower Huron Shale	4.6	24.0	74.5	5.24	16.26
44	1287.8	Lower Huron Shale	2.6	19.3	44.8	7.29	16.92
45	1289.3	Lower Huron Shale	5.0	20.0	76.1	4.03	15.35
46	1290.8	Lower Huron Shale	4.0	17.0	76.0	4.22	18.85
47	1337.5	Lower Huron Shale	1.1	3.9	19.2	3.56	17.64
48	1338.1	Lower Huron Shale	0.8	3.1	13.0	4.04	16.92
49	1339.6	Lower Huron Shale	1.0	-	-	-	-
50	1341.1	Lower Huron Shale	0.8	7.3	15.6	9.69	20.65
51	1342.6	Lower Huron Shale	1.0	2.7	13.5	2.76	14.02
52	1344.2	Lower Huron Shale	0.9	2.3	14.3	2.55	16.21
53	1348.0	Lower Huron Shale	8.5	37.3	190.4	4.39	22.43
59	1349.0	Lower Huron Shale	2.5	10.8	24.0	4.30	9.52
54	1349.3	Lower Huron Shale	5.4	12.5	87.8	2.32	16.24
55	1350.3	Lower Huron Shale	0.1	7.0	6.5	58.67	54.15
56	1351.8	Lower Huron Shale	1.3	1.3	1.7	1.01	1.32
57	1353.6	Lower Huron Shale	1.6	10.0	17.0	6.43	10.94

* - indicates value not reported; horizontal line separates stratigraphic intervals of Lower Huron Units I and II as discussed in text

Table A2. Core description for Well 566765 from Letcher County, Kentucky, focused primarily on the Ohio Shale Group.

KGS Call #: C-5668		County: Letcher
Operator Name: EQT		Formation: Ohio Shale
Well # 566765		Date: 1/17/2019
		Geologist: John M. Clymer
Depth (ft)	Comment	Formation
3720	Dark gray shale - Bedford Shale?	Sunbury Shale
3722	Black shale shift, sulfur, yellow film (drilling mud?) possible pyrite nodules	Sunbury Shale
3723-3725.3	Black shale shift, sulfur, yellow film (drilling mud?) possible pyrite nodules	Berea Sandstone
3727.3-37293.9	Black shale - top as yellow film (drilling mud?)	Berea Sandstone
3729.9-3732.2	Black shale	Berea Sandstone
3732.2-3734.6	Black shale	Berea Sandstone
3734.6-3736.8	Black shale	Berea Sandstone
3736.4-3737.8	Missing core	Berea Sandstone
3737.8-3740.7	Yellow film (drilling mud) - Black Shale - Cleveland	Cleveland Member, Ohio Shale
3740.3743.3	Yellow film (drilling mud) - Black Shale - Cleveland	Cleveland Member, Ohio Shale
3743.2-3746	Yellow film (drilling mud) - Black Shale - Cleveland	Cleveland Member, Ohio Shale
3746-3748.4	Yellow film (drilling mud) - Black Shale - Cleveland	Cleveland Member, Ohio Shale
3748.4-33751.1	Yellow film (drilling mud) - Black Shale - Cleveland	Cleveland Member, Ohio Shale
3751.1-3752.1	Missing core	Cleveland Member, Ohio Shale
3753-3756	Black shale with thin gray siltstone interbedded	Cleveland Member, Ohio Shale
3756-3759	Black shale	Cleveland Member, Ohio Shale
3759-3761.5	Black shale with thin gray siltstone interbedded	Cleveland Member, Ohio Shale
3761.5-3764.5	Missing core	Cleveland Member, Ohio Shale
3764.5-3767.5	Black shale with thin gray siltstone interbedded	Cleveland Member, Ohio Shale
3767.5-3770.5	Stained blue from t-shirt - black shale, thin gray siltstone interbedded	Cleveland Member, Ohio Shale
3770.5-3773.5	Black shale - thin gray bedding	Cleveland Member, Ohio Shale
3773.5-3776.4	Thicker gray bedding at top of section, ~8in into core (3783 ft)	Cleveland Member, Ohio Shale
3776.4-3779.5		Cleveland Member, Ohio Shale
3779.5-3782.4	Black shale with crystals leeching to surface	Cleveland Member, Ohio Shale
3782.4-3785.05	Lower portion of core missing - black shale with thin gray bedding	Cleveland Member, Ohio Shale
3785.05-3786	Missing core	Cleveland Member, Ohio Shale
3786-3789	Pyrite nodule; increase in thin gray bedding	Cleveland Member, Ohio Shale
3789-3792	Increase in thickness and frequency of gray bedding	Cleveland Member, Ohio Shale
3792-3795	Increase in thickness and frequency of gray bedding	Cleveland Member, Ohio Shale
3795-3796.5	Missing core	Cleveland Member, Ohio Shale
3796.5-3799.4	Partial missing core - black and gray interbedding	Cleveland Member, Ohio Shale
3799.4-3802.2	Black shale and gray interbedding	Cleveland Member, Ohio Shale
3802.2-3805.1	Black shale with gray interbedded	Cleveland Member, Ohio Shale
3805.1-3806.7	Partial missing core , black shale	Cleveland Member, Ohio Shale
3806.7-3809	Black shale with gray interbedded	Cleveland Member, Ohio Shale
3809-3811.9	Red/Tan bed at 3810.9	Cleveland Member, Ohio Shale
3810-3813	Cleveland/Three Lick Bed contact	Cleveland Member, Ohio Shale
3811.9-3814.85	Black shale with thin gray laminations	Three Lick Bed, Ohio Shale
3813-3816	Black shale with thin gray laminations	Three Lick Bed, Ohio Shale
3814.85-3817.8	Black shale with a single gray lamination	Three Lick Bed, Ohio Shale
3816-3819	Black shale, partial missing core	Three Lick Bed, Ohio Shale
3817.8-3819.9	Mostly missing core - black shale, interbedded gray laminations	Three Lick Bed, Ohio Shale
3819-3822	Dark gray shale	Three Lick Bed, Ohio Shale
3822-3824.4	Black shale	Three Lick Bed, Ohio Shale
3824.4-3825.4	Missing core	Three Lick Bed, Ohio Shale
3825.4-3827	Missing core	Three Lick Bed, Ohio Shale
3827-3829	Dark gray shale	Three Lick Bed, Ohio Shale
3829-3831	Reddish brown color appearing throughout dark gray shale interval, white streak on streak plate	Three Lick Bed, Ohio Shale
3831-3832.4	Dark gray shale	Three Lick Bed, Ohio Shale
3832.4-3833.4	Missing core	Three Lick Bed, Ohio Shale
3833.4-3836.5	Thick red lamination in black shale	Three Lick Bed, Ohio Shale
3836.5-4143.4	Missing core	Three Lick Bed, Ohio Shale

Table A2 (continued). Core description for Well 566765 from Letcher County, Kentucky, focused primarily on the Ohio Shale Group.

4143.4-4144.65	Very black shale - Lower Huron?	Lower Huron Huron, Ohio Shale
4144.65-4146.65	Dark gray/black shale	Lower Huron Huron, Ohio Shale
4146.55-4148	Dark black with thin dark gray lamination	Lower Huron Huron, Ohio Shale
4148-4150.9	Black shale	Lower Huron Huron, Ohio Shale
4150.9-4153.4	Black shale with yellow film (drilling mud?)	Lower Huron Huron, Ohio Shale
4153.3-4156.3	Black shale	Lower Huron Huron, Ohio Shale
4157.3-4159.3	Black shale-dark gray shale	Lower Huron Huron, Ohio Shale
4159.3-4160.7	Dark gray to black shale	Lower Huron Huron, Ohio Shale
4160.7-4163.1	Dark gray to black shale (lightens up towards 4163.1') - pyrite laminations	Lower Huron Huron, Ohio Shale
4163.1-4165	Partial missing section, medium gray shale; nodule @ ~4164.5 (pyrite?), filled in, does not effervesce. Erosional surface ~4164.5; transition back to dark gray to black, back to gray, and then back to black shale	Lower Huron Huron, Ohio Shale
4165-4167.45	Transition back to gray to light gray w/ pyrite laminae; 4165-4266.0', and to black/dark gray at 4166.5' with pyrite laminae	Lower Huron Huron, Ohio Shale
4165-4167.8	Mid gray shale with pyrite laminae at top to dark gray-black at mid to bottom of section	Lower Huron Huron, Ohio Shale
4167.8-4170.8	Dark gray at top of section, transition to mid-gray at middle, then transition to dark gray at bottom of section; thin to medium pyrite laminae throughout	Lower Huron Huron, Ohio Shale
4170.8-4173.75	Dark gray-black at top of section to brown-black shale; pyrite laminae at middle to medium gray at bottom of the section; Brown-black could be caused by t-shirt staining that was covering the core	Lower Huron Huron, Ohio Shale
4173.75-4176.5	Medium-dark gray shale at top of interval, bottom of section missing (4174.8-4176.5')	Lower Huron Huron, Ohio Shale
4176.5-4177.5	Dark gray to black shale	Lower Huron Huron, Ohio Shale
4178-4181	Dark gray to black shale, pyrite laminae	Lower Huron Huron, Ohio Shale
4184-4187	Pyrite nodules, possible filled in fracture, pyrite laminae, high amount of yellow film on surface of core (drilling mud)	Lower Huron Huron, Ohio Shale
4187.5-4190	Black shale at top of the section with large pyrite nodules to dark gray at middle of section, back to black at bottom of the section	Lower Huron Huron, Ohio Shale
4190-4191	Missing section	Lower Huron Huron, Ohio Shale
4191-4194	Core may be out of order - yellow film at surface of the core; black shale throughout with pyrite laminae	Lower Huron Huron, Ohio Shale
4194-4197	Black shale; pyrite nodules and laminae throughout, black crystals leeching to surface of core	Lower Huron Huron, Ohio Shale
4196-4199	Black shale with pyrite laminae, partially missing core (4197.5-4199')	Lower Huron Huron, Ohio Shale
4199-4201	Jumbled in box black shale with pyrite laminae throughout	Lower Huron Huron, Ohio Shale
4201-4203.2	Black shale with yellow film (drilling mud?)	Lower Huron Huron, Ohio Shale
4203.2-4206	Black shale with yellow film (drilling mud?)	Lower Huron Huron, Ohio Shale
4206-4209	Black shale, pyrite nodules	Lower Huron Huron, Ohio Shale
4209-4210	Black shale, pyrite laminae	Lower Huron Huron, Ohio Shale
4210-4212	Black shale to dark gray shale, pyrite laminae	Lower Huron Huron, Ohio Shale
4212-4215	Black shale throughout, pyrite laminations	Lower Huron Huron, Ohio Shale
4215-4218	Black shale - black crystals leached out, possible gypsum or other mineral; bladed crystals	Lower Huron Huron, Ohio Shale
4218-4221	Black shale with mid-dark gray interbedded; "Rose Gold" cross bed, possible fracture fill at 4220'	Lower Huron Huron, Ohio Shale
4221-4224	Partial missing core; black to dark gray shale throughout, pyrite or red fill laminae at top of section	Lower Huron Huron, Ohio Shale
4224-4227	Black shale; pyrite laminae	Lower Huron Huron, Ohio Shale
4227-4230	Leeching gypsum crystals at surface - black shale	Lower Huron Huron, Ohio Shale
4230-4233	Black and medium gray interbedding throughout (missing 4232-4233')	Lower Huron Huron, Ohio Shale
4233-4234.9	(Missing 4233-4233.7) black shale; pyrite laminae sparse throughout interval	Lower Huron Huron, Ohio Shale
4234.9-4236.3	Black shale, very few pyrite laminae, some dark gray interbedded	Lower Huron Huron, Ohio Shale
4236.3-4388	Missing Section	Lower Huron Huron, Ohio Shale

Table A2 (continued). Core description for Well 566765 from Letcher County, Kentucky, focused primarily on the Ohio Shale Group.

4388-4391	Black shale, thin gray interbedding	Lower Huron Huron, Ohio Shale
4391-4394	Black shale, thin gray interbedding	Lower Huron Huron, Ohio Shale
4394-4397	Black shale, pyrite laminations and inclusions; possibly iron inclusion at 4395'	Lower Huron Huron, Ohio Shale
4398-4401	Black shale	Lower Huron Huron, Ohio Shale
4401-4403	Black shale - poorly preserved/jumbled in box	Lower Huron Huron, Ohio Shale
4403-4406	Black shale, pyrite laminae	Lower Huron Huron, Ohio Shale
4406-4408.35	Black shale; pyrite laminae and nodules; iron deposits/red laminae and nodules at 4408'	Lower Huron Huron, Ohio Shale
4408.35-4410.35	Black shale	Lower Huron Huron, Ohio Shale
4410.35-4408.35	Black shale - low pyrite laminae, poorly sorted in core box	Lower Huron Huron, Ohio Shale
4412.3-4414.2	Black shale with thin gray laminae; some pyrite laminae present	Lower Huron Huron, Ohio Shale
4414.2-4421	Partial missing core; dark gray to black shale	Lower Huron Huron, Ohio Shale
4421-4423.7	4421-4422.7 missing; black to dark gray shale	Lower Huron Huron, Ohio Shale
4423.7-4426.7	Thick pyrite laminae in black shale at ~4424'; possible burrow at ~4426', filled in with pyrite in black shale; yellow excretion (drilling mud?), pyrite laminae and nodules throughout	Lower Huron Huron, Ohio Shale
4426.7-4428.5	Black shale, pyrite laminae	Lower Huron Huron, Ohio Shale
4428.65-4430.65	Black shale and dark gray interbedding; red/orange staining at 4430', goes through core (not just surface staining)	Lower Huron Huron, Ohio Shale
4430.65-4433.2	4431.5-4432.5' missing; black shale, pyrite laminae, some nodules	Lower Huron Huron, Ohio Shale
4433.2-4435	Black-dark gray shale interbedded, pyrite laminae	Lower Huron Huron, Ohio Shale
4435-4437	Black-dark gray shale interbedded, pyrite and iron laminae?	Lower Huron Huron, Ohio Shale
4437-4438.75	Black-dark gray shale interbedded, pyrite laminae and iron staining, yellow excretion/film (drilling mud?)	Lower Huron Huron, Ohio Shale
4438.75-4441	Missing 4438.75-4440.7'; black and dark gray shale	Lower Huron Huron, Ohio Shale

VITA

John Michael Clymer

Candidate for the Degree of

Master of Science

Thesis: ANALYSIS OF THE URANIUM TO ORGANIC CARBON RELATIONSHIP
IN THE ORGANIC-RICH OHIO SHALE OF EASTERN KENTUCKY

Major Field: Geology

Biographical:

Education:

Completed the requirements for the Master of Science in Geology at Oklahoma State University, Stillwater, Oklahoma in December, 2020.

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Experience:

Cimarex Energy Co., Tulsa, OK, Geology Intern from May 2019 to August 2019.

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Red Mountain Energy, Oklahoma City, OK, Geoscientist Intern from May 2017 to August 2017.

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