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XRD ANALYSIS AND PETROLEUM POTENTIAL OF THE EAGLE MILLS FORMATION AND PALEOZOIC ROCKS IN THE SUBSURFACE, SOUTH ARKANSAS

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> > North Little Rock, Arkansas 2021



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Table of Contents

List of Figures	ii
List of Tables	iii
INTRODUCTION	2
GEOLOGIC SETTING	2
METHODS	5
RESULTS AND DISCUSSION	6
X-ray Diffraction	6
Total Organic Carbon & Rock-Eval Pyrolysis	
Fragment Analysis	
CONCLUSIONS	
REFERENCES	

List of Figures

Figure 14. XRD results for Edith Mehrens et al. #1 samples.	. 18
Figure 15. Concentration of augite in Edith Mehrens et al. #1 samples	. 19
Figure 16a. XRD results for G. D. Royston #1 samples, 1,740-7,366 ft.	. 20
Figure 16b. XRD results for G. D. Royston #1 samples, 7,420-10,270 ft	. 21
Figure 17. Concentration of Plagioclase in G. D. Royston #1 samples	. 22
Figure 18. XRD results for J. H. Douglass et al. #1 samples	. 22
Figure 19. Concentration of carbonate minerals in Cabe LD Co. Inc. et al. #1 samples	. 23
Figure 20a. XRD results for Cabe LD Co. Inc. et al. #1 samples, 9,500-11,910 ft.	. 24
Figure 20b. XRD results for Cabe LD Co. Inc. et al. #1 samples, 12,000-14,025 ft	. 25
Figure 21. van Krevelen diagram for samples with >1% TOC	. 28

List of Tables

Table 1. Location information for sampled wells	8
Table 2. Rock-Eval pyrolysis data for cutting samples with >1% total organic carbon (TOC)	27
Table 3. Fragment analysis for core and chip samples from the G. D. Royston #1 and James	A.
Williams #1 wells	27

XRD Analysis and Petroleum Potential of the Eagle Mills Formation and Paleozoic Rocks in the Subsurface, South Arkansas

Ciara Mills and Peng Li

ABSTRACT

The pre-Mesozoic subsurface geology of the Gulf of Mexico basin remains largely unknown due to a limited number of wells penetrating the section. Relatively undeformed late Paleozoic carbonate and clastic rocks were discovered in the subsurface along the northern margin of the basin, piquing interest in the petroleum potential of this region over the years. Possible petroleum resources related to the Triassic Eagle Mills Formation have been identified, and potential for carbon sequestration has recently renewed interest in this region. X-ray diffraction (XRD), Rock-Eval pyrolysis, and density and porosity analyses were conducted on samples from deep wells in south Arkansas in order to determine the lithology and petroleum potential of the pre-Jurassic section.

Based on XRD analysis, the primary minerals found within both the Eagle Mills Formation and Paleozoic section are quartz and clay minerals with varying amounts of carbonate and feldspar (primarily plagioclase). The dominant rock types within each section are likely argillaceous siliciclastic rocks such as shale and siltstone, with trace to moderate amounts of carbonate. Additional significant minerals found in a few intervals within the Eagle Mills include anhydrite, halite, and augite. The occurrence of augite may indicate that diabase sills or pebbles are present. Both sections also contain intervals with significant concentrations of carbonate minerals, which are likely interbedded limestone.

Only seven samples from four wells have total organic carbon (TOC) concentrations that are greater than 1%. One sample is from the Louann Salt and the rest are from the Paleozoic section. TOC concentrations range from 1.05-3.52% and S₂ values range from 0.13-1.15 mg HC/g. Reliable T_{max} values in six samples fall between 495 and 570°C, which correspond to 1.75-3.10% R_o and therefore fall in the gas window. Hydrogen Index (HI) values in Paleozoic samples range from 9.39 to 56.19 mg HC/g TOC and reflect high maturity. Production index (PI) values from Paleozoic samples fall between 0.102 and 0.200 within the oil window. All samples plot on the type III (gas prone) kerogen curve of a van Krevelen diagram. Based on these values, any hydrocarbons present were most likely produced in the gas window.

It is unlikely that the Paleozoic section in south Arkansas contains good source rocks since S_2 values reflect poor generative potential and overall TOC concentrations are very low, with sufficient concentrations only occurring in intervals of 5-30 feet. It is also unlikely that the Eagle Mills or Paleozoic section would make good reservoir rocks for oil or sequestered carbon because the average porosity for samples from the Eagle Mills is 1.725% and the average porosity for the Paleozoic is 2.4%. However, more samples need to be analyzed in future studies to draw more comprehensive conclusions.

INTRODUCTION

Along the northern rim of the Gulf of Mexico (GoM) basin, deep wells drilled throughout Mississippi, south Arkansas, north Louisiana, southeast Oklahoma, and northeast Texas have encountered Late Triassic rocks of the Eagle Mills Formation as well as steeply dipping metamorphosed and deformed Paleozoic beds related to the Ouachita orogeny; wells south of the exposed Ouachita folded belt in Louisiana, south Arkansas, and Texas have also encountered undeformed, relatively flat-lying carbonate and clastic rocks of Permian and Pennsylvanian age (Morgan, 1952; Flawn, 1961; Vernon, 1971; Woods and Addington, 1973; Nicholas and Waddell, 1989). This sequence of pre-Jurassic rocks in the northern GoM basin has long been considered an area of interest for hydrocarbon exploration. The discovery of Permian shallowwater carbonate and clastic rocks with reservoir-quality porosities in northeast Texas and southwest Arkansas piqued speculation of a potentially large unexplored petroleum province (Vernon, 1971). Additionally, oil related to lacustrine shale of the Triassic Eagle Mills Formation was identified in late Jurassic reservoirs in northeast Texas and northwestern Louisiana (James et al., 1993). Furthermore, recent studies of the Eagle Mills Formation and equivalent subsurface Mesozoic basins in the eastern United States have identified large deposits that may be favorable for carbon sequestration (Blount et al., 2011; Zakharova et al., 2020).

Despite positive outlooks for the potential of the pre-Jurassic section, only a relatively small number of deep wells penetrate pre-Mesozoic rocks, most of which are located within 100 kilometers south and east of the exposed Ouachita orogenic belt (Thomas, 1990; Woods et al., 1991). Analyzing samples and logs from these wells is critical for gaining insight into pre-Jurassic rock types, tectonics, and depositional patterns, and may encourage additional drilling operations. The purpose of this study is to contribute to the limited available data characterizing the subsurface pre-Jurassic section in south Arkansas. Samples from the Eagle Mills Formation and Paleozoic section were collected and analyzed in order to identify rock types and determine the likelihood of a potential hydrocarbon source or reservoir existing in either section. The results presented will also provide information useful for those interested in exploring the pre-Jurassic section as a potential carbon sequestration site.

GEOLOGIC SETTING

Much of the pre-Mesozoic lithology and structure of the GoM basin remains unknown due to a limited number of wells penetrating pre-Mesozoic rocks (Woods et al., 1991). However, a few deep wells across south Arkansas, northern and western Louisiana, and eastern Texas have encountered relatively undeformed, predominantly marine Pennsylvanian through Permian carbonate and clastic rocks overlying deformed beds related to the Ouachita folded belt (Fig. 1). Numerous studies have interpreted these sequences as successor basin deposits that formed as a result of post-orogenic subsidence (Flawn, 1961; Paine and Meyerhoff, 1970; Nicholas and Waddell, 1982, 1989). Lithology varies but includes shale, siltstone, sandstone, carbonaceous sediment, fossiliferous shale and limestone, and shallow water shelf carbonate and sandstone along with occasional intrusive igneous rocks (Vernon, 1971; Woods and Addington, 1973; Woods et al., 1991).



Figure 1. Geologic map of pre-Mesozoic surface and subsurface geology in parts of Arkansas, Louisiana, and Texas. Modified after Nicholas and Waddell (1989) and Thomas (1990)

The Late Triassic Eagle Mills Formation unconformably overlies late Paleozoic deposits and is composed of fluvial, deltaic, and lacustrine "red beds" that include red and green-gray shale and siltstone as well as interbedded lithic and feldspathic sandstone (Scott et al., 1961; Dawson and Callendar, 1992). Intrusive igneous rocks (including diabase and basalt sills) along with nodular limestone, dolostone, conglomerate, and anhydrite stringers are also present (Scott et al., 1961; Chapman, 1963; Dawson and Callendar, 1992). The Eagle Mills is present in the subsurface of west-central Mississippi, southern Arkansas, and east Texas with equivalents in the subsurface of South Carolina, Georgia, northwest Florida, and south Alabama (Scott et al., 1961; Marine and Siple 1974; Chowns and Williams, 1983; Gawloski, 1983). Until recently, the predominant theory of deposition for the Eagle Mills across the basin was accumulation in rift basins and grabens that formed as a result of tensional deformation during the breakup of Pangea (Salvador, 1987, 1991a, 1991b). However, recent studies analyzing seismic data discovered riftrelated structures in Paleozoic and early Mesozoic strata in Florida, Georgia, and Alabama, but no evidence for rifting in the subsurface of Texas, Arkansas, and Louisiana. Instead, seismic data showed either unconformities with the underlying sedimentary section or accumulation in localized flexural areas (Norton et al., 2018; Snedden and Galloway, 2019; Frederick et al., 2020). Therefore, the alternative depositional model for the Eagle Mills in the north-central GoM infers post-orogenic successor basin fill similar to the underlying Pennsylvanian-Permian section.

Middle Jurassic evaporite deposits of the Werner-Louann sequence unconformably overlie the Eagle Mills in south Arkansas, north Louisiana, and adjacent parts of Texas and Mississippi (Fig. 2). The Louann is composed primarily of salt while the Werner consists of an upper anhydrite member and a lower siliciclastic member of conglomerate, shale, and sandstone (Hazzard et al., 1947; Bishop, 1967). General consensus is that these evaporites are associated with one cycle of precipitation and deposition in large, shallow hypersaline lakes in an arid sabkha environment with limited seawater influx from the Pacific or Proto-Atlantic (Hazzard et al., 1947; Salvador, 1987, 1991a; Snedden and Galloway, 2019).

The Late Jurassic in the GoM was characterized by a period of widespread marine transgression as the basin experienced continued subsidence and marine invasion (Salvador, 1991a, 1991b). This is reflected in the Smackover-Norphlet supersequence overlying Middle Jurassic evaporites. The Norphlet Formation was deposited as a terrigenous siliciclastic unit on the edge of a shallow-water basin and is composed of thin shale, sandstone, and gravel deposits in the north-central GoM and thick fluvial and eolian deposits in the northeast GoM (Hazzard et al., 1947; Snedden and Galloway, 2019). Continued marine invasion in the Oxfordian deposited marine carbonate and clastic rocks of the Smackover Formation conformably on the Norphlet along a tectonically stable, low-angle ramp on the northern margin of the GoM (Ahr, 1973; Salvador, 1987; Snedden and Galloway, 2019). The offshore onlite bars and shoals of the upper Smackover in the northern GoM transitioned conformably to anhydrite and clastic rocks of the Buckner Member of the Haynesville Formation, indicating deposition in shoreward hypersaline coastal lagoons behind carbonate barriers (Dickinson, 1968; Moore, 1984; Salvador, 1991a, 1991b). These lower anhydrite-rich beds transitioned to terrigenous clastic and carbonate rocks of the upper Haynesville Formation. A progradational sequence of marine, deltaic, and fluvial siliciclastic rocks belonging to the Cotton Valley Group was deposited on top of the Buckner in the northern GoM at the end of the Jurassic (Thomas and Mann, 1966; McGowen and Harris, 1984; Salvador, 1987, 1991a; Fig. 2).



Figure 2. Paleozoic-Jurassic stratigraphic column for southern Arkansas subsurface

METHODS

Representatives from Chesapeake Energy Corporation collected core and cutting samples from nine deep wells in south Arkansas that were drilled to late Mesozoic and Paleozoic rocks (Fig. 3, Table 1). Seven wells only had cuttings available and additional core/chip samples were collected from the G. D. Royston #1 and James A. Williams #1 wells.

Samples were sent to the Chesapeake Energy Corporation internal laboratory for analysis. X-ray diffraction (XRD) was performed on cutting samples to characterize the bulk and clay mineralogy. To streamline the results of this study, the minerals are grouped into seven categories based on chemical formula: quartz, feldspar (plagioclase and potassium feldspar), carbonate (calcite, dolomite, siderite, magnesite, aragonite, vaterite), clay (total clay minerals), anhydrite (anhydrite and gypsum), halite, and others (includes total organic carbon and accessory minerals such as apatite, pyrite, anatase, analcime, hematite, barite, hornblende, and augite). Significant fluctuations of specific accessory minerals are noted, and concentrations of all minerals are available in Appendix 1. XRD values of raw data were normalized to sum to 100%.

Organic geochemical analysis was conducted on core and cutting samples to evaluate the source rock characteristics. Total organic carbon (TOC wt%) was measured to assess the organic matter richness. Rock-Eval pyrolysis was used to evaluate the type of organic matter, thermal

maturity, and generation potential of source rocks and was therefore only carried out on samples with TOC values greater than 1%. Density and porosity analyses were conducted on core and chip samples in the G. D. Royston #1 and James A. Williams #1 wells.

RESULTS AND DISCUSSION

X-ray Diffraction

Georgia Pacific #1

One hundred and forty-six cutting samples were collected from the Georgia Pacific #1 well. The first sample was from the Louann Salt at 7,700-7,710 feet; seventeen samples from 7,800-9,310 feet were in the Eagle Mills Formation, and the remaining one hundred and twentyeight samples from 9,360-16,610 feet were in the Paleozoic section. A halite interval is present in the Eagle Mills from 8,500-8,510 feet (Fig. 4a). Higher concentrations of anhydrite in the top ~100 feet of the Eagle Mills are consistent with reports of anhydrite stringers in the upper part of the formation (Fig. 4a, Chapman, 1963). Previous studies of this well noted calcareous shale and fossiliferous carbonate in the upper 3,000 feet of the Paleozoic section that give way to shale, siltstone, sandstone, and carbonaceous material deeper in section (Vernon, 1971; Woods and Addington, 1973; Woods et al., 1991). This shift from carbonate to siliciclastic rocks is evident based on a decrease in carbonate minerals below 12,400 feet (Figs. 4a, 4b, 5). A slight increase in quartz around 14,295 feet also supports this observation and is consistent with reports of quartzitic sandstone becoming more abundant and thicker with depth (Fig. 6, Woods and Addington, 1973). The calcareous intervals sampled were likely not in pure limestone since the total concentration of carbonate for most of these samples falls between 10 and 30%. High concentrations of total clay (40-60%) across most samples are consistent with argillaceous rocks such as shale and siltstone being the dominant lithology of both the Eagle Mills Formation and Paleozoic section.

Georgia Pacific #5

Six cutting samples were collected from Paleozoic rocks between 9,750 and 10,430 feet in the Georgia Pacific #5 well. Quartz and plagioclase are the most abundant minerals while concentrations of clay minerals fall between 21 and 35% and carbonate minerals constitute less than 15% of each sample (Fig. 7). These patterns suggest argillaceous siliciclastic sandstone and/or siltstone rather than shale.

<u>Mary Currie #1</u>

Two cutting samples were collected from the Mary Currie #1 well at depths ranging from 4,890-5,470 feet. The sample at 4,890-4,900 feet was collected from the Smackover Formation and is composed predominantly of carbonate (primarily calcite) (Fig. 8). The cuttings from 5,460-5,470 feet were collected from the Eagle Mills Formation and contain significant amounts of feldspar, specifically plagioclase (Fig. 8). This sample is likely either an arkosic wacke or a plagioclase-rich igneous rock.



Figure 3. Locations of sampled wells in south Arkansas

Table 1.	Location	information	for	sampled wells	5

Well Name	Operator	API	Permit	Location SecTwp Rge.	County	Sampled Interval for XRD (ft.)
Georgia Pacific #1	Humble Oil	03-003-00047-00-00	20322	4-19S-9W	Ashley	7,700-16,610
Georgia Pacific #5	Placid Oil	03-003-10013-00-00	21989	20-15S-7W	Ashley	9,750-10,430
Mary Currie #1	Mobil Oil	03-003-10024-00-00	23129	4-19S-4W	Ashley	4,890-5,470
Brine Supply #1	Albemarle Corp.	03-027-01377-00-00	93070	33-17S-20W	Columbia	10,740-10,745
James A. Williams #1	Home Petroleum Corp.	03-003-10027-00-00	23829	6-18S-4W	Ashley	5,820-9,948
Edith Mehrens et al. #1	Amoco Production	03-043-10013-00-00	30799	9-14S-4W	Drew	7,750-9,200
G. D. Royston #1	Carter Oil	03-057-00008-00-00	16686	31-10S-24W	Hempstead	1,740-10,270
J. H. Douglass et al. #1	MRT Exploration	03-057-10004-00-00	25471	27-12S-26W	Hempstead	10,800-11,960
Cabe LD Co. Inc. et al. #1	Chevron Oil	03-099-10092-00-00	22854	35-12S-21W	Nevada	9,500-14,025



Figure 4a. XRD results for Georgia Pacific #1 samples, 7,700-11,960 ft.



Figure 4b. XRD results for Georgia Pacific #1 samples, 12,000-16,610 ft.



Figure 5. Concentration of total carbonate minerals in Georgia Pacific #1 samples



Figure 6. Concentration of quartz in Georgia Pacific #1 samples



Figure 7. XRD results for Georgia Pacific #5 samples



Figure 8. XRD results for Mary Currie #1 and Brine Supply Well #1 samples

Brine Supply #1

One cutting sample was taken from the Brine Supply Well #1 at 10,740-10,745 feet in the Werner Formation. Over 90% of the sample is made up of anhydrite.

James A. Williams #1

Ninety cutting samples were collected from intervals spanning 5,820-9,948 feet in the James A. Williams #1 well. The sample at 5,820-5,850 feet was collected from the Louann Salt, samples from 6,510-7,770 feet were collected from the Eagle Mills Formation, and the remaining samples from 7,770-9,948 feet were from the Paleozoic section. The predominant mineralogy of the first sample is anhydrite (Fig. 9a). Noticeable increases in carbonate minerals take place in three different intervals: 7,463.75-7,491 feet, 7,890-7,920 feet, and 8,190-8,790 feet (Figs. 9a, 9b, 10). These likely represent interbedded limestone. Augite begins appearing in samples between 7,680 and 7,710 feet, with spikes from 7,710-7,890, 8,130-8,190 and 9,630-9,660 feet (Fig. 11). Plagioclase follows a similar relationship: increases occur between 7,680-7,890, 8,010-8,190, 9,070-9,100, and 9,510-9,948 feet (Fig. 12). Both minerals are commonly found in igneous rocks; therefore, increases may represent diabase intrusions or detrital deposits derived from igneous sources. Total concentrations of clay minerals decrease after 6,510 feet before rising again after 8,715 feet (Fig. 13).

Edith Mehrens et al. #1

Seventeen cutting samples were collected from the Eagle Mills Formation in the Edith Mehrens et al. #1 well. Most samples are composed predominantly of quartz or a combination of plagioclase and quartz, and carbonate minerals occur in cumulative concentrations less than 11% (Fig. 14). Concentrations of clay minerals range from 11.7 to 31.6%. Significant concentrations of augite occur from 7,750-7,810 feet (Fig. 15). The augite-rich rocks at the top of the section likely reflect igneous intrusions, which are known to exist in the Eagle Mills as diabase dikes and sills (Scott et al., 1961; Dawson and Callender, 1991). The lack of carbonate minerals and moderate amount of clay minerals suggest moderately argillaceous siliciclastic rocks for this section of the Eagle Mills.

<u>G. D. Royston #1</u>

Sixty-five cutting samples were collected from the G. D. Royston #1 well. One sample from 1,740-1,750 feet was collected from the Cotton Valley Formation while samples from 1,930-8,800 feet were from the Eagle Mills Formation and the remaining samples were collected from the Paleozoic. An earlier study of this well described 1,210 feet of Pennsylvanian carbonate and clastic rocks (including shale, sandstone, fossiliferous carbonate, and carbonaceous rock) above 336 feet of highly tilted and eroded Ouachita facies rocks (Woods and Addington, 1973; Woods et al., 1991). Plagioclase concentration shows an overall decreasing trend with depth while total clay and quartz values remain relatively consistent at 40-60% and 20-50% respectively with a few outliers (Figs. 16a, 16b, 17). Carbonate minerals are not abundant in this well, but some samples yield isolated values over 10%. These results suggest argillaceous rock types (most likely shale and siltstone) throughout most of the Eagle Mills and Paleozoic section, and are in agreement with reports of shale in the Paleozoic; additionally, there is little evidence for previously reported additional carbonate due to low concentrations of carbonate minerals (Woods and Addington, 1973).



Figure 9a. XRD results for James A. Williams #1 samples, 5,820-8,460 ft.



Figure 9b. XRD results for James A. Williams #1 samples, 8,460-9,948 ft.



Figure 10. Concentration of total carbonate minerals in James A. Williams #1 samples



Figure 11. Concentration of augite in James A. Williams #1 samples



Figure 12. Concentration of plagioclase in James A. Williams #1 samples



Figure 13. Concentration of total clay in James A. Williams #1 samples



Figure 14. XRD results for Edith Mehrens et al. #1 samples



Figure 15. Concentration of augite in Edith Mehrens et al. #1 samples

J. H. Douglass et al. #1

Twelve cutting samples were collected from the J. H. Douglass et al. #1 well. Samples from 10,800-10,810 feet were from the Eagle Mills Formation and the remaining samples were from the Paleozoic section. The most abundant minerals are quartz and clay (concentrations fall between 38-64% and 23-46% respectively), and all but one sample have a cumulative concentration of carbonate minerals below 10% (Fig. 18). The majority of these samples are likely argillaceous sedimentary rocks such as siltstone rather than shale since the total concentration of clay minerals per sample falls below 50%.

Cabe LD Co. Inc. et al. #1

Forty-nine cutting samples were collected from the Cabe LD Co. Inc. et al. #1 well. Samples from 9,500-10,400 feet were taken from the Eagle Mills Formation and the cuttings from 10,500-14,025 feet were collected from the Paleozoic. Carbonate minerals are more abundant in the Paleozoic section between 11,700 and 13,500 feet, implying either limestone or calcareous siliciclastic rocks (Fig. 19). Quartz and clay are the most abundant minerals with concentrations of each falling between 20 and 50% in most samples (Figs. 20a, 20b).



Figure 16a. XRD results for G. D. Royston #1 samples, 1,740-7,366 ft.



Figure 16b. XRD results for G. D. Royston #1 samples, 7,420-10,270 ft.



Figure 17. Concentration of Plagioclase in G. D. Royston #1 samples



J. H. Douglass et al. #1 XRD

Figure 18. XRD results for J. H. Douglass et al. #1 samples



Figure 19. Concentration of carbonate minerals in Cabe LD Co. Inc. et al. #1 samples

Total Organic Carbon & Rock-Eval Pyrolysis

Average total organic carbon (TOC) values for samples from each well range from 0.05 to 0.46%, and average TOC concentrations for the Eagle Mills and Paleozoic are 0.11% and 0.36% respectively (Appendix 1). Of the nine wells, only four produced samples containing more than 1.0% TOC: the Georgia Pacific #1, James A. Williams #1, G. D. Royston #1, and J. H. Douglass et al. #1. One sample is from the Louann Salt and the rest are from Paleozoic strata (Table 2). Generally, source rocks with greater than 1.0% TOC are considered to have "good" generative potential while TOC values greater than 2.0% are preferable (Peters, 1986). Therefore, Rock-Eval pyrolysis was only performed on samples with TOC values in excess of 1.0% (Table 2). TOC values for these samples ranged from 1.05-3.52%. It is important to note that results and interpretations from Rock-Eval pyrolysis data are very limited for this study given that only seven samples from four wells contained sufficient TOC values to warrant further analysis.

 S_1 represents the free, thermally extractable hydrocarbons of source rocks. The S_1 values of the studied samples range from 0.03 to 0.10 mg HC/g. S_2 represents the remaining hydrocarbon generative potential of source rocks. Values of 2.00-5.00 HC mg/g rock indicate fair source potential and values greater than 5.00 mg HC/g rock are indicative of good source potential (Espitalié, 1982), although these values are diminished with increasing thermal maturity. The S_2 values from analyzed samples range from 0.13 to 1.15 mg HC/g rock. Thus, S_2



Figure 20a. XRD results for Cabe LD Co. Inc. et al. #1 samples, 9,500-11,910 ft.



Figure 20b. XRD results for Cabe LD Co. Inc. et al. #1 samples, 12,000-14,025 ft.

yields indicate that the samples have poor generative potential. T_{max} is the temperature of a maximum rate of evolution of S₂ hydrocarbons, and is used as a measure of maturity

(Espitalié et al., 1977, 1985). Since vitrinite reflectance (R_o %) measured from visual kerogen analysis was not available for this study, the thermal maturity of the samples has been interpreted primarily based on T_{max} values. T_{max} values are affected by low organic matter content, which correlate to low S₂ peaks. When S₂ values are lower than 0.20 mg/g, T_{max} values are not usually reliable (Peters, 1986). Therefore, the T_{max} values with low S₂ from the thermal maturity interpretation were excluded. The T_{max} value from the sample in the Louann Salt Formation is 423°C, which corresponds to 0.454% R_o (immature) according to a conversion formula (calculated $R_o = 0.0180 \text{ x } T_{max} - 7.16$) by Jarvie et al. (2001). T_{max} values of the samples in the Paleozoic fall within the range of 495 to 570°C, which correspond to 1.75 to 3.10% R_o (gas window).

The hydrogen index (HI = S_2 /TOC x 100) is the normalized hydrogen content of a sample. Like S_2 , HI decreases as the sample matures. The HI value for the immature sample in the Louann Salt is 102.8 mg HC/g TOC, indicating type III gas prone kerogen (Jones, 1984). HI values of the samples in the Paleozoic section range from 9.39 to 56.19 mg HC/g TOC. The low HI values are consistent with a high level of thermal maturity.

The production index (PI = $S_1/(S_1+S_2)$) is another measurement of thermal maturity (Peters, 1986). PI values of less than ~0.1 indicate immature stage, and values of approximately 0.4 are at the bottom of the oil window. The PI value of the sample in the Louann Salt is 0.050, which is indicative of an immature stage and is consistent with the thermal maturation interpretation from the T_{max} value. PI values of the samples in the Paleozoic range from 0.102 to 0.200, which fall within the oil window and thus are inconsistent with the T_{max} interpretation. The anomalously low PI values in the Paleozoic samples imply that hydrocarbons have been expelled from source rocks (Espitalié et al., 1977).

A van Krevelen diagram was constructed to further characterize kerogen type (Fig. 21). Samples from both the Louann Salt and Paleozoic section fall along the type III (gas prone) kerogen curve, which is consistent with the T_{max} interpretation for the Paleozoic samples and HI interpretation for the Louann Salt.

Fragment Analysis

Core chip samples were collected from intervals in the Eagle Mills Formation in the G. D. Royston #1 well and four core samples were collected in the James A. Williams #1 well, two each from the Eagle Mills and Paleozoic sections. All were analyzed for bulk density, dry grain density, and porosity (Table 3). Porosity values for all samples range from 0.3-2.8%, with average porosities of 1.725% in the Eagle Mills Formation and 2.4% in the Paleozoic. Petroleum reservoirs are generally considered good quality with 15-20% porosity, although 8% and 5% porosities are the practical cutoffs for oil sandstone and limestone respectively (Tiab and Donaldson, 2012). Porosities never rise above 2.8% in the samples collected. Therefore neither the Eagle Mills nor the Paleozoic section would make a good reservoir rock for hydrocarbons or carbon sequestration.

Table 2. Rock-Eval pyrolysis data for cutting samples with >1% total organic carbon (TOC)

Well	Depth Range	Depth Range Ro	Formation	S ₁	S ₂	S ₃	T _{max}	S.+S.	тос	н	OI	PI	NOC
	(ft.)	(%)		(mg/g)	(mg/g)	(mg/g)	(°C)	01102	(% wt)				
Georgia Pacific #1	13940-13950	0.634*	Paleozoic	0.05	0.21	0.51	433*	0.26	1.14	18.42	44.74	0.192	4.39
James A. Williams #1	5820-5850	0.454	Louann Salt	0.06	1.15	1.10	423	1.21	1.07	107.48	102.8	0.050	5.61
James A. Williams #1	8850-8880	0.256*	Paleozoic	0.04	0.20	0.63	412*	0.24	2.13	9.39	29.58	0.167	1.88
G. D. Royston #1	9850-9860	3.1	Paleozoic	0.06	0.53	0.36	570	0.59	3.52	15.06	10.23	0.102	1.70
G. D. Royston #1	9900-9910	3.298*	Paleozoic	0.03	0.13	0.58	581*	0.16	1.35	9.63	42.96	0.188	2.22
J. H. Douglass et al. #1	11395-11400	1.768	Paleozoic	0.09	0.59	0.49	496	0.68	1.05	56.19	46.67	0.132	8.57
J. H. Douglass et al. #1	11710-11715	1.75	Paleozoic	0.10	0.40	0.38	495	0.50	1.10	36.36	34.55	0.200	9.09

*: unreliable values due to low S₂.

 $HI = Hydrogen Index; OI = Oxygen Index; PI = Production Index; NOC = Normalized Oil Content = (S_1/TOC) x 100 (Jarvie and Baker, 1984)$

Table 3. Fragment analysis for core and chip samples from the G. D. Royston #1 and James A. Williams #1 wells

Well	Depth (ft)	Bulk Density (g/cc)	Dry Grain Density (g/cc)	Porosity (% of BV)
G. D. Royston #1	5968	2.742	2.805	2.8
G. D. Royston #1	6396	2.602	2.663	2.4
G. D. Royston #1	6444	2.73	2.788	2.3
G. D. Royston #1	6916	2.74	2.803	2.5
G. D. Royston #1	6950	2.724	2.778	2.3
G. D. Royston #1	7366	2.762	2.773	0.8
James A. Williams #1	7463.8	2.711	2.719	0.4
James A. Williams #1	7491	2.713	2.72	0.3
James A. Williams #1	8713.1	2.654	2.719	2.5
James A. Williams #1	8715.3	2.693	2.749	2.3



Figure 21. van Krevelen diagram for samples with >1% TOC

CONCLUSIONS

XRD analysis indicates that quartz and clay are the most common minerals within both the Eagle Mills and Paleozoic sections. Additionally, feldspar (primarily plagioclase) and carbonate occur in varying amounts. High overall concentrations of quartz and clay minerals suggest that the most common rock types within both sections are argillaceous siliciclastic rocks such as shale and siltstone. Concentrations of feldspar increase in a few intervals in the Eagle Mills, and may represent an arkosic wacke. Augite is also present in varying amounts in the Eagle Mills, which is consistent with previous reports of diabase intrusive rocks. Intervals containing high concentrations of carbonate minerals exist in both sections, suggesting that carbonate rocks such as limestone may be interbedded with the siliciclastic rocks.

TOC concentrations for the majority of samples are very low, with average TOC values in each well below 0.5%. Only seven samples (one in the Louann Salt, six in the Paleozoic) from four wells contained a sufficient concentration of TOC to warrant further analysis with Rock-Eval pyrolysis. S₂ values range from 0.13-1.15 mg HC/g and indicate poor generative potential. Results on a van Krevelen diagram and R_o values calculated from T_{max} place kerogen type in the gas window. HI values also corroborate gas prone kerogen by reflecting a high level of thermal maturity. PI values placed kerogen type in the oil window, but this is likely misleading given that the majority of the evidence reflects gas prone kerogen.

Poor generative potential, low TOC values, and tendency toward gas prone kerogen lead to the conclusion that the Paleozoic subsurface rocks in south Arkansas are not economically viable source rocks. Additionally, sufficient TOC concentrations are only present in intervals of 5-30 feet. Fragment analysis on core chip samples from two wells give porosities of less than 3% for both the Eagle Mills and Paleozoic section, indicating that these intervals would not make effective reservoir rocks for hydrocarbons or carbon storage. However, this conclusion only reflects results from ten samples across two wells. Additional sampling throughout the pre-Jurassic in south Arkansas may lead to the discovery of potential source rocks for hydrocarbon exploration or adequate porosities for carbon storage.

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