GAMMA SPECTROMETRY AND GEOCHEMICAL INVESTIGATION OF THE MISSISSIPPIAN (CHESTERIAN) FAYETTEVILLE SHALE AND IMO SHALE, ARKOMA BASIN, ARKANSAS

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TABLE OF CONTENTS

CHAPTER PAGE

LIST OF TABLES

TABLE PAGE

LIST OF FIGURES

CHAPTER I

1.1 INTRODUCTION

Conventionally limestone and sandstone are well known as reservoir rocks as they have been well studied and much is known about their geology. On the contrary, shales are conventionally known as seals and source rocks and as such, they have been lightly studied. Recently, shales have received more attention because of their dual characteristics as both source and reservoir rock. The provenance of shale has generated many questions in the past and has resulted to a lot of debate and unanswered questions. The foremost of the questions include: (1) what is the source/origin of the mud-forming shale?, (2) what are the paleoconditions of deposition (anoxic or oxic)?, (3) is color a proper diagnostic feature to identify shales origin?, (4) what is the environment of deposition (terrestrial or marine)? and (5) did black shales originated from sediments deposited in shallow or deep water?

Black shales can be defined as dark gray to black, organic-carbon-rich, laminated, carbonaceous strata that are characterized by low amounts of benthic faunas or devoid of metazoan life (Arthur and Sageman, 1994). The formation of black shale requires an adequate supply of organic matter, conditions conducive for preservation of the organic material and depletion of dissolved oxygen in waters above the sediment-water interface.

Black shale is described as “hot shale” when the gamma ray values equal or greater than 200 American Petroleum Institute (API) units (Luning et al., 2000)

Organic matter, which is the main cause of the dark coloration in shales, is the most important thing that distinguishes black shales from all other mudrocks. The amount, type and maturity of organic carbon determines the color of shales as shales containing a few percent of immature amorphous organic matter exhibit more brown (lighter color) than black coloration; highly oxidized or thermally matured strata containing about 1-2% organic carbon are mostly black. The closeness/ proximity of terrestrial sources of organic matter and marine productivity predominantly control the type of organic matter that is found in black shale deposits (Arthur and Sageman, 1994).

Oxygen demand relates to surface bio-productivity and when the demand for oxygen in water column exceeds the supply, the state of anoxia exists. Oxygen-constrained environments are identified in the geological record by their association with diagnostic sedimentological and geochemical characters. A fissile black shale lithology enriched in organic matter and trace elements such as uranium (Wignall and Myers, 1988) is particularly characteristic of dysaerobic to anoxia environments. Geochemical and sedimentological evidences suggest that potential oil source beds have been deposited in the following anoxic settings: large anoxic lakes, anoxic silled basins, upwelling induced anoxia and anoxic open ocean (Demaison and Moore, 1980)

Large anoxic lakes have permanent stratification, maximum water depth of about 1,500 m, anoxia below 150 m, varved sediments and H_2S is present in the water (euxinic). Here sediment with shallow oxygenated waters contains 1-2% organic carbon while sediments within anoxic waters contain about 7-11% total organic carbon (TOC) (Demaison and Moore, 1980).

Anoxic silled basins are characterized by several physical barriers that restrict vertical mixing, hence stratification of the basin. Their water balance have a strong salinity contrast between fresh out-flowing surface water and deeper in-going more saline and nutrient-rich oceanic water. However, positive water balance also acts as nutrient traps enhancing productivity and preservation of organics. They are also characterized by permanent or intermittent anoxia, permanent halocline marking oxic and anoxic boundary, anoxic boundary of about 250 m around edges and 150 m at the center and presence of H_2S in the anoxic waters (Demaison and Moore, 1980).

Upwelling induced anoxia develops when surface bio-productivity demand is far more than the oxygen supply from the deep water. Anoxic organic rich sediments contain very high TOC value between 5-20%. Organic-rich sediments contain high concentration of uranium, phosphorus, copper, and nickel (Demaison and Moore, 1980).

Anoxic open oceans are the most complex and least understood of all settings for developing organic sediment. The anoxia is believed to be caused by biochemical oxygen demand causes or formed by high plankton productivity (Demaison and Moore, 1980).

Anoxic shales are generally characterized by the following: thinly laminated beds, high TOC of between 1-20%, lack of bioturbation (they lack benthics), presence of pelagic fauna such as sharks, ammonoids, conodonts, planktonic foraminifera, radiolarians and nanoplanktons, authigenic minerals such as pyrite, phosphate, cherts and carbonate concretions. In contrast dysoxic shales are clay-rich cotaining, minor bioturbation (Chondrites), and may have benthic fauna in addition to pelagic component (Demaison and Moore, 1980).

Black shales have been recently viewed as forming from slow, uniform deposition under anoxic conditions in deep water settings. Black shales remain an enigmatic sedimentary deposit and recent progress in the understanding of their depositional dynamics has enhanced the traditional view and promoted the complexity of their geology.

This study was done to further enhance the general understanding of the provenance of shales using both the Fayetteville Shale and the Imo Shale as the study platform. This work focuses on the sediment source and environment of deposition with less emphasis on the lithostratigraphy and fossil content. Many other problems involving shales remain to be addressed and it is hoped that additional study/ research will be conducted to answer the knows and future unanswered questions.

1.2 Objectives

The primary goal of this project is to determine the sediment source and environment of deposition of the Fayetteville Shale and the Imo Shale. The Mississippian Fayetteville and Imo shales are lightly studied and as a result very little are known about their geology, internal stratigraphy, depositional setting and geochemistry. As a result of its unconventional gas production, the Fayetteville Shale has been the focus of more studies than the Imo Shale. The majority of work completed on the Fayetteville was done mainly for hydrocarbon exploration purposes. This project is designed to help establish the sediment source and depositional settings of these shales topics that have not been adequately addressed previously. Specific objectives include:

- Analyze and describe the lithological characteristics of Fayetteville and Imo shales.
- Estimate environment of deposition and source through detailed gamma ray and TOC analysis
- Determine clay mineralogy

Ultimately, this study will definitely lead to a deeper understanding of the depositional environment, sediment source, clay mineralogy and organic matter content of the Fayetteville Shale and the Imo Shale.

1.3 Location of the Study Area

The study area includes three primary outcrops located in three counties in northern Arkansas on the northern flank of the Arkoma Basin. (Fig.1). The first outcrop is located in Marshall, Searcy County (Fig. 2). Exposed here are the middle to upper Fayetteville and lower part of the Pitkin Limestone. The outcrop is located on the east side of U.S. Highway 65 about 1 mile south of Marshall in T. 14 N., R. 15 W., Searcy County, Arkansas. The Marshall outcrop exposes about 52 m (169 ft) of the Fayetteville Shale and the lower part of the Pitkin Limestone. The Fayetteville Shale is in gradational contact with the Pitkin Limestone. The Fayetteville Shale here is characterized by two distinct layers, the lower black fossiliferous shale and the upper interbeded micritic limestone and shale. The contact between the two formations is marked by a change from gray to light gray bioclastic and oolitic carbonates. The oolitic-bioclastic lower part of the Pitkin Limestone contains thin black shales alternating with thick beds of carbonates. This outcrop only provides the upper contact of the Fayetteville because the underlying unit is not exposed.

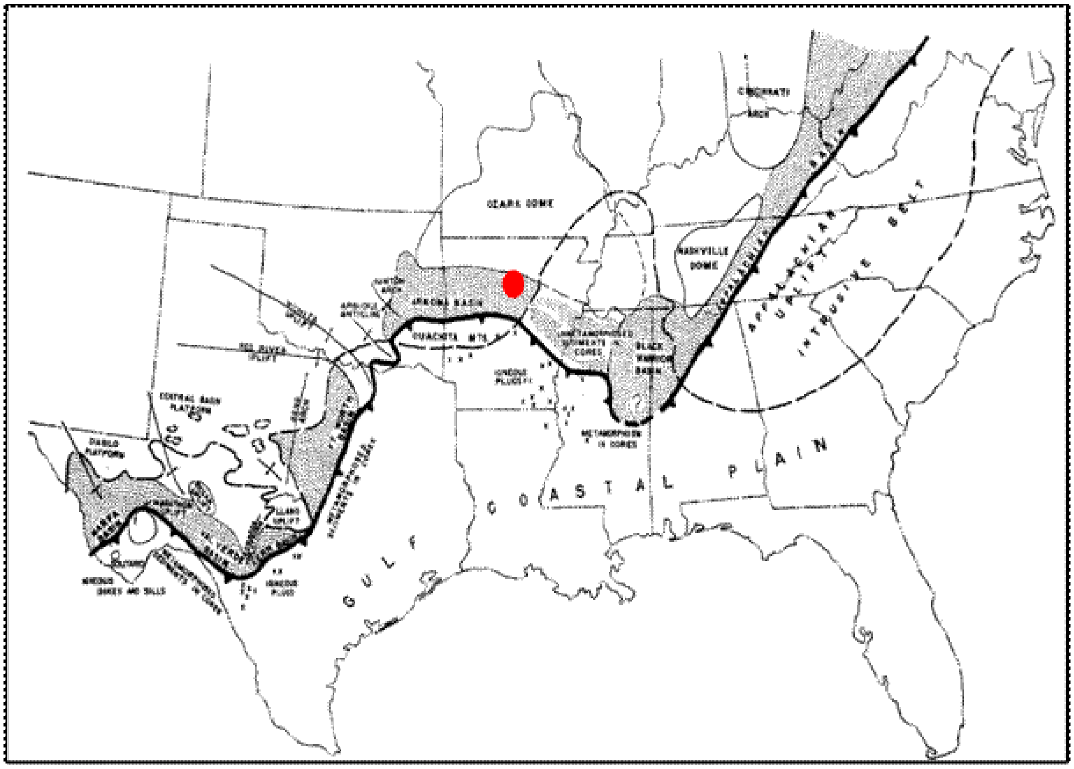


Figure 1: The study area (red dot) within the Arkoma Basin (modified from Branan, 1968)

The second outcrop is located in Spring Valley, Washington County, Arkansas. This outcrop is along the west side of U.S Highway 412 J in T. 17 N., R. 28 W, Washington County, Arkansas (Fig. 2). Here the contact between the Fayetteville Shale and the upper Hindsville Limestone is exposed. The Mississippian Hindsville Limestone is predominantly grainstone with intercalations of thin shale beds. It contains fossils such as brachiopods, crinoids and algal-coated grains (oncolites). This outcrop contains a channel that truncates the limestone. At the base of the channel, the limestone contains abundant quartz, which makes it sandy. In this section, about 4.0 m (13 ft) of Fayetteville Shale is exposed. The Fayetteville Shale is black, very fissile and clay rich and unconformably overlies the Hindsville Limestone.

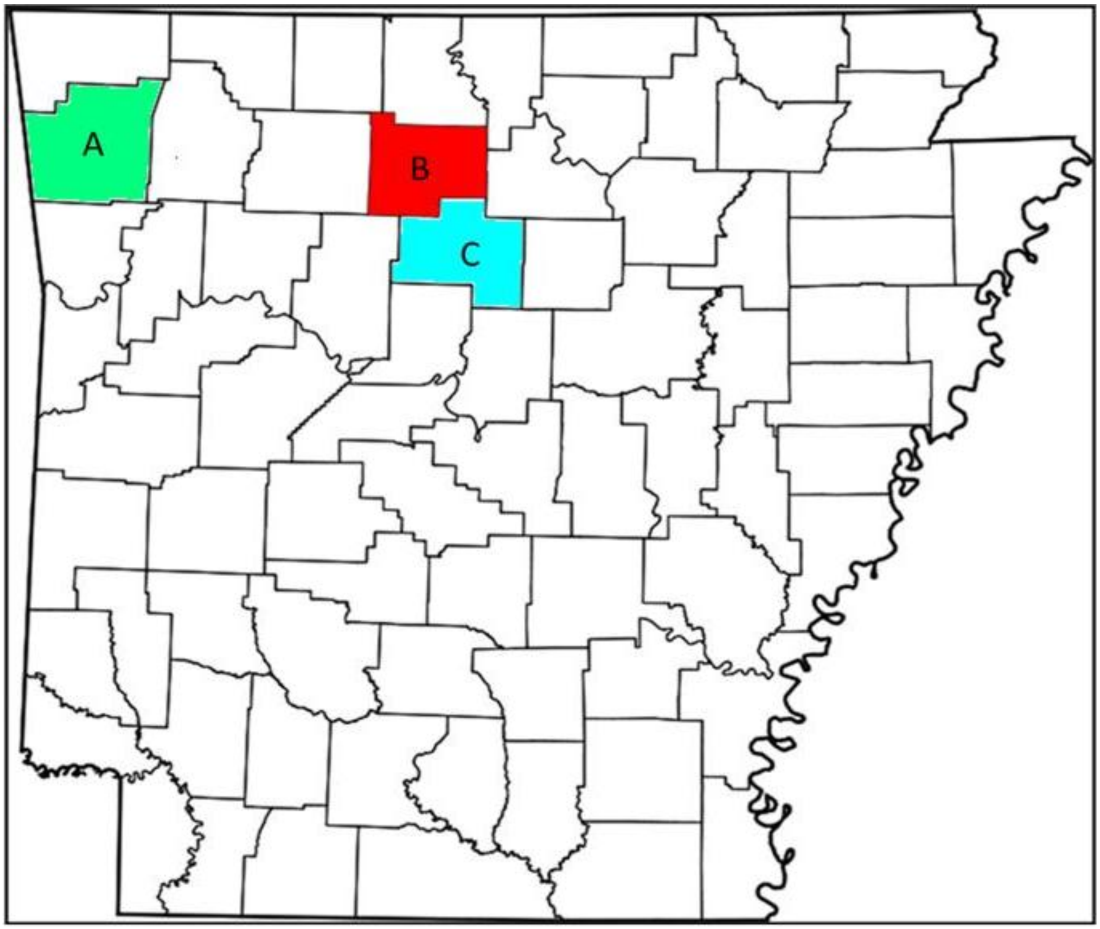


Figure 2: Map of Arkansas showing the study area counties: A= Washington, B=Searcy and C= Van Buren

The third outcrop is a road cut on the east side of U.S. Highway 65. It is located about 3.5 miles south of Leslie, Arkansas and 0.3 mile south of the Searcy-Van Buren County line in T. 13 N., R.15 W. Van-Buren County, Arkansas (Fig. 2). The outcrop starts directly south of the Peyton Creek Bridge and contains about 42 m (140 ft) of the upper part of the Pitkin Limestone and the entire Imo Shale. The upper part of Pitkin Limestone is a series of oolitic crinozoan grainstones with thin shale interbeds.

Conformably overlying the Pitkin Limestone is the Imo Shale. The Imo Shale is the youngest Mississippian in the study area (Boardman, 2010 (personal communication)). The Imo Shale is dark gray-very black, fissile, fossiliferous and concretious shale with massive sandstone and thin beds of siltstone. The dominant fossils are brachiopods and crinoids. The Imo contains a thin resistive conglomeratic crinozoan layer that is approximate 5 inches thick. This outcrop is heavily weathered and covered in part by thick forest.

1.4 Stratigraphic Relations

Stratigraphically, the succession found in the Chesterian stage includes the Hindsville, Fayetteville, Pitkin and the Imo formations (Fig. 3). Stratigraphically, the Fayetteville Shale conformably rests on the Chesterian Batesville sandstone or Hindsville Limestone (Spring Valley) or unconformably on the Meramecian Moorefield in northeastern Arkansas or the Osagean-Meramecian Boone Limestone in areas where the Batesville and the Hindsville Limestone are not present (Meeks, 1997). The basal part of the Fayetteville Shale is black shale. The middle part where exposed contains a sandstone unit called the Wedington Sandstone Member (Washington County) (Quinn, 1966). The upper part contains shale with interbeded limestone in a rhythmic pattern (Handford, 1986). This upper Fayetteville unit was once called Koger Member of the Fayetteville Formation (Taylor, 1964).

The type section exposed in Washington County, Arkansas has been described as thin bed of black limestone by McCaleb et al. (1964). This limestone is conglomeratic in places and the unit may represent a western continuation of the reef complex of the eastern Boston Mountains (Quinn, 1966). The Fayetteville Shale is conformably overlain by the Chesterian Pitkin Limestone all through its extent except in places where post-Mississippian erosion has allowed a contact with younger formations (Sutherland and Manger, 1979).

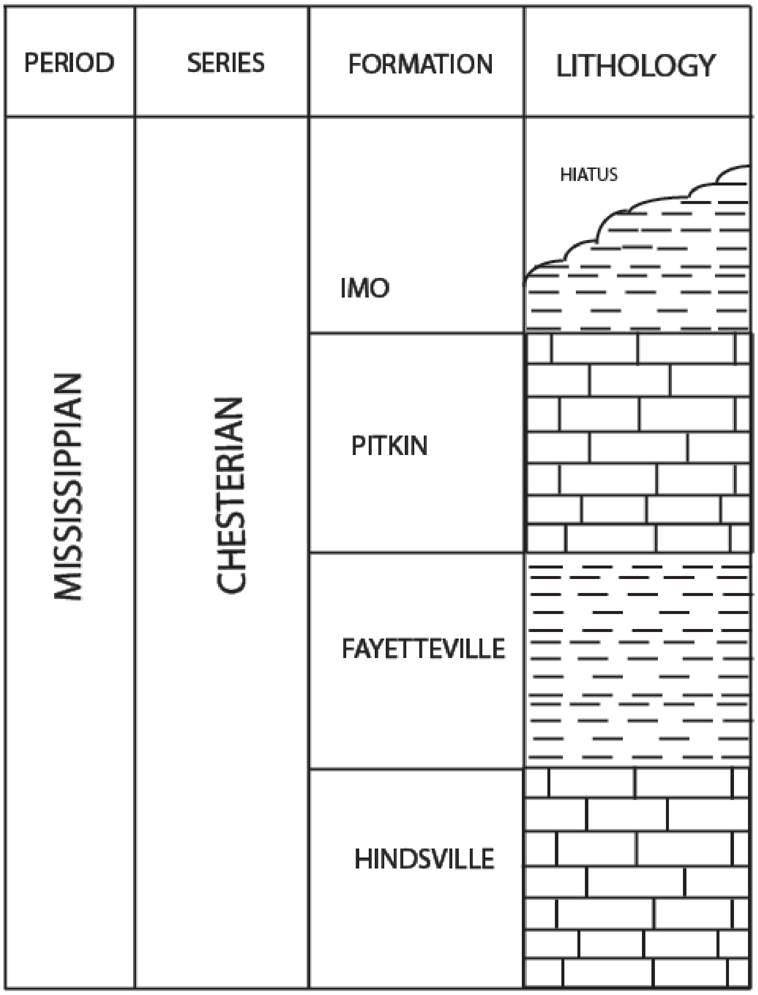


Figure 3: Generalized stratigraphic section of the Chester Series of the Ozark Uplift Northeastern Arkansas

According to biostratigraphy, the base of Fayetteville Shale is time transgressive with its oldest development in the Batesville region of northeastern Arkansas (Gordon (1965). The Pitkin Limestone contains predominantly limestone with thin lenses of shale. It is considerably less than 100 feet thick. The limestone contains *Archimedes* but goniatite cephalopods are not reported (Quinn, 1966). Quinn (1966) believed the formation is bounded above by a Late Mississippian age erosional unconformity. In the eastern portion of the Boston Mountains the stratigraphic position of the Pitkin Formation appears to be occupied by a much thicker sequence of strata including silt and shale beds as well as limestone. They also contain numerous *Archimedes* like the limestone of the Pitkin Formation (Quinn, 1966). Conformable overlying the Pitkin Limestone is the fossil-bearing black shale unit of the Imo Formation (the youngest Mississippian strata in north-central Arkansas (Dr. Boardman personal communication)). It is a highly fossiliferous, pyritic and fissile black shale. Overlying this shale unit is the grey shale unit which is followed by series of flaggy siltstones, succeeded by massive sandstones and concretious shale. *Pseudoparalegoceras* was recovered from the sandstone indicating Atokan age for the unit (Quinn, 1962). The stratigraphic interval represented by the Imo Formation corresponds with the hiatus displayed by the widespread Mississippian-Pennsylvanian unconformity across many North American sequences (Webb and Sutherland, 1993) (Fig. 3).

1.5 Depositional Setting

The depositional model for the Chesterian sequence has been described as a mesothemic cycle (Saunders et.al 1979). A regional regressive phase affecting the entire upper Chesterian in the Ozark region began with the deep-water Fayetteville Shale, advanced through the shallow-water Pitkin Formation, and ended with the gap (hiatus) at the top of the Imo Shale (uppermost, nearshore) (Webb and Sutherland, 1993).

The depositional remnants of the shallow-marine Ozark shelf are represented by the Pitkin Limestone, a largely oolitic and bioclastic facies, which conformably overlies the Fayetteville Shale (Handford, 1986). The Hindsville, Fayetteville and Pitkin form a conformable, carbonate shelf cycle of transgression followed by regression (Fabian, 1984). The Hindsville and the Batesville Sandstone were deposited in a shallow shelf environment during the beginning stages of a transgression. As the transgression continued, there is an increase in the water depth and the open marine muds of the Fayetteville were subsequently deposited on the shelf.

By middle Fayetteville time, sediments of the deltaic Wedington Sandstone were deposited in northwestern Arkansas. The end of Fayetteville time represents the time of maximum transgression along with subsidence of the Wedington and eventual inundation of the carbonate clastic source (Glick, 1979). Bioclastic carbonate mud developed on topographic highs at the end of the upper Fayetteville. By early Pitkin, there was regression of seas, water depth decreased, thereby bringing the bottom water into the photic zone, which lead to carbonate deposition over the shelf (Fabian, 1984). Easton (1942) suggested that the deposition of Pitkin sediments began in the southeastern part and spread to western Arkansas in middle Pitkin time, and receded to the east and south in late Pitkin time.

In the Marshall outcrop, the Fayetteville Shale grades into the bioclastic-oolitic Pitkin Limestone. The mudstone and the wackestone of Pitkin Limestome at Marshall were interpreted to have been deposited in relatively deeper water based on their closeness to the basin and quiet water fauna associated with them (Handford, 1986).

The Fayetteville Shale and Pitkin Limestone generally display and represent a single shoaling-upward progradational system (Jehn and Young, 1976; Handford, 1986). The black lower shale unit of the Fayetteville Shale represents deposition on a deep shelf, while the rhythmic upper limestone unit represents deposition on a storm-dominated, muddy shelf (Handford, 1986). Oolitic grainstones of the Pitkin Limestone reflect deposits formed in a lower shoreface environment that prograded over the Fayetteville Shale. The Pitkin Limestone at Peyton Creek contains leaf molds and fossilized wood. These were interpreted as deposits of lagoonal and marsh environments (Jehn and Young, 1976).

The Chesterian Imo Shale of northern Arkansas represents the youngest Mississippian strata present on the Ozark platform and contains a unique, coral fauna that is transitional between Mississippian and Pennsylvanian assemblages (Webb and Sutherland, 1993). The fauna of the Imo Formation of north-central Arkansas in North America represents one of the most fossiliferous Mississippian intervals reported (Webb and Sutherland, 1993). The stratigraphic interval represented by the Imo Formation corresponds with the hiatus displayed by the widespread Mississippian-Pennsylvanian unconformity across many North American sequences (Webb and Sutherland, 1993). The goniatite fauna in the Imo Shale has been used to determine the age and establish correlations (Saunders, 1973). The Imo is correlated with the late Chesterian conodont assemblage zone that extends through ammonoid-bearing interval at the Peyton Creek road cut (Mapes and Rexroad, 1986).

The Imo coral fauna characteristically contains elements that are characteristic of both the Mississippian and Pennsylvanian period (Webb 1987; Webb and Sutherland, 1993) and no species present in Imo has been reported in the underlying Pitkin Formation (Webb and Sutherland, 1993). Hawkins (1983) noted evidence of a brackish environment in the collected corals in the upper part of the Imo Shale. Also, the sandstone unit of the

Imo Shale contains terrestrial plant fragments. As a result, the environment of deposition is interpreted as a relatively low-energy, shallow-water environment undergoing slow, and incessant deposition of terrigenous materials with intermittent higher energy invasion of carbonate sediments (Webb and Sutherland, 1993). Webb (1987) noted that the Imo coral fauna is very distinct from that of the Pitkin Limestone. This is probably the result of different environments of deposition. Imo corals occur in shale, while most of the Pitkin corals occur in shallow-water, high-energy oolitic and bioclastic grainstones (Webb and Sutherland, 1993). Imo shales are rich in terrigenous materials because they are associated with a regressing shoreline. This suggests that Imo-like coral assemblages, containing *Lophophyllidium*, *Amplexizaphrentis*, and *Bradyphyllum*, show diagnostic features of environments with muddy substrates (Webb and Sutherland, 1993).

1.6 Previous Work Done in the Areas

This section will discuss considerable numbers of published work available on the following Chesterian Stage formations: Hindsville Limestone/Batesville Sandstone, Fayetteville Shale, Pitkin Limestone and Imo Shale.

1.6.1 Batesville Sandstone/Hindsville Limestone

Quinn (1966) described the Moorefield (Ruddell) and Batesville Formations as most extensively and characteristically developed in the eastern part of the Boston Mountains and are not clearly identified in the western part.

Batesville Sandstone in the western part of the Boston Mountain is represented by a unit described as the Hindsville Member of the Batesville Sandstone (Purdue and Miser, 1916). Overlying the Batesville Sandstone is the Fayetteville Shale and this crops out across the entire Boston Mountains front from the vicinity of Oil Trough, eastern Arkansas into western Oklahoma (Quinn, 1966).

Purdue and Miser (1916) described a thin limestone resting on shale, conglomerates and sandstone that lies between Fayetteville and Boone rocks in Washington County, Arkansas. This limestone was named the Hindsville Member of the Batesville Formation (Purdue and Miser, 1916). The same limestone was also reported by Adams and Ulrich (1904) to belong to the Fayetteville Formation although it contains a Moorefield-Batesville fauna. "Because of this fauna and the unfounded assumption that the limestone belongs to the Fayetteville Formation it has been supposed the base of the Fayetteville is of Moorefield age and the formation spans the Namurian-Visian boundary" Quinn (1966). The "basal limestone" belongs with the rocks below, which are referred to as the Hindsville Formation (Quinn, 1966).

1.6.2 Fayetteville Shale

There is a considerable amount of published work available on the depositional environment, stratigraphy, structures, geomorphology, geochemistry, and fossil content of the Fayetteville Shale. The significant work done in this area includes that of the following authors. According to Meeks (1997), Owen (1858) was the first to study the lithology of the Fayetteville Shale, but he did not give it the name "Fayetteville". Owen (1858) correctly described the lithology and interpreted the age as sub-carboniferous. According to Meeks (1997), Branner (1891) proposed the name Fayetteville shale.

Gaughan (1913) described the Fayetteville Shale near Fayetteville Arkansas and discussed the origin, formation and growth of the concretions.

Spreng (1967) described submarine slump structures in the Fayetteville Shale northwestern Arkansas. He noted the slump balls (limestone mounds or rolls), slump sheets (irregular shaped beds), sharply cut off beds, depression of beds under the mounds, and chert and limestone breccias.

Quinn, (1966) reported the occurrence of vascular plants collected from Fayetteville Shale and Imo Shale in Arkansas. He also noted that the Fayetteville fauna is very uniform and is entirely Namurian in character (Quinn, 1966).

Taylor and Eggert (1967) reported the occurrence of petrified plants from the Chesterian Fayetteville and Imo shales.

Steele and Lamb (1977) carried out geochemistry analysis of the Fayetteville in northwestern Arkansas and reported the geochemical properties exhibited by the upper and lower Fayetteville shale suggest a similar source and depositional environment as the Devonian-Mississippian Chattanooga Shale.

Handford (1986) described hummocky cross-stratification and related storm-generated features in limestones from the upper Fayetteville shale and Pitkin limestone and used interpretations of these shelf-carbonate storm deposits to construct depositional model of the late Mississippian shelf environments in northern Arkansas.

Meeks (1997) described the taphonomy of the cephalopods and ammnoids that occur in the Fayetteville Shale in Arkansas.

Murthy et.al (2004) described the rare-earth element chemistry of phosphate nodules across Fayetteville Shale of Oklahoma and Arkansas to interpret paleoenvironment and geochemistry during.

Ratchford and Bridges (2006) characterized organic geochemistry and thermal maturation of Fayetteville Shale.

1.6.3 Fayetteville Shale Hydrocarbon History

The Arkoma Basin has a long history of known large conventional gas accumulations. However, recently it has become a hot spot for unconventional hydrocarbon exploration. It is estimated that the Arkoma Basin contains over 4 trillion cubic feet of undiscovered conventionally trapped natural gas, mostly within shallow marine to deltaic Pennsylvanian sandstones of the Atokan Formation (Cemen et.al, 2009). Over the past decade, the focus of exploration has shifted from these conventional reservoirs to the Fayetteville Shale which is approximately age equivalent to the Barnett Shale in the Fort Worth Basin and Caney Shale in Oklahoma (Fig. 4).

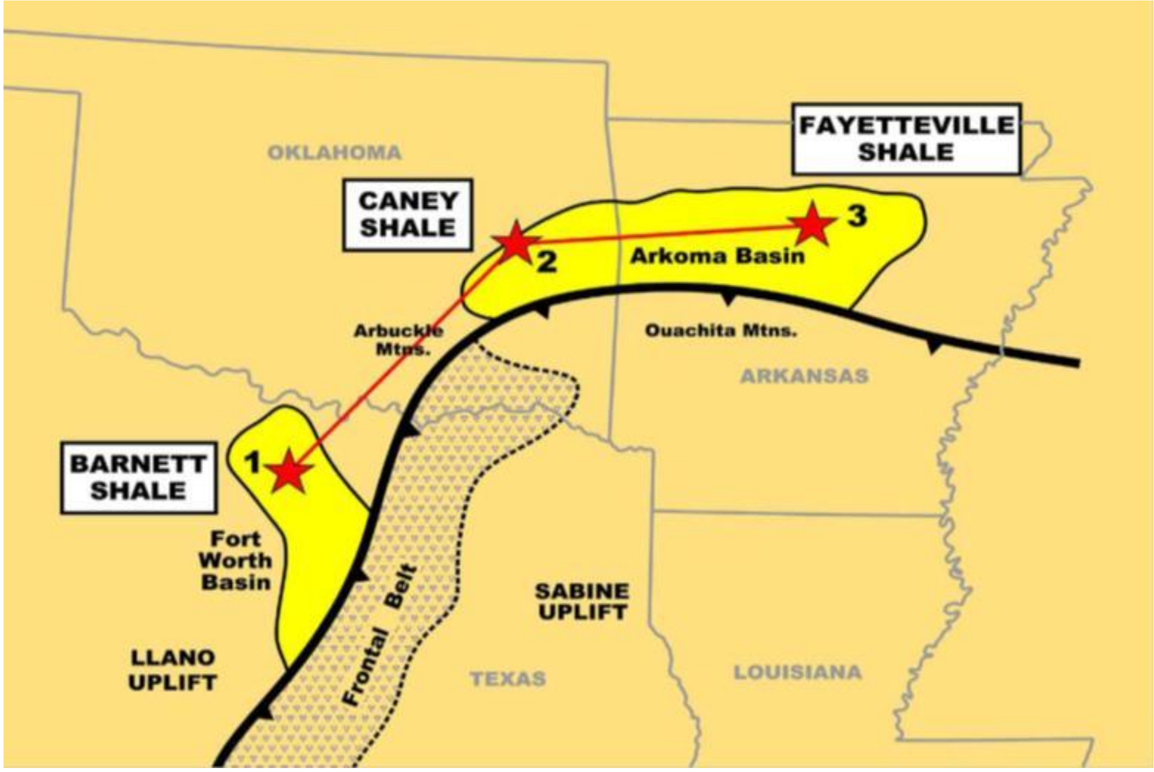


Figure 4: Fayetteville Shale in Arkoma Basin and its equivalent in Oklahoma end of the Arkoma Basin (Caney Shale) and Fort Worth Basin (Barnett Shale) (Shelby, 2008)

The Fayetteville Shale play in Arkansas is among the most active shale-gas play in the US today (Table. 1).

Deep part of the Arkoma Basin has shown that with tight sandstone reservoir and unconventional shale gas play, the basin may be a continuous basin-centered gas accumulation (Brown, 2009). During much of the Paleozoic, the Arkoma Basin was a passive, south-facing margin of the Ouachita orogeny. The Ouachita orogenic belt loads the margin during the Late Mississippian which led to progressive break down of the passive margin northward thereby forming a foreland basin. This foreland was filled by sediments off the Ouachita Orogenic belt (McGilvery and Housekenecht, 2000; Brown, 2009).

Parameters	Barnett shale(Core)	Woodford Shale	Haynesville Shale	Marcellus Shale	Fayetteville Shale	Moesian Platform Silurian Shale
Depth, ft TVD	6500-9000	6000-13000	10500-13500	5000-8,500	1500-6500	11000-19000
Average Thickness, ft	100-500	150	200-240	50-200	20-200	700-2,200
Average total porosity, %	4.1-6.1	6.1-8	8.1-12	2.1-8	2.1-8	1.0-2.0
GIP, BCF/Section	20-50	40-120	150-250	25-65	25-65	70-90
Average TOC, wt%	3.5-8.1	3.1-10	3.1-5	4.0-9.5	4.0-9.5	4.48

Table 1: Major Shale Gas Play in North America (Deutsche Bank and XTO Energy)

The reservoirs of the Arkoma Basin are thermally matured such that the water legs were destroyed by thermal maturation. In deep areas of the basin, wells never encounter water and it is either there is porosity that is gas filled or no porosity at all (Brown, 2009). Oils in the reservoir in Arkoma Basin were turned to wet and subsequently to dry gas before 300 ma. Generally, the present gas in the basin was charged about 310 ma (Byrnes and Lawyer, 1999).

Drilling history in Arkoma Basin has revealed that the basin contains a channelized turbidites at depth. Hitting these channels produces gas very low on the structure with no water. If these are anything to go by, future drilling in well evaluated zones in Arkoma basin is more likely to be a success (Brown, 2009).

In 2008 the United States government indicated that annual U.S. gas demand could increase from 22 Tcf (trillion cubic feet) to 24 Tcf by the year 2016 and then decline to 23 Tcf by 2030. Before 2006, domestic gas production was flat and the gas production increased from 2007 to by 9% with Barnett Shale providing larger percentage of the growth (Curtis, 2009). Production of Shale gas in the United States starts as early as 1821 and it is now rapidly increasing, accounting for about 7% of the US annual production. By 2025, it is believed that shale gas production will account for 50% of the total production (Curtis, 2009). This assumption is supported by the developing shale gas resources in the Appalachian, Anadarko, Arkoma, Ft. Worth, and Permian basins (Fayetteville, Haynesville, Marcellus plays and Eagle Ford plays) (Table 1).

Southwestern Energy started producing from drilling Fayetteville Shale in July of 2004 and currently over 500 wells are producing from the Fayetteville and about 460 of these wells are horizontal. Total production to date from the Fayetteville shale is well over 52 Bcf and daily production averaged over 230 MMcf (Shelby, 2008). Drilling activities within the Fayetteville Shale Play is growing at a rapid pace as Southwestern Energy, Chesapeake Energy, XTO, Petrohawk and other companies having over 45 rigs in operation. Currently Fayetteville is producing from southern Van Buren, Cleburne, northern Conway, northern Faulkner, and northern White Counties in north-central Arkansas (Shelby, 2008). Improving exploration, completion, and production technologies has made Shale gas technically recoverable and economically viable.

Southwestern Energy started drilling in the Fayetteville play in July of 2004 in northern Conway County. At the onset, wells in Fayetteville Shale were all vertical wells, no 3-D seismic, no single conventional play and Nitrogen foam fracs were greatly in use (Shelby, 2008).

By February of 2008, all Fayetteville Shale play is producing from horizontal wells and the lateral length increased from the initial 1200-2000 feet to about 3000-4000 feet across most of the play. Also by this time, almost all the Fayetteville fracs are slickwater, 3-D programs was introduced by Chesapeake and several good conventional wells are producing. Production results of the Fayetteville Shale play from day one have continued to improve, more slickwater fracs are performed and then lateral lengths have also increased (Shelby, 2008). The developing Fayetteville Shale play is becoming the largest gas-producing interval in Arkansas.

1.6.4 Pitkin Limestone

The Pitkin Limestone of Arkansas was first recognized by D. D. Owen, who named it “Archimedes limestone”, but it was later named the “Pitkin limestone” by E. O. Ulrich in 1904 from outcrop exposed near the town of Woolsey (formally called Pitkin), in Washington County (Easton,1943).

Adams and Ulrich (1904) were the first to use the term Pitkin Limestone in place of the older “Archimedes Limestone” in order to comply with the rules of stratigraphic nomenclature.

Easton (1942) proposed the name changing from Pitkin Limestone to Pitkin Formation having realized that it contained a considerable proportion of shale and some lenticular sandstone bodies.

Snider (1915) did detailed paleontological studies of the Chesterian series. He discussed the generalized lithologies of the Mississippian strata as well as the trends associated with the Mississippian-Pennsylvanian unconformity.

Buchanan (1927) discussed the distribution and correlation of the Pitkin Limestone in Oklahoma, while Roth (1929) established the regional relationships of the Pitkin when he correlated the Mississippian faunas of Oklahoma and Arkansas. Also Laudon (1941) described crinoids in the Pitkin and Hale Formations in northeastern Oklahoma.

Easton (1942 and 1943) studied the fauna and stratigraphy of the Pitkin in Arkansas and suggested that the deposition of Pitkin sediments began in the southeast and spread to western Arkansas in middle Pitkin time, and receded to the east and south in late Pitkin time.

Other studies that discussed the biota, depositional environment and stratigraphy include: Laudon (1958), Lane (1967), Lane and straka (1974), Sutherland and Manger (1977), Quinn (1966), Jehn and Young (1976), Fabian (1984), Handford (1986) and Heydari et.al (1993).

1.6.5 Imo Shale

The name “Imo” was proposed for this formation by Mackenzie Gordon in 1964 for sequence of late Mississippian shale with interbedded sandstone and conglomerate above the Pitkin Limestone and below the Cane Hill Member of the Hale Formation (Webb and Sutherland, 1993; Hutto and Smart, 2010).

Gordon realized that this unit contains indisputable Mississippian-age fossils, but dropped the name in the same publication it was first proposed due to concurrent mapping by Glick. Glick erroneously included this unit in his Cane Hill Formation which crossed the Mississippian-Pennsylvanian boundary (Hutto and Smart, 2010). This was due to the difficulty delineating its upper contact in the field which is typically a shale-shale contact. In 1964, the Geologic Names Committee of the USGS adopted the name Cane Hill Formation officially and the name Imo Formation was officially abandoned (Hutto and Smart, 2010).

Quinn (1966) questioned the usage of Cane Hill in place Imo and as a formation in Arkansas. Also Hawkins (1983) provided stratigraphic and lithologic evidences indicating that Cane Hill Formation and Imo Shale could be consistently differentiated. Hence, the name Imo was reinstated and the name Imo has continued in recent literature.

Recently, geologic mapping for the STATEMAP Program (2006-2009) has delineated the Imo interval and to date, the Imo has been mapped in five counties totaling about 73 square miles of outcrop area. And it has been distinguished lithologically and paleontologically from the Cane Hill on a regional scale (Hutto and Smart, 2010).

Over the years Imo fossils has received a lot of taxonomic and biostratigraphic attention from several authors. Quinn (1966) reported the occurrence of vascular plants collected from Fayetteville Shale and Imo Shale in Arkansas. Also Taylor and Eggert (1967) one of the early investigators to work on the paleobotanical discovery in the Fayetteville Shale and Imo Shale in Arkansas reported the occurrence of petrified plants from the Chesterian Fayetteville and Imo shales.

Mapes et.al (1986) reported an unusual occurrence of colony of microcrinoids of the Late Mississippian from the Imo Formation of Arkansas. They noticed specimens of Rayonnoceras that shows evidence of a repaired shell, indicating that a significant part of the body chamber had been broken away and subsequently repaired. This indicates that large predators that could cause huge shell damage were present in Imo seas. On the contrary, the fragment could have been reworked or redistributed into the sediment.

Hawkins (1983) provided stratigraphic and lithologic evidences indicating that Cane Hill Formation and Imo Shale could be consistently differentiated. Hence, the name Imo was reinstated. He also noted evidence of brackish environment in the collected corals in the upper part of the formation. Also the sandstones in the formation contain terrestrial plant fragments. As a result, the environment of deposition is interpreted as a relatively low-energy, shallow-water environment undergoing slow, and incessant deposition of terrigenous materials with intermittent higher energy invasion of carbonate sediments (Webb and Sutherland, 1993).

(Webb, 1987) noted that the Imo coral fauna is very distinct from that of the conformably underlying Pitkin Limestone. This is probably as a result of different environments of deposition. Imo corals occur in shale, while most of the Pitkin corals occur in shallow-water, high-energy oolitic and bioclasticgrainstones (Webb and Sutherland, 1993).

Webb and Sutherland, (1993) extensively described distinctive coral fauna of the Imo Formation north-central Arkansas, which includes 10 solitary rugose species and one tabulate coral species and this is represented by over 300 specimens. The following genera were included: *Bradyphyllum, Amplexizaphrentis, Barytichisma, Lophamplexus, Lophophyllidium*, and *Tectamichelinia*. This study produced a better understanding of the age and correlation of the Imo Formation

CHAPTER II

2.1 Origin of the Arkoma Basin and Sedimentation

The Arkoma basin was formally referred to as the “Arkansas-Oklahoma Coal Basin”, “Arkansas Valley Basin,” and the “McAlester Basin”. Over the years, for the purpose of literature and clarity, the Geologists of the two states adopted the name “Arkoma Basin” (Branan, 1968). The Arkoma Basin includes portions of west-central Arkansas and southeastern Oklahoma and includes an area of about 33,800 sq. mi. The maximum length of the province is about 315 mi, east-west, and the maximum width is about 175 mi, north-south. The Arkoma Basin is approximately 250 miles long and about 50 miles wide.

During the Ouachita Orogeny, collision of the North American Plate and a southern landmass known as Llanoria formed the Arkoma Basin and Ouachita Mountains (Houseknecht and Kacena, 1983) (Fig. 5) In Arkansas the province is bounded on the north by the Ozark Uplift and in Oklahoma it is bounded on the north by the Cherokee Platform. The northern part of the province is a major foreland basin. The Arkoma Basin developed in front of and north of the Ouachita Fold and Thrust Belt. It is characterized by down-to-the-south normal faults which affect Early Pennsylvanian and older rocks (Houseknecht and Kacena, 1983; Byrnes and Lawyer, 1999).

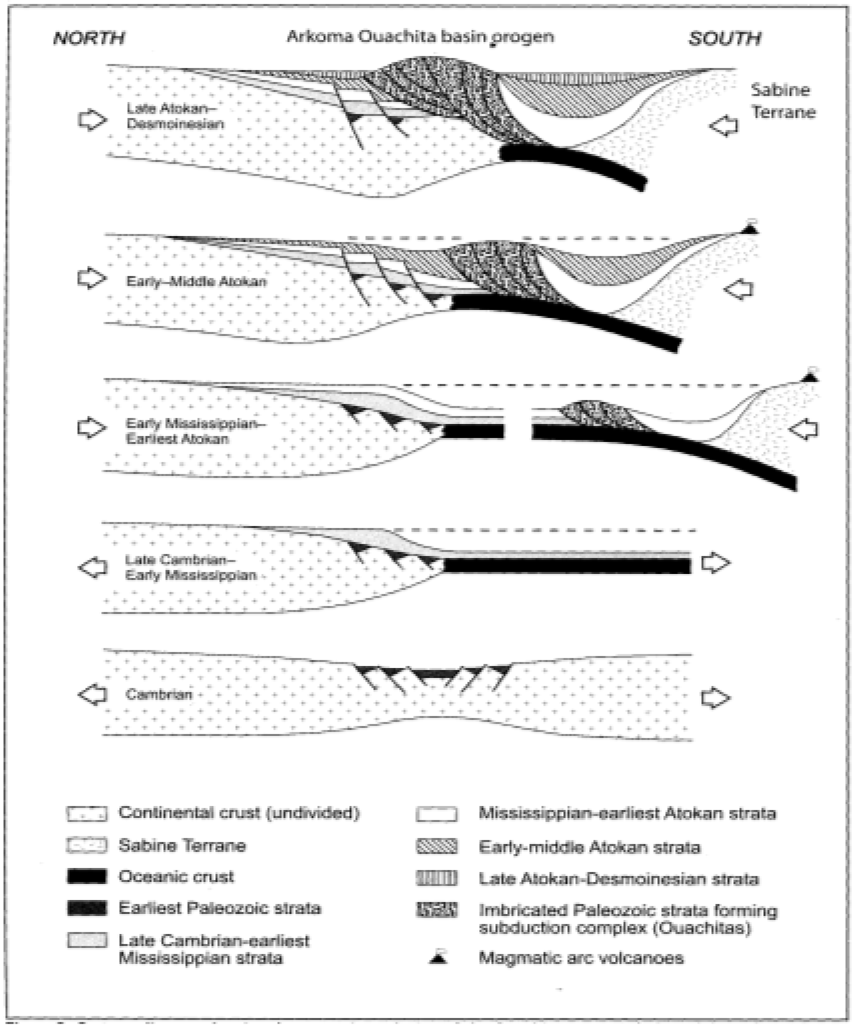


Figure 5: Tectonic evolution of the Arkoma Basin with structural cross section drawn from North to South. A)Mid-Late Cambrian (510Ma), B) Devonian (345Ma), C) Mississippian (345Ma), D) Early Pennsylvanian (315Ma), E) Late Pennsylvanian (300Ma).(after Houseknecht and Kacena, 1983 and Keller, 2009)

Sedimentary rocks in the Arkoma Basin range in thickness from 3,000 to 20,000 ft and consist primarily of pre-Mississippian carbonate shelf deposits, organic-rich Mississippian marine shales and Pennsylvanian fluvial deposits (Byrnes and Lawyer, 1999).

The Arkoma Basin was formed in the Carboniferous as a result of the Ouachita orogeny. The Pennsylvanian Ouachita Orogeny is also responsible for the generation of other foreland basins such as the Black Warrior (Mississippi and Alabama) and Fort Worth (Texas), which all lie landward along the Ouachita fold thrust belt (Fig 6). These basins are related both stratigraphically and tectonically (Branan, 1968). The Basin trends in an east-west direction with the Ozark Uplift and the Oklahoma Platform on the northern side and the Choctaw and Ross Creek Faults on the south (Houseknecht and Kacena, 1983; Byrnes and Lawyer; 1999).

During the early Cambrian to early Pennsylvanian, Arkoma basin was part of a continental shelf on the boundary of a passive continental margin (Houseknecht, 1986 and Sutherland, 1988). This shelf was transformed into a foredeep basin in the Middle Pennsylvanian as a result of continental convergence. From the Cambrian to the Middle Mississippian, shallow water carbonates of Arbuckle Group as well as the Viola and Hunton groups were deposited on the shelf. In the southern Arkoma Basin, black shales and cherts were deposited (Houseknecht and Kacena, 1983; Byrnes and Lawyer, 1999). The basin is characterized by the presence of growth faults, anticlines and synclines (Branan, 1968; Houseknecht and Kacena, 1983; Byrnes and Lawyer, 1999). Clastic invasion interrupted carbonate deposition in the Middle Ordovician, this deposition brought about the Simpson Group. Some parts of the Hunton, Viola and Simpson Groups were removed as a result of erosional events of regional extent which took place in the Middle and Late Devonian. Overlying the unconformity created by the erosional event is the Sylamore Sandstone and the Woodford Shale (Byrnes and Lawyer; 1999). In the Middle Mississippian, the Arkoma shelf, although stable at this time, began to experience subsidence due to the pressure exerted on it by the thrust sheets from the south. Subsequently, there was the deposition of the Jackfork and Stanley Groups. Terrigeneous sediments were deposited along the Shelf margin of the Arkoma Basin. This was followed by the formation of growth faults, which changed the Shelf into a foreland basin and the deposition of lithic arenites. (Byrnes and Lawyer, 1999). Following the cessation of fault movement, deltaic systems moved west and south of the foreland basin (Sutherland, 1989). With the cessation of deposition, subsequent folding took place on a regional level (Byrnes and Lawyer, 1999).

2.2 Stratigraphic Setting of the Arkoma Basin

The Arkoma Basin is a foreland basin formed during the Pennsylvanian Ouachita Orogeny. It is an east-west trending arcuate foreland basin bounded on the north by the Ozark Uplift and Oklahoma Platform and on the south by the Choctaw and Ross Creek Faults which separates it from the Ouachita Foldbelt. It is bounded on the west by the Arbuckle Mountains and on the east by the Mississippi Embayment (Byrnes and Lawyer, 1999) (Fig 6).

The Arkoma Basin contains sedimentary rocks that date from the Cambrian to the middle Pennsylvanian. Deposition in the Arkoma Basin occurred in three unique depositional periods starting from the Cambrian. The first depositional period was about 5,000 ft. miogeoclinal deposits from the Cambrian to Early Atokan (Houseknecht and McGilvery, 1990). This followed by 18,000 ft. Middle-Late Atokan strata which were deposited as a result of syndepostitional growth fault movement. And the 8,000 feet Pennsylvanian Desmoinesian Series strata of the late stages of the basin formation (Houseknecht and Kacena, 1983).

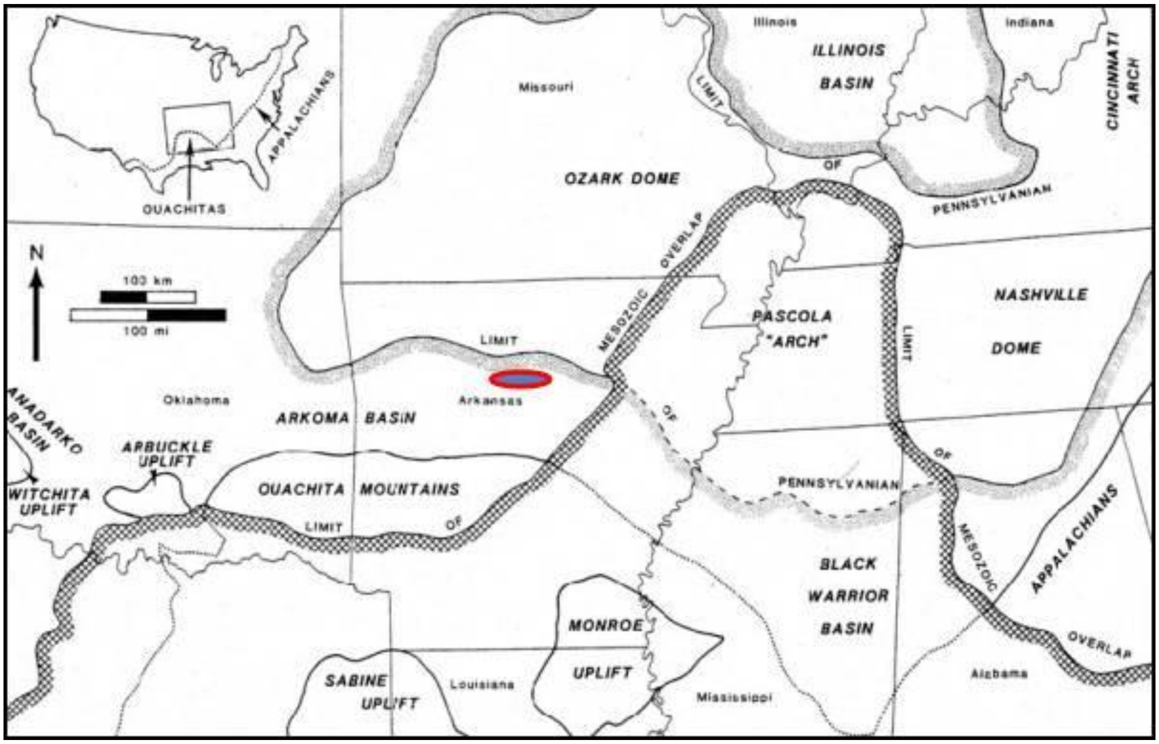
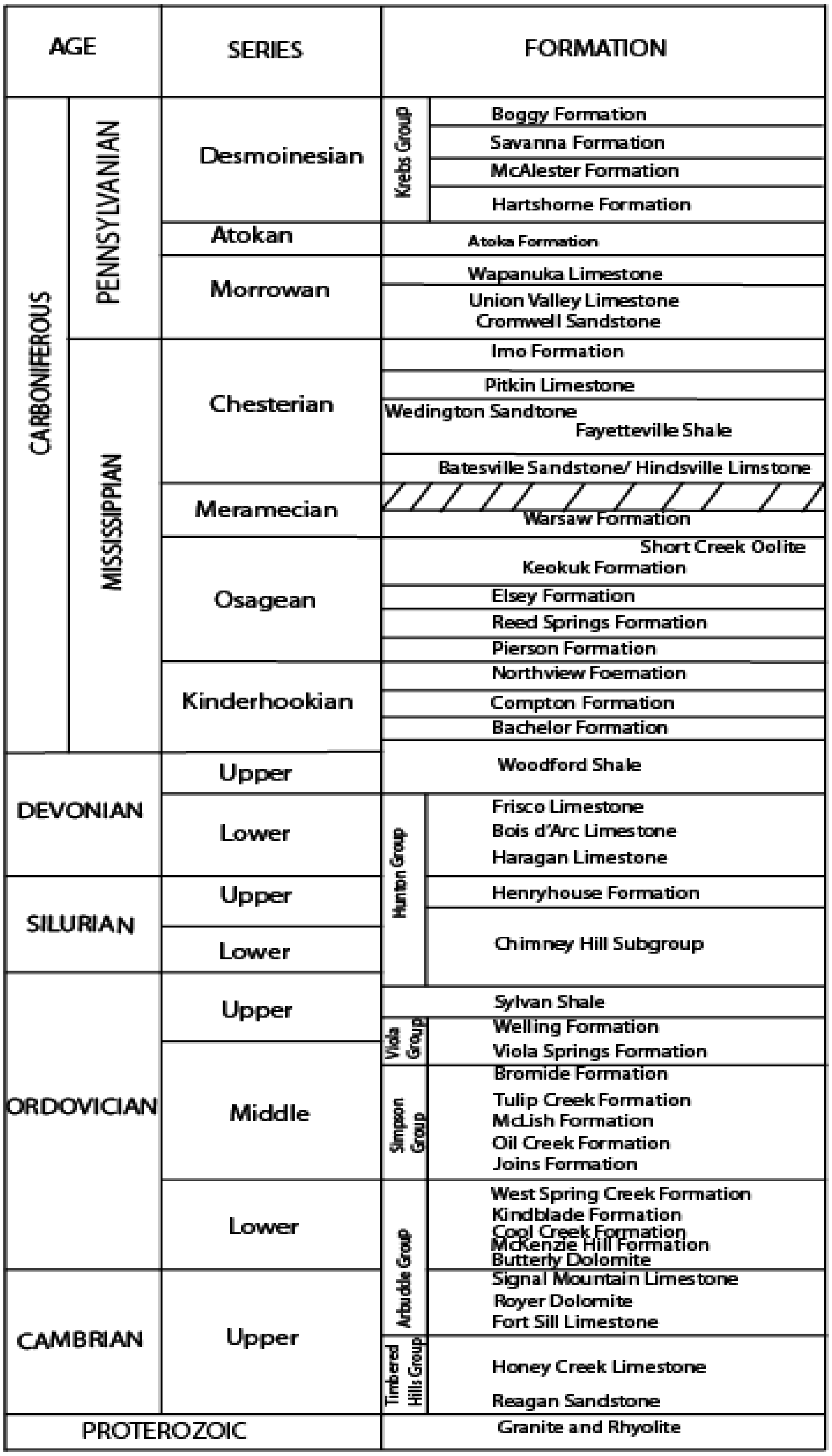


Figure 6: Structural position of the Arkoma Basin and the red spherical dot is showing the approximate position of the study area within the basin (Houseknetch, 1986)

The Arkoma Basin is underlain by Proterozoic crystalline basement. This is followed by Reagan Sandstone which first and widespread strata of the Arkoma Basin. It is deposited unconformably above the basement rocks. The Early Ordovician consist predominantly shallow marine deposits of the Arbuckle Group. During this period, deposition on the shelf consisted predominantly of a southward-thickening sequence of predominantly shallow-water carbonates of the Arbuckle Group about 1,000 to 6,500 feet thick (Byrnes and Lawyer, 1999).This is overlain by the Middle Ordovician Simpson Group, which contains shoaling-upwards sequences (Ham, 1969). The Middle to Late Ordovician represented by the shallow marine carbonate deposits of the Viola Group. The Late Ordovician contains the Sylvan Shale and the Keel Formation of Chimneyhill Subgroup of the Hunton Group (Sutherland, 1988) (Fig. 7)



AGE		SERIES	FORMATION	
CARBONIFEROUS	PENNSYLVANIAN	Desmoinesian	Krebs Group	Boggy Formation
				Savanna Formation
				McAlester Formation
				Hartshorne Formation
		Atokan		Atoka Formation
		Morrowan		Wapanuka Limestone
				Union Valley Limestone Cromwell Sandstone
	MISSISSIPPIAN	Chesterian		Imo Formation
				Pitkin Limestone
				Wedington Sandtone Fayetteville Shale
				Batesville Sandstone/ Hindsville Limstone
		Meramecian		Warsaw Formation
		Osagean		Short Creek Oolite Keokuk Formation
				Elsey Formation
				Reed Springs Formation
				Pierson Formation
		Kinderhookian		Northview Foemation
				Compton Formation
				Bachelor Formation
DEVONIAN		Upper		Woodford Shale
		Lower	Hunton Group	Frisco Limestone Bois d'Arc Limestone Haragan Limestone
SILURIAN		Upper		Henryhouse Formation
		Lower		Chimney Hill Subgroup
ORDOVICIAN		Upper		Sylvan Shale
			Viola Group	Welling Formation Viola Springs Formation
		Middle	Simpson Group	Bromide Formation Tulip Creek Formation McLish Formation Oil Creek Formation Joins Formation
		Lower	Arbuckle Group	West Spring Creek Formation Kindblade Formation Cool Creek Formation McKenzie Hill Formation Butterly Dolomite
CAMBRIAN		Upper		Signal Mountain Limestone Royer Dolomite Fort Sill Limestone
			Timbered Hills Group	Honey Creek Limestone Reagan Sandstone
PROTEROZOIC				Granite and Rhyolite

Figure 7: Stratigraphic nomenclature of the Arkoma Basin (Modified from Sutherland 1988 and Johnson 1988)

The Silurian and Lower Devonian strata are represented by the Hunton Group. The Hunton group (Limestone) rests unconformably on the Sylvan Shale. After the deposition of Hunton Group, there was an epeirogenic uplift which caused a major unconformity that separates the Hunton Group from the overlying Woodford shale (Johnson, 1988). The Woodford is a Late Devonian-Early Mississippian black, organic rich shale (Ham, 1969). It is fossiliferous and evidently deposited in a deep marine setting (Suneson et al., 2005).

There was a severe change of conditions during the Mississippian as thick turbidites were deposited into the basin (Sutherland, 1988). Mississippian strata are predominantly black, organic-rich Caney Shale and the Chesterian Series. The Late Mississippian is represented by Springer Shale. It also represents a major detachment surface between Pennsylvanian extensional and compressional tectonics. By the middle Mississippian, Arkoma Basin stable shelf began to subside as result of load of thrust sheets coming from the south. To the south of the basin, in the Ouachita Trough, Stanley and Jackfork Groups were deposited. They are thick flysch-type deposits originated from the east and southeast Ouachita orogenic belt (Byrnes and Lawyer, 1999). To the north on the Arkoma Shelf, terrigenous sediments were deposited, originated predominantly from the Illinois Basin region to the northeast.

Upper Mississippian Chesterian Series are exposed in the southern Ozark area (Northwest Oklahoma to North central Arkansas). They consist of interbeds of shallow marine limestone and shale (Sutherland, 1988). The Chesterian Series from the oldest to the youngest include upper Moorefield, Hindsville, Fayetteville, Pitkin and Imo formations. The Fayetteville Shale and the Imo Shale are the main rock units studied in this thesis. During the Chester period, the southern limit of carbonate deposition takes place in the subsurface and south of this line, as such there is an abrupt facie change to shale as the outer shelf deepens eastward. The Caney Shale is a continuous shale sequence at the subsurface to the west of the Arkoma Basin in Oklahoma underlying the Lower Pennsylvanian Cromwell Sandstone. Caney is subdivided into Mississippian Caney and Pennsylvanian Caney (Sutherland, 1988). At the end of the Mississippian, there is upwarping of the transcontinental arch and the Ozark dome and sinking of the Ouachita trough. As a result, the sea began to regress and subsequently led to the southward tilting of the Arkoma shelf north of the trough. This was all occurring as the southern landmass known as Llanoria was encroaching upon the North American plate. Due to the collision, the Chesterian Series was progressively truncated creating a regional angular unconformity at the base of the Pennsylvanian (Houseknecht and Kacena, 1983 and Sutherland, 1988). The Pennsylvanian rock units of the Arkoma Basin are highly productive reservoir sands. They include the following: Morrowan Series, Atokan Series, and Desmoinesian Series (Sutherland, 1988).

By middle Atokan time, there was a down-to-the-south normal fault which affects early Pennsylvanian and older rocks (Branan, 1968; Housekenecht and Kacena, 1983; Byrnes and Lawyer, 1999). This fault transformed the southern Arkoma Shelf into a foreland basin. Afterwards, Thick sequences of lithic arenites, sourced mainly from the uplifted and eroding Ouachita orogenicfoldbelt were deposited to the south and southeast (Houseknecht and Kacena, 1983; Byrnes and Lawyer, 1999). Major fault movement stopped by the end of Atokan time and thick Late Atokan and Desmonesian strata spread westward and southward over the basin. By the end of the Desmoinesian,major deposition ceased and this was subsequently followed by a period of regional folding. From the early Mesozoic to the recent, erosional events led removal of a considerable large thickness of stratigraphic section from both the Arkoma Basin and the Ouachita Foldbelt (Byrnes and Lawyer, 1999). The general stratigraphic history of the Arkoma Basin can be represented by extremely faulted a thin early Paleozoic section of carbonates and organic-rich shale overlain by a thick section of interbedded sandstone and shale (Byrnes and Lawyer, 1999).

2.3 Structural Framework of the Arkoma Basin

The Arkoma Basin is a synclinorium foreland basin that formed along the North American side of the Ouachita mountain belt during Carboniferous orogenesis (McGilvery and Houseknecht, 2000). It is an arcuate structural feature located in southeastern Oklahoma and northwestern Arkansas. It is bounded to the south by the Ouachita Mountains, to the north by the Ozark Uplift, to the northwest by the Cherokee Platform. It is bounded to the west by the Hunton Arch, to the southwest by the Arbuckle Mountains, and to the east by the Reelfoot Rift and Mississippian Embayment (Cemen et.al, 2009). According to Branan (1968) the sedimentary rock thickness ranges from 3,000 feet on the northern shelf of the basin about 30,000 feet along southern part of the basin. The Arkoma Basin is approximately 250 miles long and about 50 miles wide. During the Ouachita Orogeny, collision of the North American Plate and a southern landmass known as Llanoria formed the Arkoma Basin and Ouachita mountains (Houseknecht and Kacena, 1983). The combination of the following forces has made the rocks of the basin to be highly deformed: The tensional forces resulting from the stability of the Ozark Plateau on the north during basin subsidence caused evolution of major block faulting in the basin. Some of these faults developed synchronously with deposition of Lower Pennsylvanian beds; Ouachita mountain building during Early Permian on the south compressed beds of the Arkoma basin into a chain of long, narrow, east-west anticlinal and synclinal folds. Some of the folds have surface expressions extending for several miles and overthrusting along anticlinal axes near the mountain front is common (Branan, 1968).

The evolution of the Basin started during the late Pre-Cambrian and into the Cambrian with the major rifting event that triggered the opening and closing of an early Paleozoic ocean in the Mid-Cambrian (Houseknecht and Kacena, 1983) (Fig. 5). By early Paleozoic rifting started, rift arms failed and the Southern Oklahoma Aulacogen and Reelfoot Rift were created. This rifting event caused the southern part of North America to evolve into an Atlantic type passive margin with miogeoclinal deposits. The rifting continued into the Mid-Paleozoic time and sediment accumulating during this period includes shelf facies and off-the-shelf facies. The shelf facies include carbonates, shale, and sandstone and the off-the-shelf facies are predominantly limestone, sandstone, and bedded chert (Houseknecht, 1986).

During Devonian and Mississippian, the Iapetus Sea started closing as a result of a southward dipping subduction zone. The subduction followed when the North American plate collided with a southern plate. The evidences for this subduction lie in the copious volcanic tuffs and volcaniclastic sandstones which indicate orogenic processes (such as the Ouachita Orogeny) (Houseknecht, 1986). By Mississippian to early Atokan time, there was a slow sedimentation which eventually formed shales, sandstones and carbonates (Houseknecht and McGilvery, 1990). Uplift along the Ouachitas as a result of continued convergence led to rapid deposition of flysch sediments of more than 5.5 km (18,000 feet) (Houseknecht and McGilvery, 1990).

By the beginning of Atokan time, flexural bending occurred resulting from pushing of subducted ocean basin, and the other parts of the subduction complex to the rifted continental margin of North America. During this time, flexural bending of the overriding plate caused normal faults, originally formed in the Cambrian to Devonian, to be reactivated, deepening the basin and causing an abrupt increase in the thickness of sediments (Branan, 1968, Houseknecht and Kacena, 1983, and Johnson, 1988). This flexural bending caused the development of normal faults, striking parallel to the Ouachitas. Atokan muds and sands were deposited by a series of submarine fans syndepositional with the fault. Throughout the Atokan, shallow marine, deltaic and fluvial sediments were deposited and abundant peat-bearing molasses were deposited from the upper Atokan through the Desmoinesian. This change in depositional style reflects the change of the basin from a passive margin to a foreland basin (Houseknecht, 1986). The structural style of the basin reflects rheology and geometry of the stratigraphic units described.

2.4 Brief Hydrocarbon History of Arkoma Basin

The Arkoma Basin is a prolific gas-producing arcuate foreland basin that is formed in the Carboniferous as a result of the Ouachita Orogeny (Byrnes and Lawyer, 1999). Arkoma Basin is one of six thrust belts and foreland basins in North America and it is the most structurally deformed hydrocarbon-bearing basin of the Ouachita trend with production from combination of both stratigraphic and structural traps (Coleman, 2008).

Foreland basins are widely researched by geologist across the world because of their reservoir potential. The basin was once a part of the large Ouachita geosyncline, and now is one of several structural basins that lie along the northern margin of the Ouachita mountain system, which traverses the southern and southeastern United States (Cemen et.al, 2009). According to Byrnes and Lawyer (1999), the increasing maturation from west to east across the basin is mainly as a result of increasing overburden and subsequent surface erosion from west to east. Most part of the basin is overmature for oil production especially from intervals below the Spiro Sandstone, except to the north and northwest. Empirical and theoretical data suggest that nowhere in the basin has sufficiently thermally matured to result in methane destruction (Byrnes and Lawyer, 1999).

Hydrocarbon-generation history for most part of the Arkoma Basin was brief with principal source rocks generating mainly during the period from Pennsylvanian (315 to 310 Ma), however to the south may have been generating as early as Late Mississippian (330 to 320 Ma). Pre-Mississippian sources primarily contain a Type II or Type I oil-prone kerogen. Marine shales from Mississippian and younger strata typically contain dominantly Type III gas-prone kerogen, although lesser amounts of Type II also may occur (Byrnes and Lawyer, 1999).

Sedimentary strata in the basin are predominantly dark-gray shale of the Lower Pennsylvanian Atokan Series. The Arkoma basin is essentially a dry-gas province with the gas being approximately 95 per cent methane. There are well over 25 gas-producing zones in the basin, ranging in age from early Desmoinesian to Simpson (Branan, 1968).

In 1902, natural gas was discovered in the basin at Mansfield, Sebastian County, Arkansas. The first significant deep gas in the basin was discovered in 1930 at Cartersville in western LeFlore County, Oklahoma and the second in 1951, at Haskell County, Oklahoma. Regular development did not start until 1959 when gas was found in the deep Red Oak and Spiro Sands in Latimer County, Oklahoma (Branan, 1968). This discovery marked the beginning of an intensive gas exploration and drilling in the basin. Trapping in the Arkoma Basin is both structural and stratigraphic but with more prospecting the stratigraphic traps. There is no oil production on the Arkansas side of the Arkoma basin and very little on the Oklahoma side. The basin is essentially a dry-gas province.The gas resembles a coal or marsh gas and is almost pure methane (Branan, 1968)

CHAPTER III

3.1 Methodology

The methodology for this project involved is based on the collection of samples from the field, and laboratory analysis of these samples. The field component included spectral gamma ray survey, section measuring and sampling. The laboratory analysis included, total organic carbon (TOC) and powder X-ray diffraction (XRD). A total of 156 samples were collected and analyzed during this investigation

3.2 Field Techniques

Field work involving gamma ray survey, section measuring, description and sampling was carried out in the spring and summer of 2010. A composite gamma-ray profile of the entire outcrop was constructed from the measured values. The study sections were surveyed on a foot by foot basis and the gamma ray survey included the Hindsville Limestone (Spring Valley), Fayetteville Shale (Spring Valley and Marshall), Pitkin Limestone (Marshal and Peyton Creek) and Imo shale (Peyton Creek).

Equipment and materials used included the SAIC GR-320 ENVISPEC gamma ray spectrometer, and typical items including field notebook, sample bags, rock hammer, paleopick, measuring tape, Jacob staff, indelible markers, hand lens and camera. The outcrops were measured from the base to the top with particular attention to the physical parameters such as bed thicknesses, color, macrofossil contents, sedimentary structures, bedding geometry and contact relationships. Measurements were taken and recorded every foot using the gamma ray spectrometer. The gamma ray spectrometer is designed to detect and measure radionuclide components of uranium (U), thorium (Th) and potassium (K) present in the rocks and the total radiation given off by these radionuclides. The gamma ray spectrometer consists of a rugged handy detector, transmitting cable, and a box shaped processor. The detector is held against the surface of the rock to measure the emitted radiation (Fig. 8). Signals from the detector are transmitted to the processor through a cable. The processor separates the acquired data into individual radionuclides. The gamma ray spectrometer is suited for the field work as it makes a complete measurement in 60 seconds. During the spectral survey, bed thicknesses were measured with the measuring tape and Jacob staff. The paleopick was used for trenching to exposed fresh outcrop and chipping out fresh samples for laboratory analysis. Samples of 500g-700g for each bed of interest were collected, labeled and sealed in the sample bags.

Figure 8: Marshall Outcrop showing the gamma ray spectrometer in use. Note the rugged handy detector mounted against the surface of the rock to measure any emitted radiation by the rock

3.3 Laboratory Analysis

The collected samples for laboratory analysis were prepared by drying and crushing the samples into powder. All samples were prepared for TOC, whereas selected samples representing intervals of high gamma ray response were prepared for XRD. Twenty seven (27) samples were prepared for XRD analysis; the detail preparation processes are discussed below.

The TOC analysis was accomplished using the coulometer in the Geochemistry laboratory, Boone Pickens School of Geology, Oklahoma State University (OSU). TOC is determined by subtracting the measured total inorganic carbon from (TIC) from total carbon (TC) (TOC=TC-TIC). The total carbon is determined using a CM5014 CO_2

coulometer manufactured by UIC Inc. The coulometer is designed to provide highly accurate and absolute amount of carbon in any CO_2 containing gas stream. It is equally designed to detect carbon in the range of 0.01ug to 100mg. The coulometer cell is filled with a propriety solution containing monoethanolamine and calorimetric pH indicator. Cathode and anode electrodes are positioned in the cell. This machine workability is based on the principles of Faraday's law. In the coulometer, each faraday of electricity expended is equivalent to 1GEW (gram equivalent weight) of CO_2 titrated.

The CM 5300 furnace is a component of the CM5014 CO_2 coulometer. It is designed to combust powdered samples in oxygen and convert organic and inorganic form of carbon to carbon dioxide (CO_2). It operates at a temperature range of 950^0C-1100^0C to completely oxidize all forms of carbon present. Its combination with CM5014 CO_2 detector can effectively determine carbon levels from less than 100ppm to 100%. To determine the TC, an aliquot of each of each collected sample was crushed into powder using a SPEX ball mill. A small portion of each crushed sample was loaded in a small ceramic boat and placed into the CM 5300 furnace via a glass tube. The total analysis time per sample from loading to readout is approximately 20 minutes.

The total inorganic carbon is determined using the CM 5130 acidification module. The CM 5130 acidification module traps all evolving forms of inorganic carbon from acidified powdered samples. The samples are acidified in a heated flask to evolve all forms of inorganic carbon as carbon dioxide. The instrument can determine carbon level from parts per million (ppm) to pure carbonate when connected to CM5014 CO_2 coulometer. To determine the TIC, weighed powdered samples were placed in a glass flask and about 5ml of perchloric ($HClO_4$) acid were added through the acid dispenser.

This mixture was analyzed approximately for 15 minutes in order to determine the total inorganic carbon present in the sample. To quicken the CO_2 evolution during sample heating the sample is magnetic stirred.

3.4 X-ray diffraction -Clay Mineralogy

Twenty seven (27) samples were selected across the Fayetteville and the Imo formations and were analyzed for their clay mineral content using powder x-ray diffraction. The x-ray analysis was conducted in the Boone Pickens School of Geology using the Philips (PANalytical) PW 3710 instrument. The analyses included both bulk and extracted clay. Bulk analysis determines the total mineralogical constituents of the rock. The extracted clay analysis is designed to identify only the clay minerals.

Rock samples to be analyzed were powdered using ceramic mortar and pestle and ceramic ball mill vial. For the bulk analysis, powdered samples were mounted on a metal slide. Extracted samples were prepared by placing 15-20g of each powdered sample to a 250ml plastic centrifuge tube and adding approximately 100ml of sodium acetate (NaOac) solution to remove rock forming minerals such as calcite. Each sample was stirred well and heated up to 80^0C in a water-bath for atleast 30 minutes. Each sample was then centrifuged at 1500 rpm for 5 minutes and decanted. Centrifuging allows clay particles to suspend while lager particle settle at the bottom of the tube. Samples containing carbonate were typically treated several times with sodium acetate (NaOac) solution until the reaction stopped. Samples were rinsed using osmosis laboratory water and centrifuged until clay particles remain suspended. Following centrifuging, the suspended particles were pipetted onto a glass slide and allowed to sit until the liquid evaporated. Following x-ray of the clay smear, the slides were put in a glycolator to facilitate the expansion of expandable clays. After glycolating 24 hours, the samples were x-rayed. Following glycolating and x-ray, the clay smears were heated up to 500^0C for 30 minutes to collapse swelling clays. The samples were subsequently x-rayed to determine if expandable clays were present

3.5 Gamma Ray and its Significance

A gamma-ray spectrometer can be used to measure the abundance of uranium, potassium and thorium, the radionuclide that produce the bulk of natural radioactivity, and hence gamma radiation, in rocks. The response of a normal gamma ray log is made up of combined radiation from uranium (U), thorium (Th) and potassium (K) and a number of other associated daughter products of radioactive decay (Asquith and Krygowski, 2004). Gamma-ray profiles can be used to distinguish between rock types. It measures the relative abundance of interstitial clay and shale. Shales produce relatively large amounts of gamma radiation compared to other common sedimentary rocks such as sandstone, limestone, or coal (Andrews and Suneson, 2002).

Gamma ray logs are meter for identifying lithologies for example, a shale-free zone or sandstone and carbonate will have relative low gamma ray readings compared to a shale-rich zone. The concentration of radioactive material in shale is relatively high as such an increase in shale content means an increase in the gamma ray readings.
Gamma ray logs can be used to calculate shale volume, radioactive mineral-rich sandstone, differentiate radioactive reservoirs from shale, evaluate source-rock and potash deposits, correlate between formations and identify lithologies. Black shale is described as “hot shale” when the gamma ray values equal or greater than 200 API (Luning et al., 2000)

The uranium content in shales is made up of detrital and authigenic components (Yu et.al 1999; Lüning and Kolonic 2003) However, significant variations exist depending on the detrital source material. Reduction and precipitation of authigenic uranium are important mechanisms in many oxygen-deficient systems and can lead to an increase in the total uranium content of the sediment that can exceed by many times the detrital uranium component (Wignall and Myers, 1988; Stocks and Lawrence, 1990).

Uranium and its daughters have shown to be good geochronometers and paleoceanographic proxies (Yu et.al 1999; McManus et.al, 2004). Uranium generally exhibits conservative behavior in oxygenated ocean waters. Uranium is reactive in some marine environments such as anoxic basins, coastal oceans, turbidite and pelagic sediments (Yu et.al 1999; McManus et.al, 2004). For sediments in upwelling areas, a relatively high influx of particulate organic matter can easily make the regions suboxic or anoxic environments. Thus uranium is able to behave in a non-conservative manner (Yu et.al 1999). The diagenetic behavior of uranium in sediments is affected by continuous upwelling activity, high bio productivity and amount of oxygen (O_2) depleted waters.Thorium (Th), is located and locked in the lattice structure of minerals and it is mainly derived from constituents through eolian and riverine pathways (Yu et.al 1999). Therefore its presence would indicate input of lithogenic (terrigenous) materials into the formation. Virtually all thorium in marine sediments are lithogenic (Yu et.al 1999). High concentration of uranium in deep-sea sediments has been attributed to hydrothermally active zones and in reduced sediments (Yu et.al 1999). Due to no record of hydrothermal inputs in this formation, it is not likely that high uranium content in the study area is caused by hydrothermal activity. Rather it has probably been added to the sediments as result of reducing conditions at time of deposition.

Authtigenic uranium is derived/incorporated into anoxic organic-rich marine sediments from two main processes (1) biogenic fixation of U in water column and scavenging of U by microorganisms (2) precipitation of U at the water-sediment interface where high bacterial activity is enhanced thereby serving as a trap for U directly or indirectly by reducing the redox potential during the early diagenesis of organic matter (Yu et.al 1999; McManus et.al, 2004).

Variations in percent authigenic U corresponds well to the variations in percent TOC. The sharp increase in authigenic U coincides with increase in percent TOC (Yu et.al 1999; Lüning and Kolonic 2003; McManus et.al, 2004).

Since only total U content of the sediments can be measured, it is necessary to derive the authigenic U contents of these sediments by an indirect means. A formula for calculating authigenic uranium content in marine mudrocks from spectral gamma-ray data introduced by Wignall (1994) is given as $U_{authigenic}=U_{measured} - Th_{measured}/3$, where $Th_{measured}/3$ approximates the detrital U component. Calculation of $U_{authigenic}$ using this formula is useful in shale successions with variable carbonate and detrital uranium contents whereas it is of less importance in pure shale succession with fairly constant detrital composition (Lüning and Kolonic, 2003). Increase in authigenic U in sedimentary record connote periods of more reducing oceanic conditions (Yu et.al 1999; Lüning and Kolonic 2003; McManus et.al, 2004). However, sedimentary reducing conditions are facilitated by at least two factors (1) low bottom water oxygen concentrations and (2) high organic carbon rain rates. (Yu et.al, 1999, Lüning and Kolonic, 2003; McManus et.al, 2004).

High concentration of U in sedimentary basin may indicate oxygen depleted bottom water, concentrations, higher organic carbon rain, or combination of both (Yu et.al 1999; Lüning and Kolonic 2003; McManus et.al, 2004). This combination of factors that influence authigenic U accumulation certainly complicates interpretations of the sedimentary record. However, it has been reported that higher authigenic uranium corresponds with high organic carbon (e.g Yu et.al 1999; Lüning and Kolonic2003; McManus et.al, 2004). In black shale systems, the organic-richness can easily be estimated by measuring the uranium content using spectral gamma-ray techniques (Lüning and Kolonic 2003).

Many hydrocarbon source rocks are enriched in authigenic uranium which precipitates at the sediment-water interface under anoxic conditions and accumulates together with organic matter (OM) at the time of deposition (Wignall and Myers, 1988; Stocks and Lawrence, 1990). In some black shale systems, a linear relationship between concentrations of TOC and uranium have been reported based on local calibrations; therefore uranium can be used as a proxy to predict the TOC content regionally (Lüning and Kolonic, 2003).

3.6 Total Organic Carbon and its Significance

The TOC is a measure of the total amount of organic matter present in the rock (Ronov, 1958). The TOC content of sediment is expressed as a weight percent. In order for a sedimentary basin to be considered a good petroleum system, high total organic carbon content greater than 2.0 (Table. 2) along with other properties such as the presence of source and reservoir rocks, traps and seals, thermally matured and economically feasible formation thickness must be present within the system. Organic materials are sourced from the remains of dead phytoplankton and zooplankton. High concentration of organic matter makes shales black and they are often seen as a good hydrocarbon source rocks whereas poor or fair organic-rich shales are often lighter (gray-light gray) than the very good organic-rich ones (Lüning and Kolonic, 2003; Arthur and Sageman, 1994).

When using TOC, the hydrocarbon generating potential and organic carbon richness is commonly interpreted using Table 1 (Jarvie, 1991). Although a good source rock should have a high TOC, not all organic matter is created equal. Some organic matter will generate oil, some will generate gas, and some will not generate anything (Tissot et al., 1974). Therefore, TOC by itself is not necessarily a good indicator of how much hydrocarbon a rock can generate. For organic matter to generate hydrocarbons, the carbon has to be associated with hydrogen. The more hydrogen associated with the carbon, the more hydrocarbons it can generate (Dembicki, 2009). As a result, there is need to determine the amount of hydrogen present in the organic matter. Hydrogen content of an organic matter can be determined by indirect means such as Rock-Eval pyrolysis (Espitalie et al., 1977a). By combining TOC and Rock-Eval pyrolysis, we can get an idea of how much organic matter is present and how much hydrogen is associated with it (Dembicki, 2009). As a source rock generates and expels hydrocarbons, the amount of organic matter in the source rock will decrease (Daly and Edman, 1987). This means that the TOC will decrease as the amount of reactive kerogen gets consumed. The amount of hydrogen will also decrease resulting in a decrease in Rock-Eval S2 (Espitalie et al., 1977b).

As a source rock matures, it will gradually look less like a source rock. When it reaches the main stage of gas generation, rich oil-prone immature sediments may look like leaner, gas-prone sediments. We must be cautious not to condemn an overmature sediment because we don't know its original organic matter content. There is more to source rock richness than just TOC, both the carbon and hydrogen contents of the organic matter are needed to determine how much hydrocarbon can be generated from a source rock. As such knowing about the maturity of the source rock is necessary for proper interpretation (Dembicki, 2009).

According to (Dembicki, 2009), source rock evaluation consists of assessing the hydrocarbon generating potential of sediments by looking at the sediment's capacity for hydrocarbon generation, type of organic matter present and what hydrocarbons might be generated, and the sediment's thermal maturity and how it has influenced generation. The analytical methods most frequently used for this purpose are total organic carbon (TOC) content analysis, Rock-Eval pyrolysis, and vitrinite reflectance analysis.

Richness	TOC in Shales (wt.%)	TOC in Carbonates (wt.%)
Poor	0.0-0.5	0.0-0.2
Fair	0.5-1.0	0.2-0.5
Good	1.0-2.0	0.5-1.0
Very Good	2.0-5.0	1.0-2.0
Excellent	>5.0	>2.0

Table 2: Source Richness Interpretation by Total Organic Carbon (TOC wt. %) (from Jarvie, 1991)

CHAPTER IV

4.1 Observations

This chapter will be focusing on the description of the outcrops at Marshall (Fayetteville Shale and Pitkin Limestone), Spring Valley (Hindsville Limestone and lower Fayetteville Shale) and Peyton Creek (upper Pitkin Limestone and Imo Shale.) as well as the gamma spectrometry and TOC characteristics and their relationships. It will also discuss the clay mineralogy, the uranium: thorium ratio as well as components of uranium and their use in the establishment of the source and maturity of the studied area.

4.2 Definitions:

Black shales can be defined as dark gray to black, organic-carbon-rich, laminated, carbonaceous strata that is characterized by poor amount of benthic faunas or devoid of metazoan life (Arthur and Sageman, 1994). The formation of black shale require adequate supply of organic matter, conditions conducive for preservation of the organic material and depletion of dissolved oxygen in waters above the sediment-water interface. Black shale is described as “hot shale” when the gamma ray values equal or greater than 200 API (Luning et al., 2000)

Organic matter which is the main cause of the dark coloration in shales is the most important thing that distinguishes black shales from all other mudrocks. The amount, type and maturity of organic carbon determines the color of shales as such shales containing few percent of immature amorphous organic matter exhibit more brown (lighter color) than black coloration; highly oxidized or thermally matured strata containing about 1-2% organic carbon are mostly black. The closeness/ proximity of terrestrial sources of organic matter and marine productivity predominantly control the type of organic matter that is found in black shale deposits (Arthur and Sageman, 1994).

Oxygen demand relates to surface bio-productivity and when the demand for oxygen in water column exceeds the supply, the state of anoxia exists. Oxygen-constrained environments are identified in the geological record by their association with diagnostic sedimentological and geochemical characters. A fissile black shale lithology enriched in organic matter and trace elements such as uranium (Wignall and Myers, 1988) is particularly characteristic of dysaerobic to anoxia environments. Geochemical and sedimentological evidences suggest that potential oil source beds have been deposited in the following anoxic settings: large anoxic lakes, anoxic silled basins, upwelling induced anoxia and anoxic open ocean (Demaison and Moore, 1980)

Large anoxic lakes have permanent stratification, maximum water depth of about 1,500m, anoxia below 150 m, varved sediments and H_2S is present in the water (euxinic). Here sediment with shallow oxygenated waters contains 1-2% organic carbon while sediments within anoxic waters contain about 7-11% organic carbon.

Anoxic silled basins are characterized by several physical barriers that restrict vertical mixing, hence stratification of the basin. Their water balance have a strong salinity contrast between fresh out-flowing surface water and deeper in-going more saline and nutrient-rich oceanic water. However, positive water balance also acts as nutrient traps enhancing productivity and preservation of organics. They are also characterized by permanent or intermittent anoxia, permanent halocline marking oxic and anoxic boundary, anoxic boundary of about 250 m around edges and 150 m at the center and presence of H_2S in the anoxic waters.

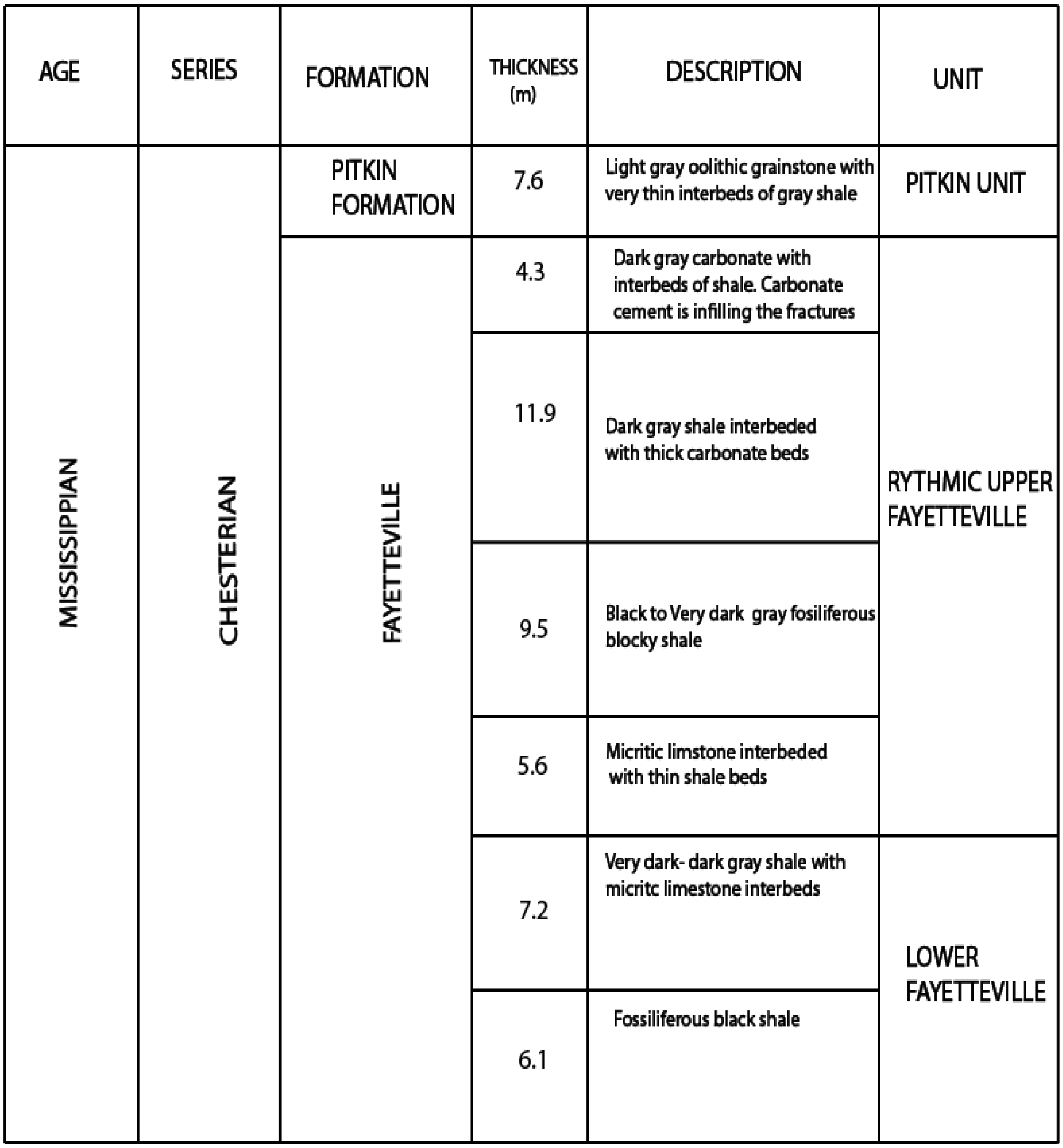
Upwelling induced anoxia develops when surface bio-productivity demand is far more than the oxygen supply from the deep water. Anoxic organic rich sediments contain very high TOC value between 5-20%. Organic-rich sediments contain high concentration of uranium, phosphorus, copper, and nickel.

Anoxic open oceans are the most complex and least understood of all settings for developing organic sediment. The anoxia is believed to be caused by biochemical oxygen demand causes or formed by high plankton productivity.

Anoxic shales are generally characterized by the following: thinly laminated beds, high TOC of between 1-20%, lack of bioturbation (they lack benthics), presence of pelagic fauna such as sharks, ammonoids, conodonts, planktonic foraminifera, radiolarians and nananoplanktons, authigenic minerals such as pyrite, phosphate, cherts and carbonate concretions. While dysoxicshales are clay-rich shales, minor, bioturbation, (Chondrites), and may have benthic fauna in addition to pelagic component.

4.3 Marshall Outcrop, Arkansas

The total thickness of beds exposed at the Marshall Outcrop, Arkansas is about 52+ m (169+ ft.). The Fayetteville and Lower Pitkin formations were measured and described (Fig. 9). This outcrop offer unparalleled exposures of the lower black shale, rhythmically bedded limestone and oolitic limestone facies. At this location the Fayetteville Shale is overlain by the bioclastic-oolitic Pitkin Limestone and the underlying unit is not exposed. The color throughout the section ranges from black to light gray. The shale is naturally fractured and most of the open fractures and natural fractures have been filled with calcite cement. The descriptions presented here produced significant bearing upon an interpretation of the Fayetteville Shale source. Based on lithology characteristics, this exposure at Marshall Arkansas is divided into three major units: the lower Fayetteville, the rhythmic upper Fayetteville and the Pitkin units.



AGE	SERIES	FORMATION	THICKNESS (m)	DESCRIPTION	UNIT
MISSISSIPPIAN	CHESTERIAN	PITKIN FORMATION	7.6	Light gray oolithic grainstone with very thin interbeds of gray shale	PITKIN UNIT
		FAYETTEVILLE	4.3	Dark gray carbonate with interbeds of shale. Carbonate cement is infilling the fractures	RYTHMIC UPPER FAYETTEVILLE
			11.9	Dark gray shale interbeded with thick carbonate beds	
			9.5	Black to Very dark gray fosiliferous blocky shale	
			5.6	Micritic limstone interbeded with thin shale beds	
			7.2	Very dark- dark gray shale with micritc limestone interbeds	LOWER FAYETTEVILLE
			6.1	Fossiliferous black shale	

Figure 9: Stratigraphic section of Marshall outcrop, Arkansas showing the three units and their relative thickness

4.3.1 Lower Fayetteville

The total thickness of this unit is about 40 ft (13.3m). It is a black to very dark gray, fissile, fossiliferous and pyritic shale unit (Fig. 11). In the lower part, it contains limonite concretions and also calcareous concretions (Fig.10) about 1.8 m (6ft) above the base of the section. It is a very black shale and highly fossiliferous. The fossils present include brachiopod, crinoids and ammnoids.

Figure 10: Photograph of Marshall outcrop showing the concretious lime within the lower Fayetteville unit

Figure 11: Photograph of Marshall outcrop showing the Black Lower Fayetteville unit. Note the pyritic layer and the laterally continuous micritic limestone bed

This unit consists of black to dark gray shale and uniformly consistent micritic limestone of about 5-8 inches thick (Fig. 11). This limestone beds are dark-gray, fine-grained and laterally continuous across this shale unit. They are fractured and give off hydrocarbon smell when broken or hit with hammer. Directly on top of it is the rhythmic upper Fayetteville Shale.

4.3.2 Rhythmic Upper Fayetteville Shale

The total thickness of this unit is about 31 m (100 ft). It is predominantly calcareous shale interbeded with micritic limestone (Fig. 12). The calcareous shale reacts upon addition of dilute (10%) HCl. This unit comformably grades into the overlying Pitkin Limestone. It is not very easy to determine the contact between this unit and the overlying Pitkin, but with facie, color and texture changes, the contact is marked the as the point where the shale unit is not more than few inches thick and the limestone unit becomes more conspicuous. Also at this point, textural changes are noticed. The red line in the (Fig.13) marks the interpreted contact separating this unit and the overlying Pitkin. The upper Fayetteville is naturally fractured, fossiliferous and pyritic in some places. Some fractures are already healed by calcite.

Figure 12: Photograph of the rhythmic upper Fayetteville unit. Note the rhythmic pattern of the beds

The rhythmic upper Fayetteville Shale is made up of alternating limestone and shale and forms a lithologic succession that displays a transition between the black shales below and the overlying Pitkin Limestone. The unit becomes more calcareous as it grades into the Pitkin Limestone.

4.3.3 Pitkin Limestone

This unit is about 7.6+ m (25+ ft) thick. It is a fine-to coarse-grained, oolitic, bioclastic limestone. It is interbeded by thin sequences of calcareous black shale (Fig. 13). Common fossils include crinoids, brachiopods, bryozoa, corals, bivalves, gastropods, cephalopods, trilobites, conodonts, and shark teeth (Handford, 1986 and other authors mentioned here). At the Marshall outcrop, the Pitkin Limestone overlies the rhythmic upper Fayetteville Shale with gradational contact. The lower part of the Pitkin Limestone consists of ooid grainstone with plane laminations thought to represent shoal and shoreface facies (Handford, 1986).

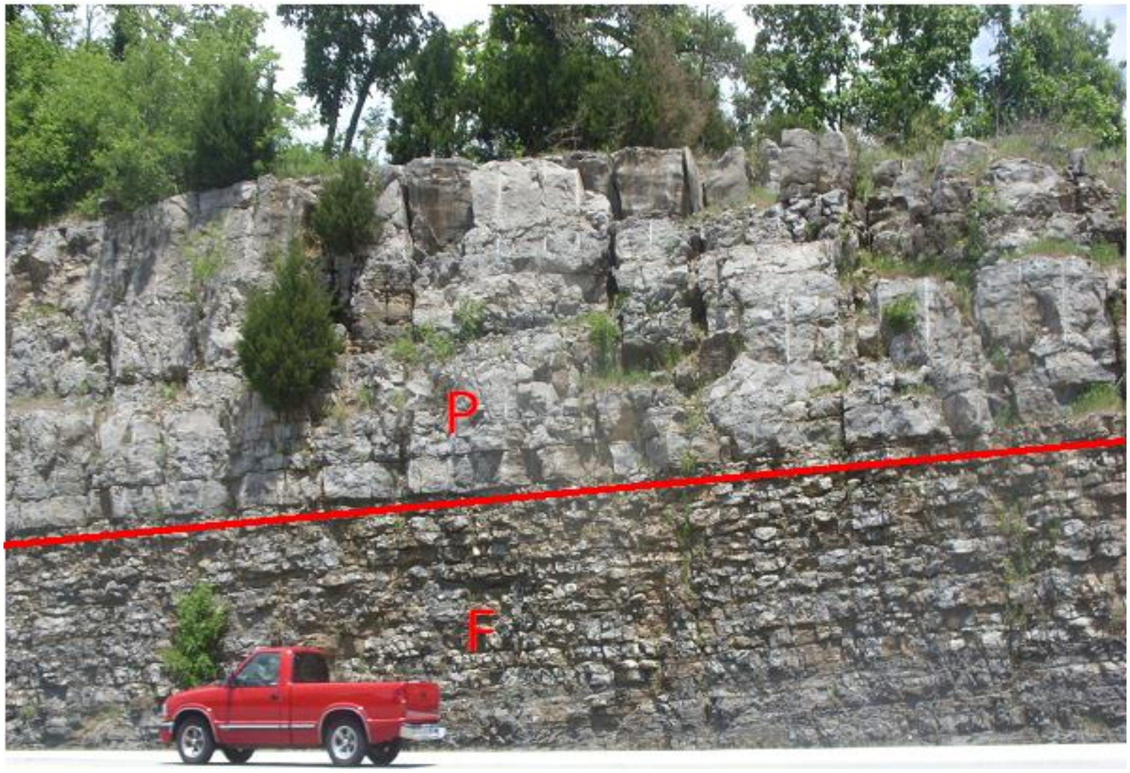


Figure 13: Photograph of Marshall outcrop showing the Pitkin Limestone (P) and upper Fayetteville (F). The red line mark indicate the observable contact between the two formations

4.3.4 Gamma Profile

The gamma ray data for the Marshall outcrop was obtained using the SAIC GR-320 ENVISPEC spectrometer. A total of 144 readings were acquired vertically across the outcrop at an interval of one foot each. The measurements were taken across both the Fayetteville Shale and the overlying Pitkin Limestone at this location. The gamma-ray characteristics exhibited by the Fayetteville Shale and Pitkin Limestone at Marshall are described in ascending order from the base of the section to the top. The Lower Fayetteville Shale unit gamma-ray values range between 86 and 245 API units. The highest values for this unit correspond with the lowermost black shale beds, whereas the lower API values corresponds with the laterally continuous carbonate beds and the limontic and carbonate concretions about 6ft above the base of the exposed section.

These carbonate beds and less radioactive materials result in the very irregular gamma-ray profile pattern of this unit (Fig. 15).

The black shale beds of this unit are hot shales as shown by Gamma-ray values reaching 234 API units. The uranium measurements for show higher uranium content than thorium; this is reflected by the uranium:thorium ratio signature (Fig. 15). Also, the shale displays higher authigenic uranium compared to detrital uranium, whereas the carbonate beds displayed no significant difference. From the above it is inferred that the shale-forming mud is deposited in a relatively deep, open-marine environment under anoxic conditions owing to the high authigenic uranium and benthic fossils reported.

The upper Fayetteville Shale starts from the point mark FT45 (appendix A) and this unit has gamma values of between 47 and 264 API units. The rhythmic carbonate beds generate the very irregular gamma-ray profile pattern. The shale interval in the lower part of this unit displays higher gamma-ray value of 264 API units, the highest in the entire outcrop (Fig. 14). In contrast, the carbonate beds have gamma-ray values as low as 45 API units. The spectral analysis shows that the uranium component all through the unit is higher than the thorium, indicating a marine source. Authigenic uranium for the shale interval is also relatively higher compared to the detrital component, which confirms a marine source

The overlying Pitkin Limestone displays very low API values that range between 5 and 49 units (appendix A). Although the uranium content is generally low, it is higher than thorium values. The difference between the authigenic and detrital uranium components is inconspicuous (Fig 15). From the gamma-ray data presented here, it is evident that the carbonate beds have lower API values and uranium content. The carbonate beds have an inconspicuously near equal amount of detrital and authigenic components.

4.3.5 Total Organic Carbon

Geochemical analysis shows that the Marshall outcrop demonstrates an inconsistent total organic carbon (TOC) value due to its heterogeneity. The general lithologic sequence of interbeded carbonate and shale beds results in an irregular pattern of the TOC signatures. The variable TOC values are attributed to the facies.

The lower black shale is organically rich with TOC content ranging between 2.4-5.3 wt.%. (Fig. 14 and appendix D) The carbonate interbeds have a TOC content ranging between 0.3-2.0 wt.% which is a very good TOC value for carbonate bed (Table 2)

The very dark gray shale interval in the upper Fayetteville has TOC values ranging between 3.0 and 6.4 wt.%. The carbonate interval has TOC values ranging between 0.5 and 3% and the Pitkin Limestone above has a TOC ranging between 0 and 0.7wt.%

Geochemical analysis show that the Fayetteville Shale has moderate to high TOC that ranges from 2.4%- 6.4 wt.% (Fig. 14).

4.3.6 TOC and Gamma Profile Relationships

A plot of the TOC and gamma-ray data from the outcrop at Marshall displayed a relatively positive relationship between the TOC and gamma-ray signature in that an increase in gamma ray values corresponds to an increase in TOC values (Fig.14). For example, the black shale interval of the upper Fayetteville Shale has a gamma-ray value of 264 API units and 6.44 wt.%, whereas the “clean”Pitkin Limestone has a gamma-ray of 5.6 API units and TOC of 0.55 wt %. The irregular pattern in the trend of the relationship chart is caused by the interbeded micritic limestone. Also variations in authigenic uranium correspond well with variation in percent TOC and increase in authigenic uranium coincides with increase in percent TOC (Fig. 15). As a result, uranium can be used as a proxy to predict the TOC content in the Fayetteville Shale. The data presented here support the general belief that high uranium content corresponds to high API values. The spectral analysis indicates an authigenic source, which is a strong indication for an anoxic environment. The basal black shale and the very dark shale interval of the upper Fayetteville exhibit a diagnostic characteristic of anoxic environments of deposition

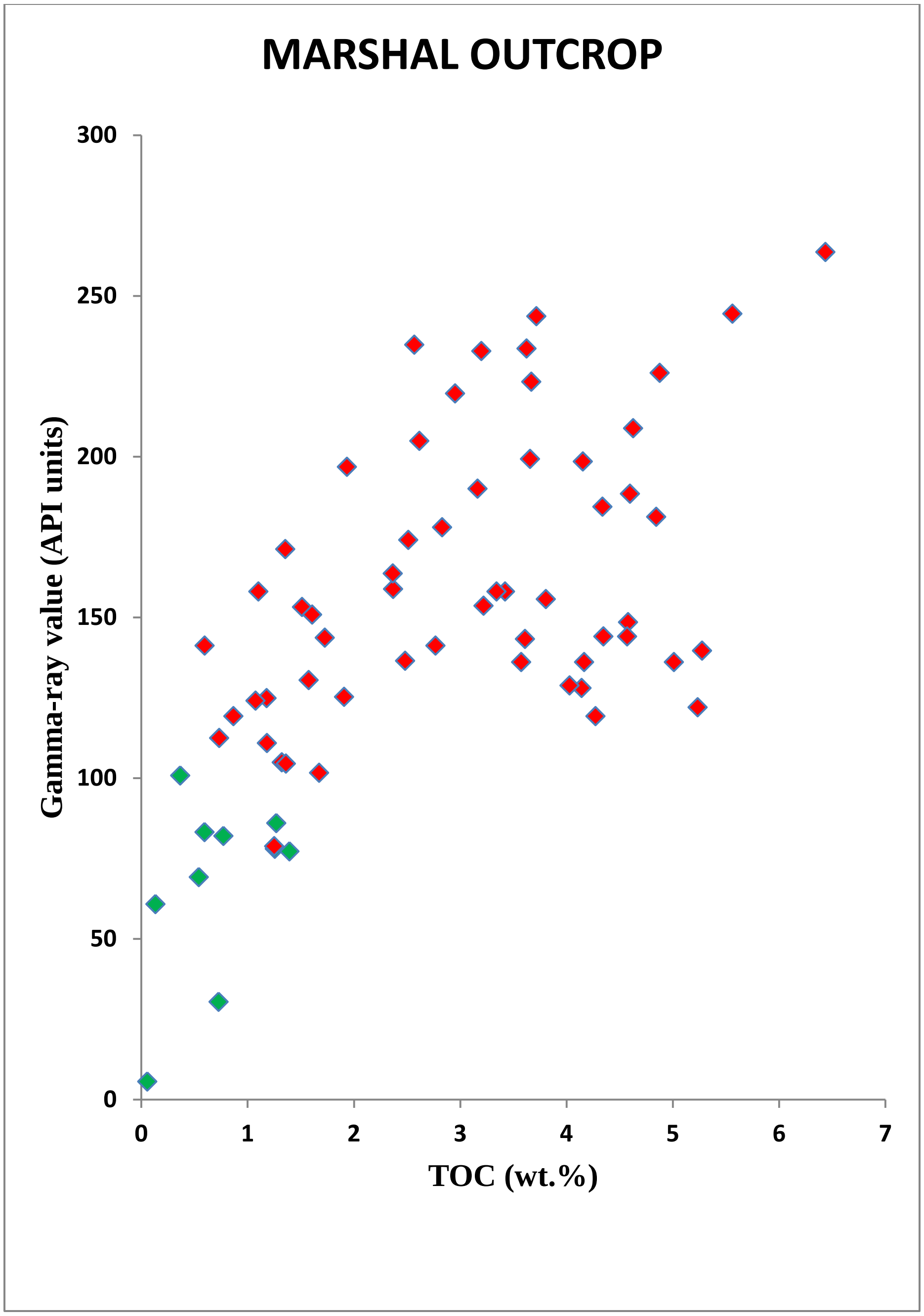


Figure 14: Relationship between gamma- ray (API units) and TOC of the Marshall outcrop. The red and green dots represent shale and carbonate respectively

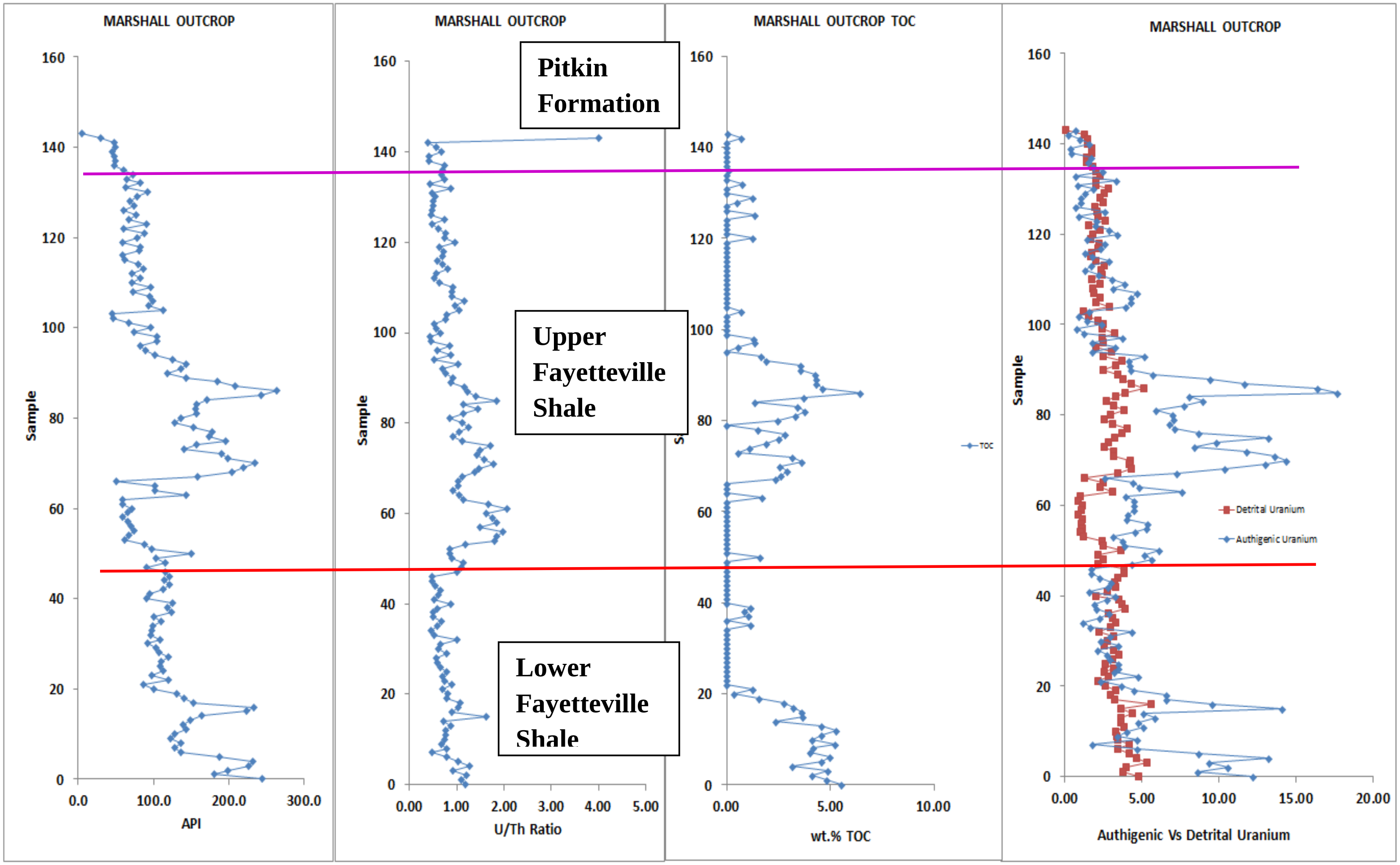
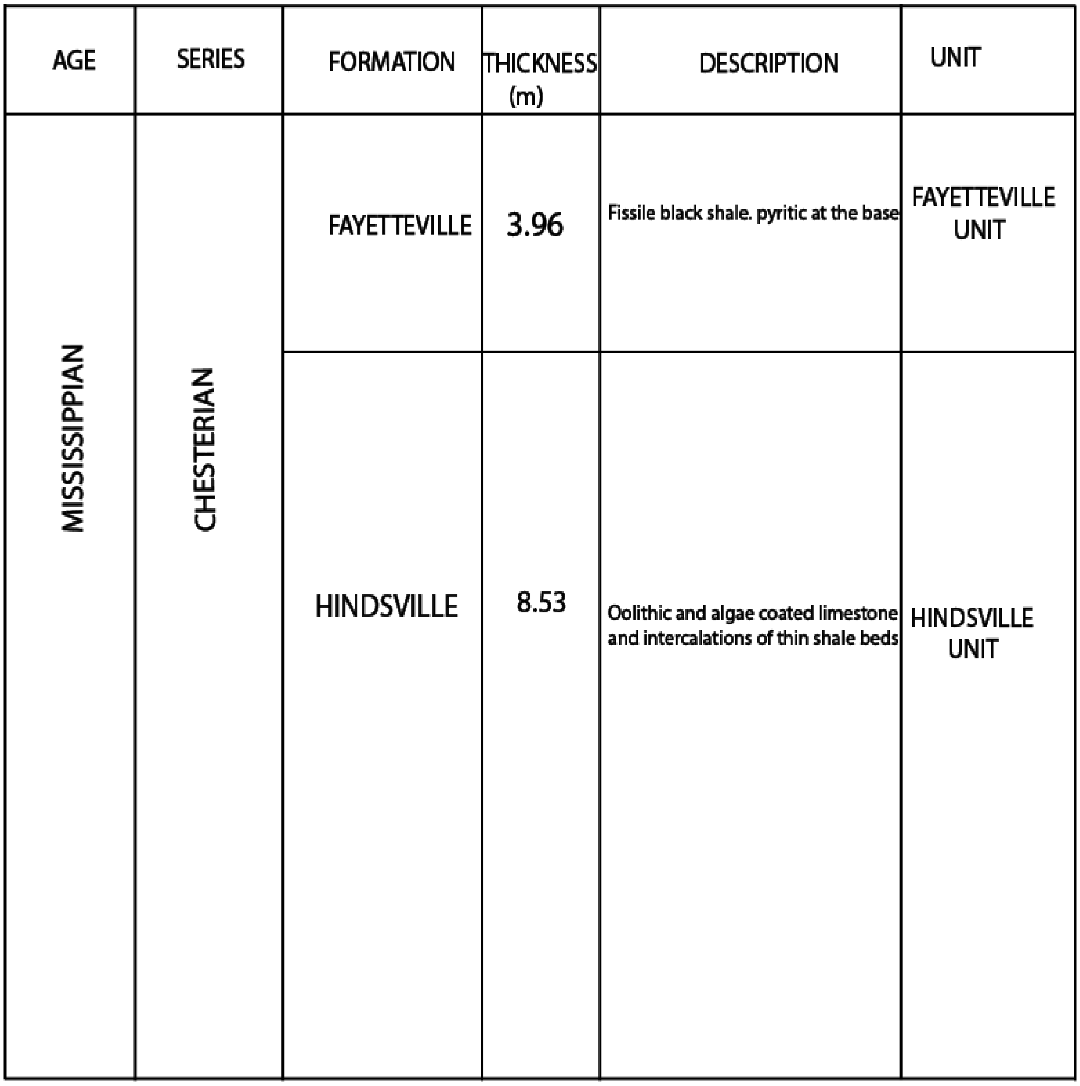


Figure 15: Relationship between gamma ray signatures, uranium (U): thorium (Th) ratio, total organic carbon concentrations and authigenic and detrital uranium signatures of the Marshall outcrop Arkansas

4.4 Spring Valley Outcrop, Arkansas

The total thickness of the beds exposed at the Spring Valley outcrop is about 12.5 m (42 ft). The units exposed here include the upper part of the Hindsville Limestone and the overlying lower part of the Fayetteville Shale (Fig. 16). The exposed section was measured, examined and described. Lithologically, this outcrop is divided into two main units: the Hindsville Limestone and the Fayetteville Shale.



AGE	SERIES	FORMATION	THICKNESS (m)	DESCRIPTION	UNIT
MISSISSIPPIAN	CHESTERIAN	FAYETTEVILLE	3.96	Fissile black shale. pyritic at the base	FAYETTEVILLE UNIT
		HINDSVILLE	8.53	Oolithic and algae coated limestone and intercalations of thin shale beds	HINDSVILLE UNIT

Figure 16: Stratigraphic section of Spring Valley outcrop, Arkansas showing the two units and their relative thickness

4.4.1 Upper Hindsville Limestone

The total thickness of the Hindsville Limestone is about 29 ft. It forms the base of the outcrop and it is predominantly oolitic grainstone, algal-coated limestone, and intercalated thin shale beds (Fig 17.) Brachiopods, crinoids and oncolites are common. Carbonate rip-up clasts are evidence of erosion and redeposition. A channel feature truncates the limestone in the lower part. At the base of the channel, the limestone has increased sand content.

Figure 17: The Hindsville Limestone at the Spring Valley outcrop, composed of the oolitic and algal-coated limestone and the intercalations of shale (light gray)

4.4.2 Fayetteville Shale

The total measured thickness of this unit is 4 m (13 ft). The Fayetteville Shale is resting uncorformably on top of Hindsville Limestone. The Fayetteville Shale is black, very fissile, pyritic and clay-rich. It becomes muddier from the base to the top of the section and generally weathers into clay. At this location, this unit is heavily weathered and covered by thick vegetation and soil. (Fig. 18)

Figure 18: Photograph of Spring Valley outcrop, Arkansas showing the fissile, pyritic and fossiliferous black Fayetteville Shale

4.4.3 Gamma Profile

A total of 42 readings were acquired vertically across the Spring Valley outcrop at an interval of one foot each. The measurements were taken across both the Fayetteville Shale and the underlying Hindsville Limestone. The gamma-ray characteristics displayed from the base to the top of the section are described as follows. The gamma-ray values of Hindsville Limestone range between 17 and 49 API units. The gamma-ray signature is irregular as a result of the intercalated beds (light grey shale) which become more conspicuous toward the top of the Hindsville Limestone. The intercalated beds lead to the irregular U:Th ratio signature (Fig.20).

The highest gamma-ray value recorded at the Spring Valley outcrop corresponds with the Fayetteville Shale, which has values ranging between 122 and 179 API units. Unlike the Fayetteville at Marshall, the black shale at Spring Valley has higher thorium than uranium content; this signifies change in terrigenous input and source. The uranium values are interpreted to indicate that the uranium component is from detrital sources. Detrital uranium is higher than the authigenic uranium across the section except at the contact between the Fayetteville Shale and the underlying Hindsville Limestone and in places where the intercalated shale is present (Fig.20). From this, it is inferred that the shale-forming muds were deposited in a relatively shallow open marine environment under dysoxic condition owing to the high thorium content.

Within the black Fayetteville Shale unit, the uranium content decreases up section, while the thorium content increases (appendix B) signifying terrestrial input. It is evident from the gamma spectrometer analysis of this Fayetteville shale that it is deposited in proximity to the brink of the basin and the organic matter present here are derived from terrestrial sources.

4.4.4 Total Organic Carbon (TOC)

Geochemical analysis shows that the Spring Valley outcrop have TOC values ranging from 1.3-7.0 wt.% (appendix E). The Fayetteville Shale has excellent TOC value as high as 7wt.% but it is evident from the very high thorium content and detrital uranium content that the organic matter here is sourced from terrestrial sources

4.4.5 TOC and Gamma Profile Relationships

A plot of the TOC and gamma data from the outcrop at Spring Valley demonstrates a positive relationship between TOC and gamma ray signature (Fig.19). The increase in the TOC values corresponds to an increase in gamma-ray values. For example, the Fayetteville shale has a maximum gamma-ray reading of 179 API unit and 7 wt.% TOC , whereas the Hindsville Limestone unit averages 17 API units and 0.58 wt %.. However, the higher gamma-ray values cannot be attributed totally to higher uranium content as the uranium content is lower than thorium. The thorium values show a significant increase relative to uranium toward the top of the section whereas TOC decreases. Since detrital uranium is tied to thorium variations in detrital uranium corresponds to variations in percent TOC and the U:Th ratio (Fig. 20). As a result, uranium can be used as a proxy to predict the TOC content and hydrocarbon source potential in the Fayetteville Shale. The U:Th ratio indicates an increased terrigenous source toward the top of section, which may corresponds to a possible oxic/suboxic environment during deposition. As such, the Fayetteville Shale at Spring Valley is interpreted as a more proximal depositional facies in which U was diluted or less effectively preserved.

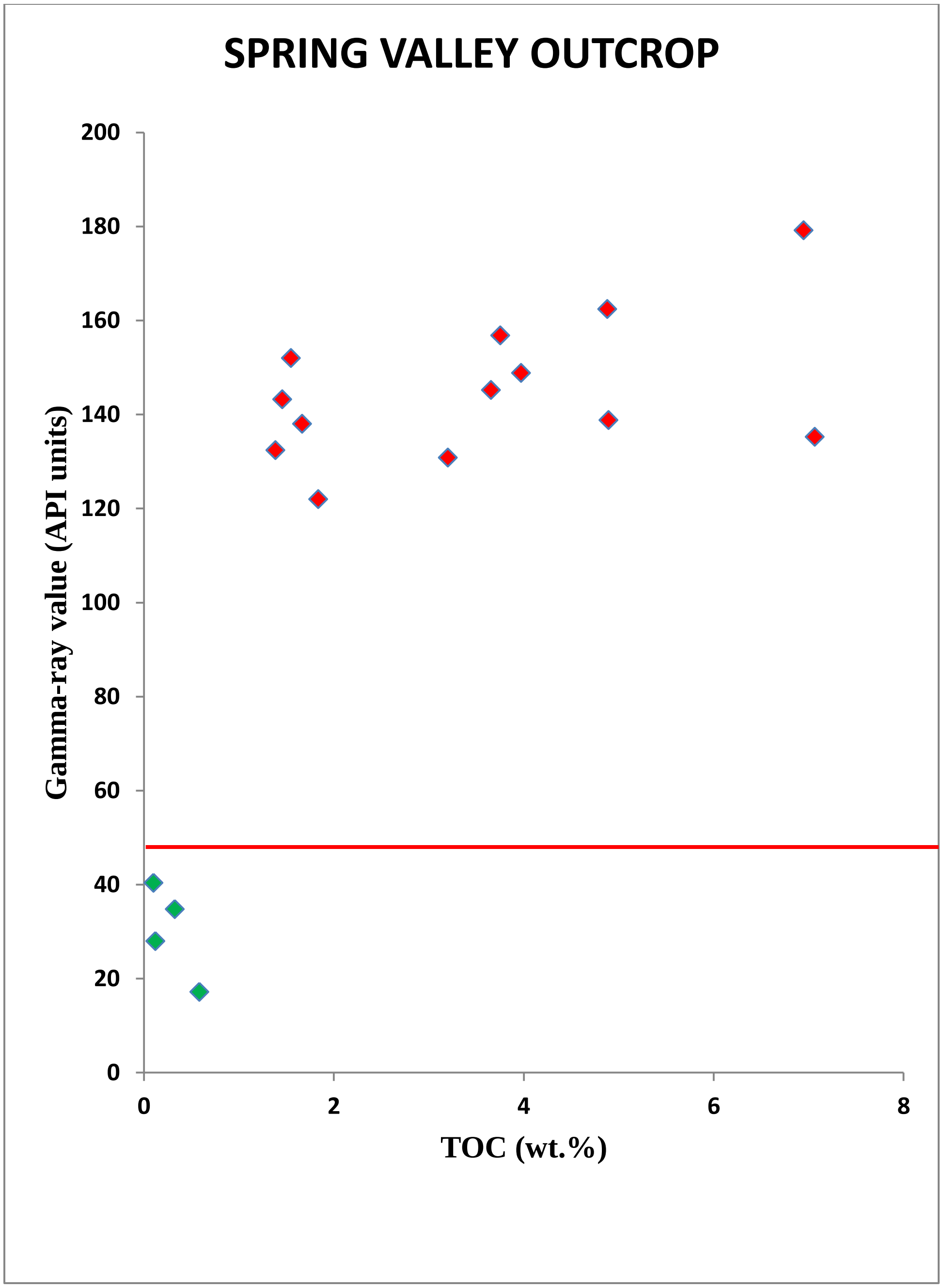


Figure 19: Relationship between Gamma- ray (API units) and TOC of the Spring Valley outcrop. The red and green dots represent the Fayetteville Shale and the Pitkin Limestone respectively.

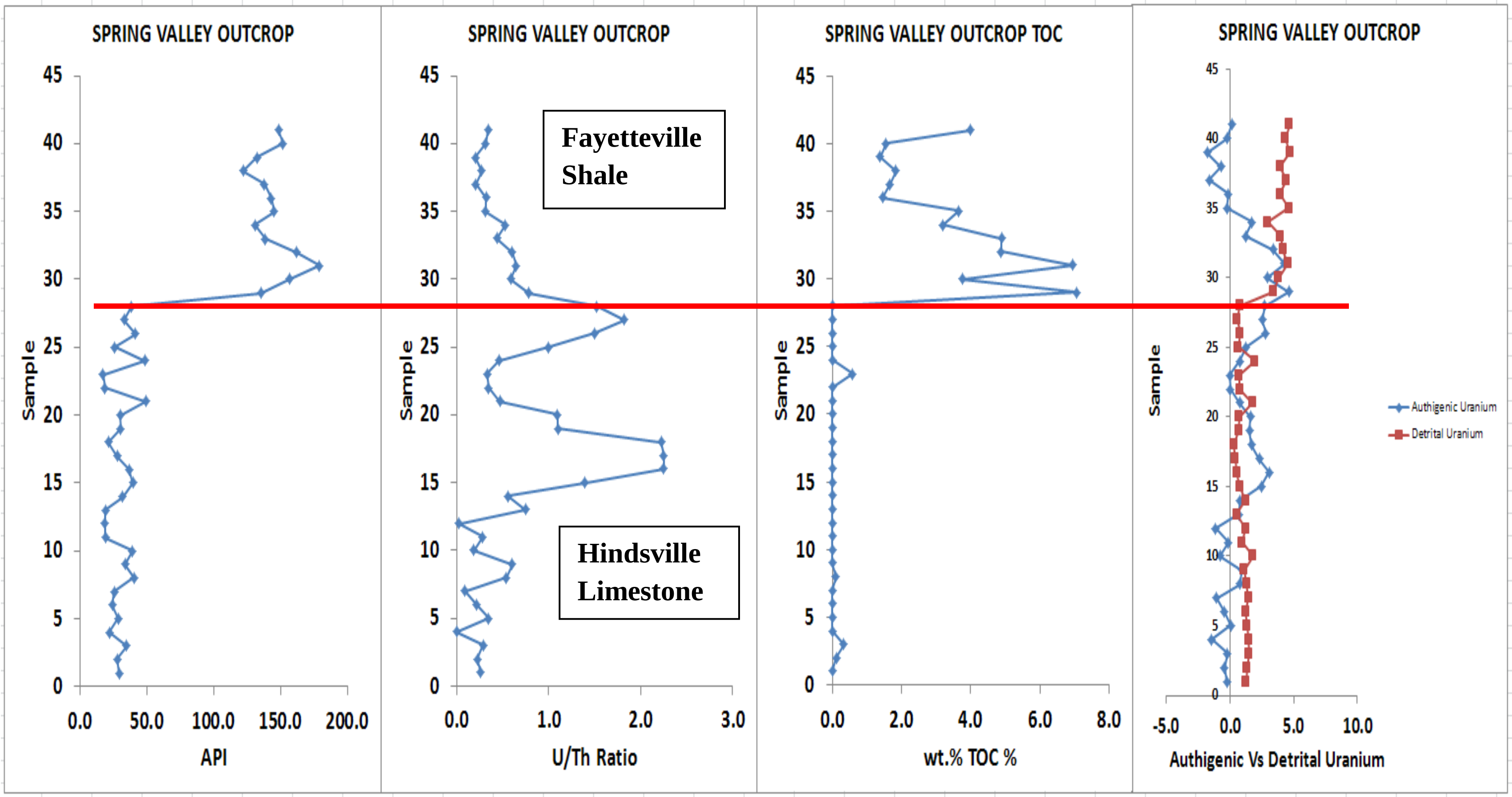


Figure 20: Relationship between gamma ray signatures, uranium (U): thorium (Th) ratio, total organic carbon concentrations and authigenic and detrital uranium signatures of Spring Valley outcrop

4.5 Peyton Creek Outcrop Arkansas

The total thickness of beds exposed in the Peyton Creek outcrop is about 42 m (140 ft). This outcrop extends from a point near the bridge across Peyton Creek, up the hillside for a considerable distance. The section was examined, measured and described. The lithostratigraphic units at Peyton Creek are the upper Pitkin Formation and the entire Imo Shale. Stratigraphically, above the Pitkin limestone is the fossiliferous and pyritic black shale unit of the Imo (Fig. 21). Directly on top of the black shale is the gray shale unit of about 4.6 m (15 ft) thick. This is followed by series of thin siltstones and massive sandstones approximately of 8.0 m (26 ft) thick. The exposed section is divided into two main units: upper Pitkin limestone, and the Imo Shale.

AGE	SERIES	FORMATION	THICKNESS (m)	DESCRIPTION	UNIT
MISSISSIPPIAN	CHESTERIAN	IMO FORMATION	12.5	Concretionary, blocky, muddy shale with interbeds of conglomeratic crinozoan grainstone and thin bedded sandstone-siltstone	CONCRETIONARY SHALE UNIT
			4.9	Concretionary dark gray shale with thin siltstone bed	
			4.9	Concretionary gray shale with conglomeratic resistant bed	
			8.0	Fine-grained sandstone-siltstone with concretionary shale interbeds and siltstone lenses. It is heavily weathered at the top	SANDSTONE UNIT
			4.6	Blocky dark to light gray shale	GRAY SHALE UNIT
			3.3	Fossiliferous fissile black shale	BLACK SHALE UNIT
		PITKIN FORMATION	3.1	Oolithic grainstone with thin interbeds of light gray shale	PITKIN
			0.6	Silty shale	

Figure 21: Generalized stratigraphic section of Peyton outcrop, Arkansas showing the two main formations, their subunits and their relative thickness

4.5.1 Upper Pitkin Limestone

The total thickness of the Pitkin Formation exposed at the Peyton Creek is about 3.7 m (12 ft). This exposure is massive and contains thin calcareous shale at the base of the section (Fig. 22). It contains fossils (fauna and flora) such as brachiopods, crinoids, shell fragments and plant rootlets (Fig. 23). The Pitkin Limestone also contains depositional features such as cross bedding and irregular bed contacts.

Figure 22: Photograph of Peyton Creek outcrop, Arkansas showing massive carbonate upper part of Pitkin Limestone. Note the irregular bed contacts and the gamma spectrometer

Figure 23: Photograph of Peyton Creek outcrop, Arkansas showing the highly fossiliferous bed of the upper Pikin limestone

4.5.2 Imo Shale (Formation)

The total measured thickness of this unit is about 28.2 m (126 ft) and consists predominantly of a dark-gray to black, fissile, clay shale with interbedded discontinuous sandstone, limestone, and conglomerate. The shale weathers from dark gray to brown and it ranges from calcareous to non-calcareous. It often contains platy fossiliferous to non-fossiliferous resistant concretionary intervals. Common fossils in the shale include bivalves, gastropods, cephalopods (including *Rayonnoceras*, *Reticycloceras*, and *Tylonautilus*), brachiopods, crinoids, trilobites, corals (solitary and colonial) and plant materials. (Webb and Sutherland, 1993) The Imo Formation at this location can be subdivided into the following from the base to the top of the section: the basal black shale, the grey shale, the flaggy siltstone and massive sandstone, and the concretionary dark to light gray shale.

The basal black shale of about 3.3 m (11 ft) directly overlies the upper Pitkin limestone. It is a black, fissile, pyritic and fossiliferous shale (Fig. 24). Fossils include brachiopods ammnoids and crinoids. It has highly fossiliferous thin resistive layers. The shale unit directly above the underlying resistant unit is highly fossiliferous (brachiopods) and weathers into thin flakes. Directly above this bed is the fossiliferous gray shale unit of about 4.6 m (15 ft) thick (Fig.25). At the lower part, the shale is dark gray in color and blocky in texture. The upper part is lighter in color and more fissile. It also contains dark-gray concretions.

Overlying the gray shale is the flaggy siltstone and the massive sandstone unit of about 8.0 m (26 ft) thick (Fig. 26). The sandstone unit is characteristically fossiliferous, brown to gray in color, fine to medium-grained, thin to massive bedded, and sometimes cross-bedded. The lower part of the sandstone unit contains, shale interbeds and shale siltstone with abundant bottom markings. At the upper part it is ferruginous, heavily weathered at the top of the unit and contains calcareous woody zone. Directly on this unit is the concretionary gray shale unit of about 22.5 m (74 ft.) (Fig. 27). This unit contains thin interbeds of siltstone of about 0.61m (2 ft) and thin beds of concretonary, conglomeratic, fossiliferous limestone. Common fossils found here include ammonoid, conodont, and foraminiferal faunas (Webb 1987; Webb and Sutherland, 1993; Hawkins, 1983)

Figure 24: Photograph of Peyton, Creek outcrop, showing the fissile, pyritic and fossiliferous black shale unit of the Imo Formation. Note the thin carbonate bed at the base made the transition from the upper Pitkin limestone to the Imo Shale.

Figure 25: Photograph of Peyton Creek outcrop, Arkansas showing the fissile-blocky, pyritic and fossiliferous gray shale unit of the Imo Shale

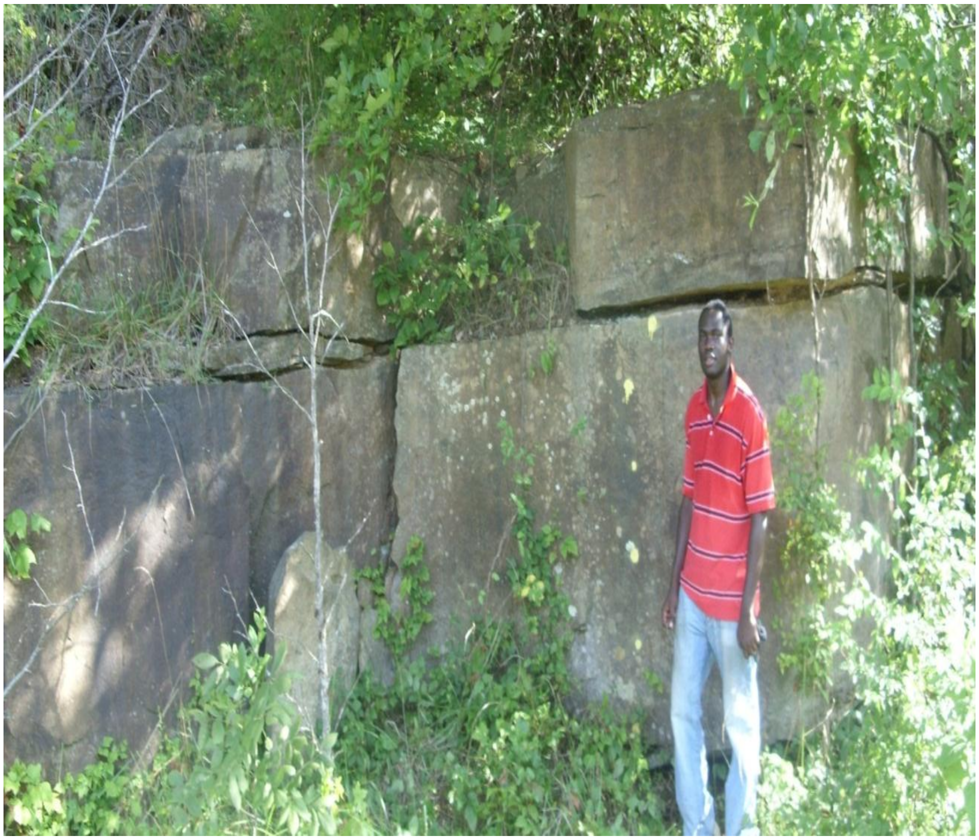


Figure 26: Photograph of Peyton Creek outcrop, Arkansas showing the sandstone unit.

The thin limestone of this unit is between 5-11 inches in thickness. It is characteristically dark gray, fine to coarse-crystalline, very thin to medium-bedded, and fossiliferous. It contains several types of marine fauna including crinoids, bryozoans, brachiopods, bivalves, corals, and nautiloids. Webb and Sutherland, (1993) described these limestones as crinoidal grainstones and packstones with varying amounts of terrigenous clay. The conglomeratic (crinoidal) bed of about 2-5inches thick is gray to black on fresh surfaces and orange-tan on weathered surfaces (Fig. 27).

Figure 27: Photograph of Peyton Creek outcrop, showing the concretionary in the dark gray unit and the concretious conglomeratic bed.

Generally, the sequence exhibited by the Imo Shale is as follows: fossiliferous gray to black shale with some fine-to coarse-grained, silty sandstone and conglomeratic limestone. Uppermost Mississippian fossils are common in some intervals and include bivalves, gastropods, cephalopods, brachiopods, crinoids, trilobites, palynomorphs and plant materials (Webb 1987; Webb and Sutherland, 1993; Hawkins, 1983). Stratigraphically, probably as a result of shale on shale contact, the upper limit of the Imo Shale is difficult locate and poorly defined whereas the basal part rests conformably on upper the Pitkin limestone. Based on the diversity of fossils and microcrinoid-bearing beds, the Imo Shale is interpreted as representing deposition in a moderately well oxygenated marine environment (Mapes et.al 1986).

4.5.3 Gamma Profile

A total of 136 readings were acquired vertically across the outcrop at an interval of one foot (appendix C). Measurements were acquired for the upper Pitkin Limestone and the entire overlying Imo Shale exposed at this location. The gamma-ray characteristics of each unit are described from the base to the top of the section as follows.

The basal part of this location is the upper Pitkin Formation. It is about 12 ft. thick and 12 readings were taking. It has gamma-ray API values ranging between 23 and 120 units (appendix C). The 120 API units correspond with the thin calcareous shale interbed at the base of the section and correlates with the increase TOC value about 4 feet above the base (Fig. 28 and 29). The uranium: thorium ratio is very low about 0.2 on the average.

The next unit in the section is the black shale unit of the Imo Shale from 13-23 feet from the base. The black shale has gamma-ray values ranging between 104 and 162 API units (appendix C and Fig. 29). The black shale, has relatively high API values but the spectral analysis shows a U:Th ratio < 1.0 and as a result the detrital uranium component is higher than the authigenic component. As a result, the black shale is interpreted as containing a high terrigenous components deposited in an open shallow marine environment.

The black shale is overlain by the gray shale unit that extends from 23 to 37 feet above the base. The gray shale has gamma-ray values ranging between 61 and 120 API units. One interesting thing about this unit is that the API values decrease upward across the gray shale. The uranium: thorium ratio is very low and terrigenous influence is indicated. The sandstone above this unit from 38 to 63 feet above the base has gamma-ray values between 17 and 116 API units. The shale unit above from 64 feet above the base to the top of the section has gamma-ray values ranging between 46 and 155 API units. The gray shale has a conspicuously irregular gamma signature that is attributed to the conglomeratic beds and the reddish-brown concretions (Fig. 29). The uranium:thorium ratio is very low and suggest a strong terrigenous sediment

On the whole, spectrometry of the Imo Shale indicates that thorium content increases across the formation from the base to the top. Also uranium concentration is low and that the shale represents deposition in an open shallow marine setting under oxic-dysoxic condition with abundant terrigenous input.

4.5.4 Total Organic Carbon (TOC)

Geochemical analysis shows that the Peyton Creek outcrop demonstrates variability in total organic carbon (TOC) values as a result of change in facies (Fig. 29). The Pitkin Limestone has a TOC content ranging between 1.1 and 2.3 wt.% (appendix F). The black shale unit is organically rich with TOC content ranging between 1.25 and 4.4

wt.%. The gray shale unit has a TOC value ranging between 0.32 and 1.2 wt.%. The sandstone unit has about 0.25 wt.% TOC and the concretions-rich gray unit has TOC values ranging from 0.2-1.67 wt.%.

4.5.5 TOC and Gamma Profile Relationships

Samples from the the Peyton Creek outcrop display a positive relationship between TOC and gamma-ray signature. (Fig. 28). For example, the black shale interval of the Imo Shale has an average gamma-ray signature of 155 API units and 6.43 wt.% TOC, whereas the Pitkin Limestone unit has has an average gamma-ray value 44 API units and 0.02 wt % TOC. Variations in uranium concentration correspond to variations in percent TOC and increases in uranium coincide with a sharp increase in percent TOC (Fig. 29). As a result, uranium can be used as a proxy to predict the TOC content in the entire section. The data from the Peyton Creek outcrop deviate from the normal pattern that high uranium causes high value of total gamma-ray (Luning and Kolonic, 2003) presented here do not conforms to the general believe that high uranium equals high API values. The spectral analysis indicates a terrigenous source, which may indicate an oxic and or dysoxic environment.

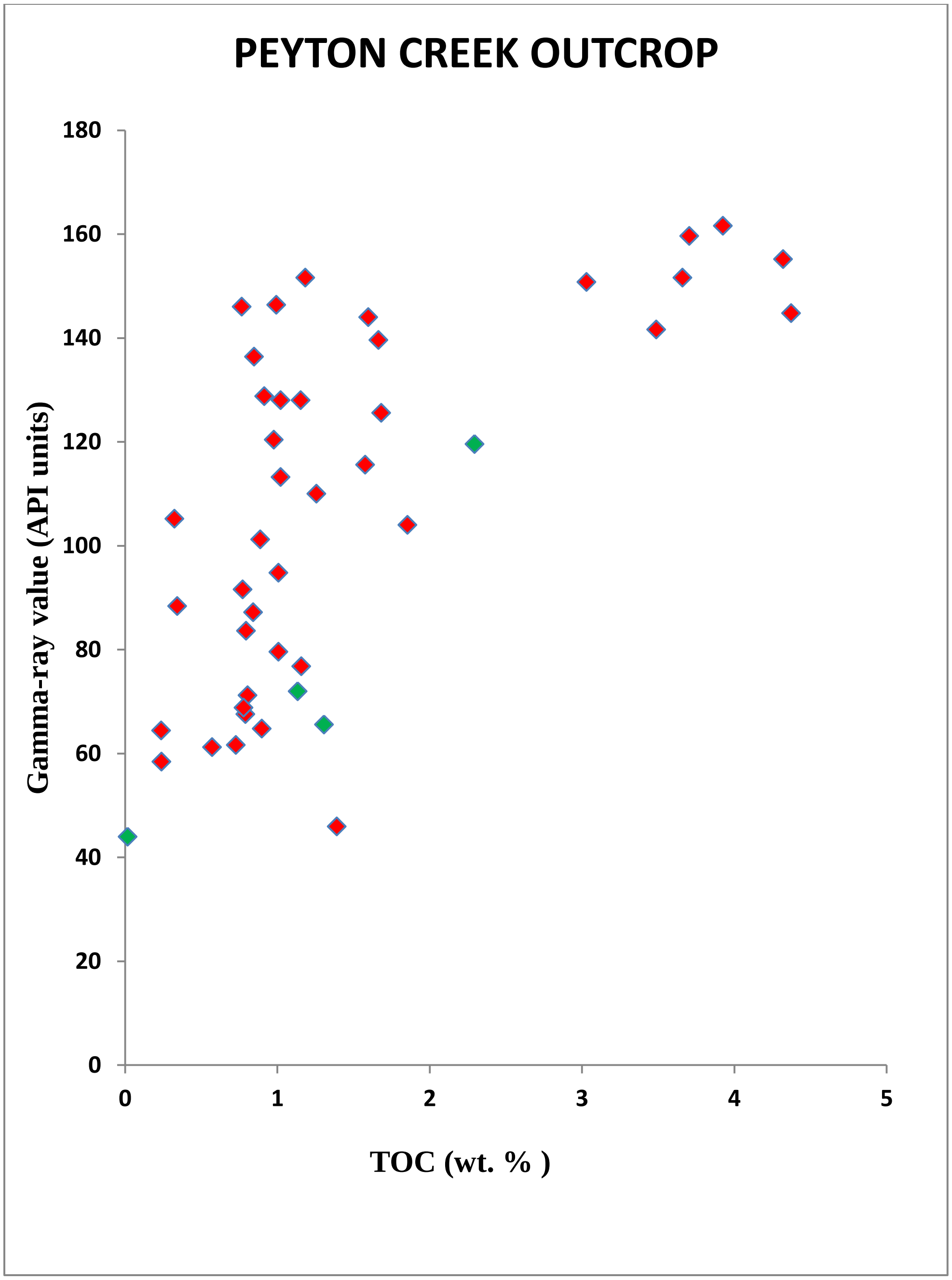


Figure 28 : Relationship between gamma-ray (API units) and TOC, Peyton Creek. The red and green dots represent the Imo Shale and the Pitkin Limestone respectively.

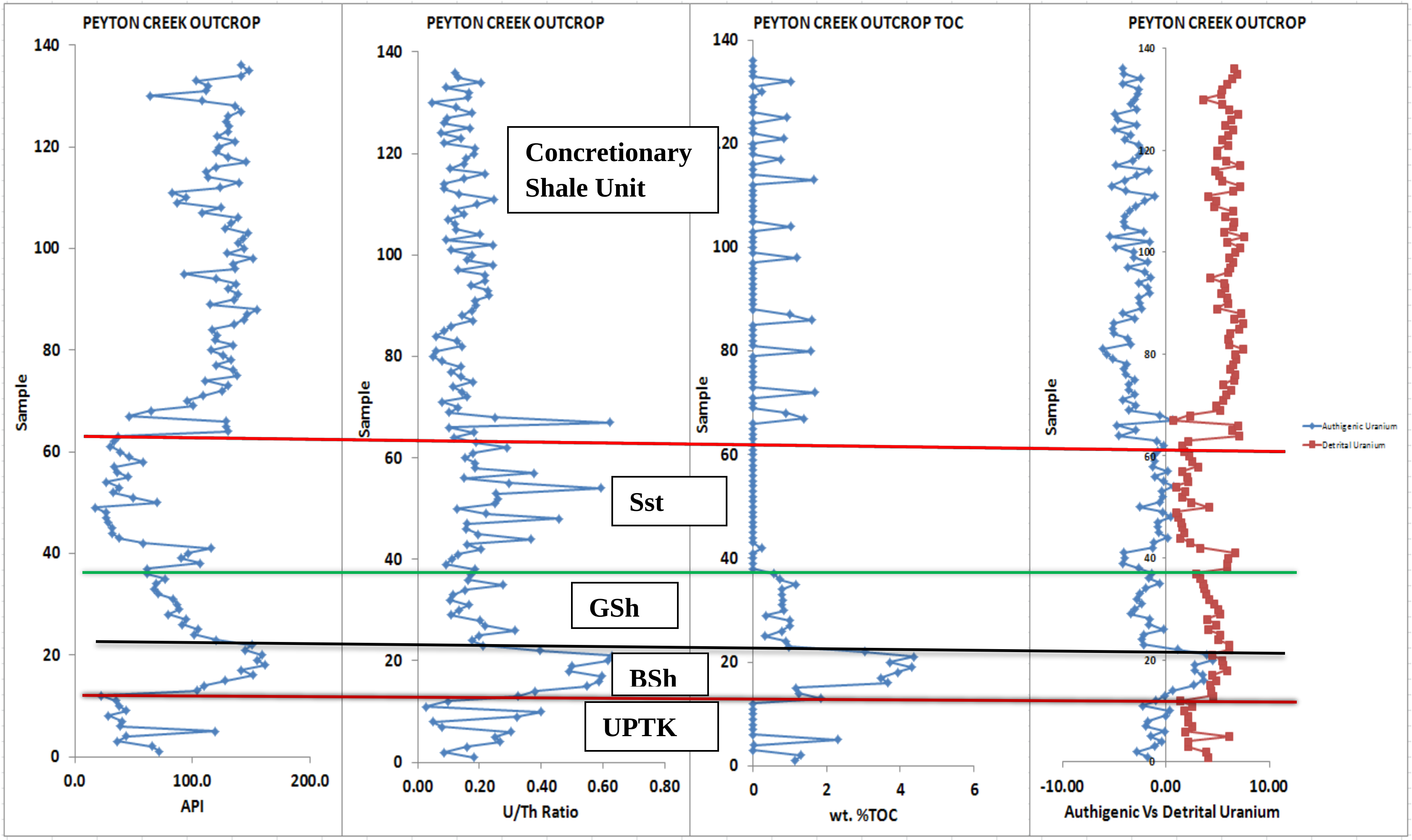


Figure 29: Total API gamma-ray, uranium (U): thorium (Th) ratio, total organic carbon concentrations and authigenic and detrital uranium signatures of Peyton Creek outcrop, Arkansas. UPTK= upper Pitkin, BSh= Black Shale, GSh= Gray Shale, Sst= Sandstone

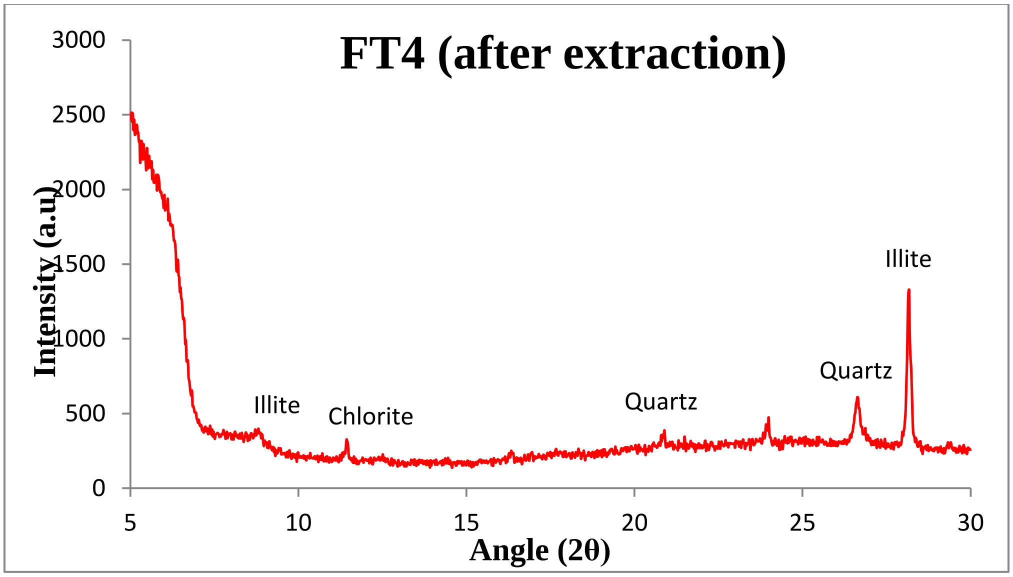
4.6 Clay Mineralogy

A total of 27 samples were collected from the three outcrops to establish the clay mineralogy for the Fayetteville and Imo shales. Shale samples were powdered and analyzed using the PANalytical x-ray diffractometer. Samples were analyzed using these treatments, air-dried, glycolated and heat treated at 500^0C (these are done when specific clays such as chlorite are to be confirmed). According to Australia X-ray Analytical Association (AXAA) (2010), there are seven common clay classes including: illite, kaolinite, smectite, chlorite palygorsite, vermiculite and sepiolite. However, there is also a series of known mixed layers in which the most common and widely studied is illite-smectite mixed layer

The classes of clay identified in the Fayetteville Shale and the Imo shale are similar and they include; illite, kaolinite, chlorite and illite-smectite mixed layer. Illite identified by a peak at 8.8^0 2θ is not affected by glycolation and heat treatment at 350^0C. The illite-smectite layer is the most difficult to identify of the series of clay and it is usually represented by a peak at approximately 8^0 2θ. Kaolinite and chlorite occupy similar positions (12.3-12.5 2θ) and can be present in the same sample. kaolinite survives heat treatment at 350^0C, but not at 500^0C whereas chlorite survives heat treatment at 500^0C. Chlorite and kaolinite are not affected by glycolation Smectite is a diverse group of clays that expands uniformly with glycolation and the peaks sharpen and increase. They collapse on heating at 500^0C to illite-like peaks (AXAA, 2010).

Twenty seven samples from both Fayetteville Shale (Marshall and Spring Valley) and Imo Shale (Peyton Creek) were analyzed for clay mineralogy. The shales conatain kaolinite, chlorite and illite with amount varying from trace amount to sufficient quantity to generate small peaks in clay-extracted samples. These clay minerals are identified on diffractograms of representative samples representative samples (Fig 30 and 31). The clay composition of the Fayetteville Shale at Marshall is represented in three diffractograms: extracted, glycolated and heated (Fig. 30). The top diffractogram for the extracted sample contains peak at 2θ value of 8.8, 12.3, 20.9 and 26.6. The first two very small, but distinct peaks indicate illite and chlorite respectively. The two peaks at 2θ values of 20.9 and 26.6 indicate quartz. The Fayetteville Shale at Spring Valley is dominated by illlite, and chlorite.

The clay composition of Imo Shale at Peyton Creek is predominantly illite, smectite, kaolinite, and chlorite and (Fig. 31). There is no significant difference in clay mineralogy between the Fayetteville Shale (Spring Valley) and the Imo shale (Peyton Creek.



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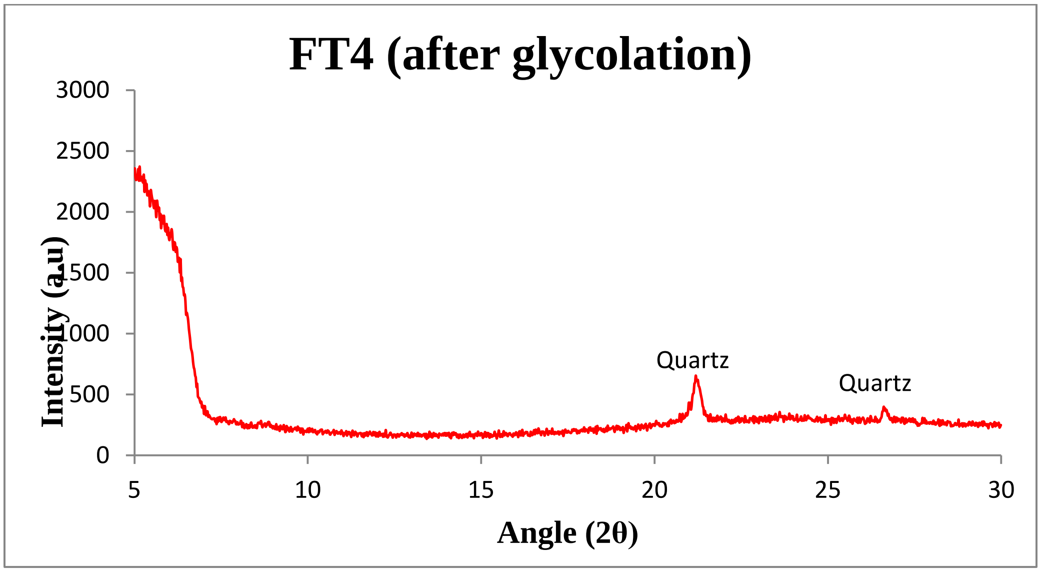

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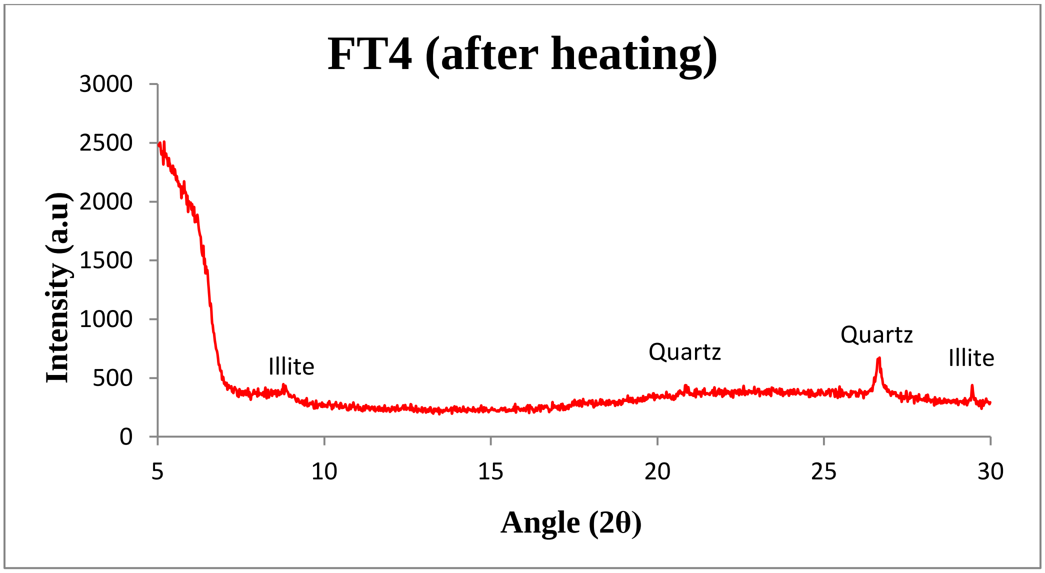

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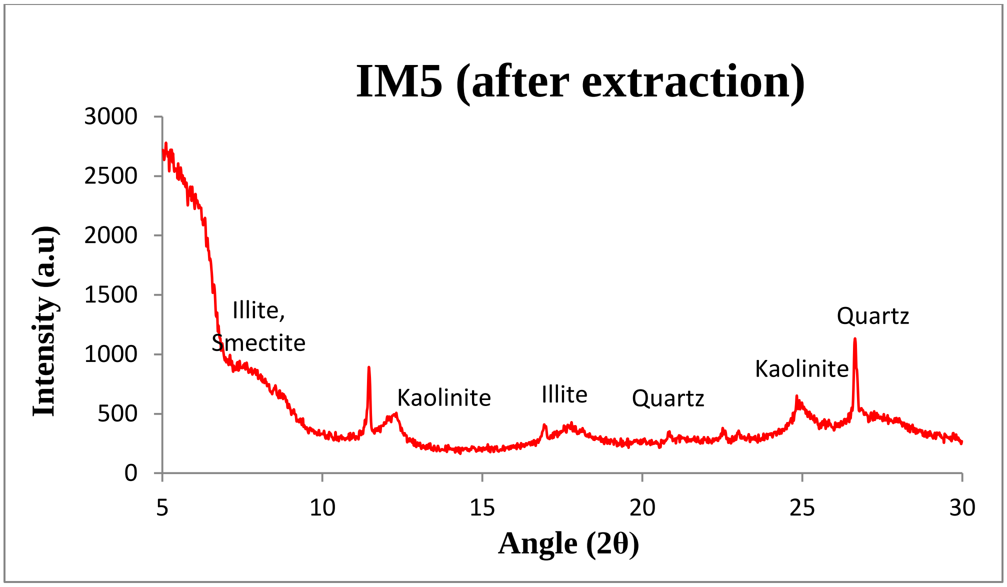
Figure 30: X-ray diffractogram of the Fayetteville Shale, Marshall, Arkansas after: (a) extraction, (b) glycolation and (c) heating.


IM5 (after extraction)
Intensity (a.u)
3000
2500
2000
1500
1000
500
0
5
10
15
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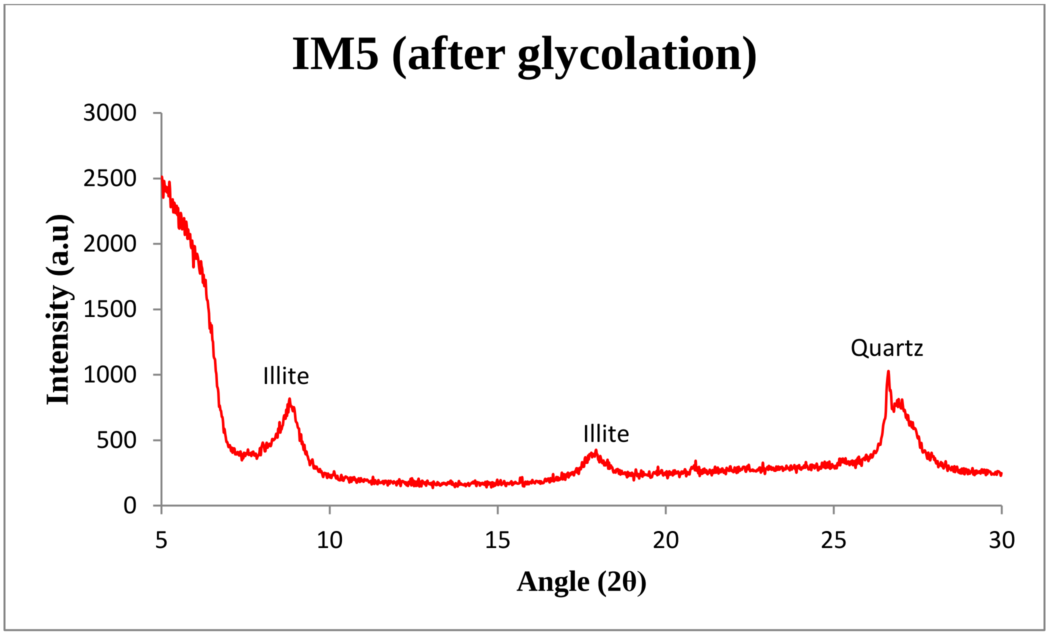
Angle (2θ)
Illite,
Smectite
Kaolinite
Illite
Quartz
Kaolinite
Quartz

a


IM5 (after glycolation)
Intensity (a.u)
3000
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Angle (2θ)
Illite
Illite
Quartz

b

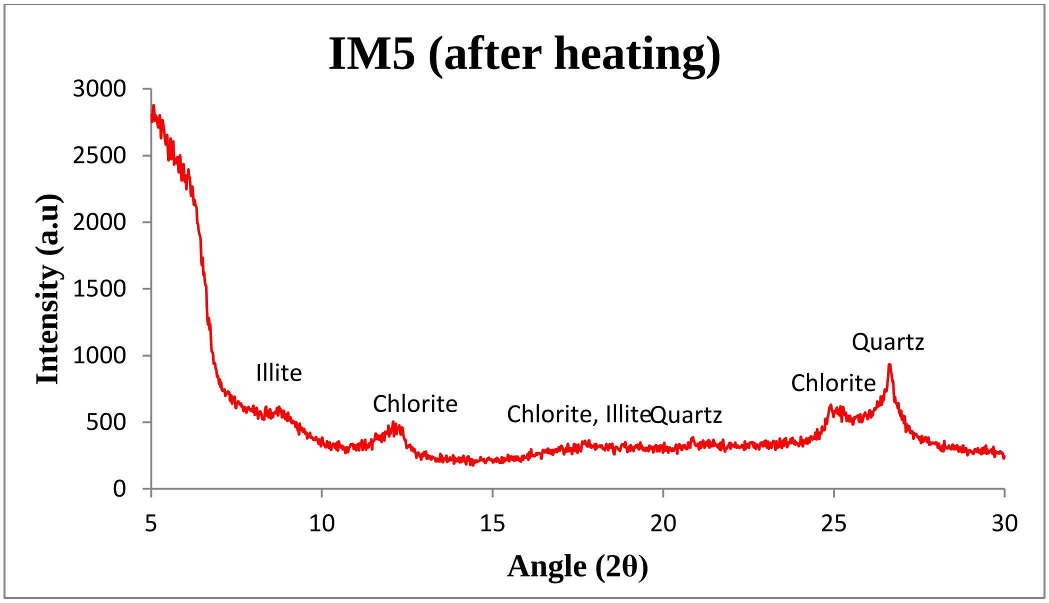

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Figure 31: X-ray diffractogram of the Imo Shale, Peyton Creek, Arkansas after: (a) extraction, (b) glycolation and (c) heating

4.7 Interpretation

Marshall Outcrop

Lower Fayetteville Shale

The black shale beds of this unit are hot shales as shown by higher API values reaching 234 API units. The uranium measurements for this unit show that the shale has higher uranium content than thorium; this is reflected by the uranium:thorium ratio signature (Fig. 15). Also, the shale displays higher authigenic uranium compared to detrital uranium, whereas the carbonate beds displayed no significant difference. From the above it is inferred that the shale-forming mud was deposited in a relatively deep open marine environment under anoxic conditions. This interpretation is supported by the lack of a sessile fauna in this unit.

Upper Fayetteville

The shale interval in the lower part of this unit displays the highest gamma-ray values (264 API units) of the entire outcrop (Fig. 14). In contrast, carbonate beds have gamma-ray values as low as 45 API units. The spectral analysis shows that uranium component across the unit is higher than the thorium, indicating marine source (Yu et.al, 1999; Luning and Kolonic, 2003; McManus et.al, 2004). Authigenic uranium for the shale interval is also relatively high compared to calculated detrital uranium, which supports the interpretation of a marine source and deposition under anoxic conditions

Pitkin Limestone

From the spectral analysis and total gamma-ray data presented here, it is evident that the carbonate beds have lower API values and uranium content. The carbonate beds demonstrate an inconspicuously equal amount of detrital and authigenic uranium indicative of a more open marine oxic conditions

Spring Valley

The gamma spectrometry survey of the organically rich Fayetteville at Spring Valley reveals that thorium concentration closely related to TOC with low values in Hindsville Limestone and higher values in the Fayetteville Shale. However, within the Fayetteville Shale thorium concentration remains relatively flat and TOC varies between 1-7 wt.%. In contrast, a positive relationship is evident between uranium and TOC that is not considering the thorium concentration (Fig. 20). As a result, uranium can be used as a proxy to predict the TOC content and source in the Fayetteville shale. High thorium concentrations towards the top of the outcrop are interpreted as an indication of increasing terigenous input and a strong indication for an oxic/suboxic environment. As such, the upper part of the Fayetteville Shale is interpreted as a proximal deposit, whereas the lowermost shale represented deeper and more distal deposition.

Within the black Fayetteville Shale unit, the uranium content decreases up section, while the thorium content increases (appendix B) signifying terrestrial input. It is evident from the gamma spectrometry analysis of this Fayetteville shale that it is deposited in a proximal position on the basin margin.

Peyton Creek

Black Shale

The spectral analysis for this unit shows that terrigenous input and the detrital uranium component were prominent. This is interpreted as indicating more lithogenic materials and a detrital source. The black shale has relatively high total gamma-ray (>160 API units) values even though the detrital uranium component calculates higher than the authigenic one. The black shale is interpreted as an open-shallow-marine deposit.

On the whole, the Imo Shale spectrometry shows that thorium content increases across the formation from the base to the top. The Imo is interpreted to represent deposition in an open-shallow-marine setting under oxic-dysoxic conditions with abundant continental sediments entering the system

4.8 Depositional Cycle

Handford (1996) described Fayetteville shale as shelf storm deposits. He interpreted the Fayetteville shale as a transgressive system tract that drowned the carbonate shelf sequence of the Hindsville Limestone and siliciclastic deltaic sequence represented by Batesville Sandstone.

The Fayetteville Shale is regarded as a transgressive and highstand sequence that represents a significant portion of the Chesterian record. The transgression was initiated by replacement of the carbonates by black shales of the Fayetteville Shale as the maximum flooding event was achieved. Regression returned carbonates to the region to form the Pitkin Limestone.

From the gamma spectrometry survey, the Fayetteville Shale shows two major depositional cycles: The lower Fayetteville shale and the upper Fayetteville shale. The black shale interval of the lower Fayetteville was deposited in a relatively deeper initially anoxic environment. This supports the interpretation of Handford, (1996) and Meek, (1997) that the Fayetteville represents deposition within anoxic/dysoxic bottom conditions on a deep to very deep shelf. Continuing compaction of the Wedington deltaic complex, particularly its prodelta muds and the lower Fayetteville shale allowed the seas to transgress further and thus the beginning of the second depositional cycle represented by the upper Fayetteville Shale (Meek, 1997).

The second depositional cycle begins with an increase in the water depth as represented by the deposition of the black shale interval of the upper Fayetteville shale. As the water depth decreases, the carbonate intervals were deposited. The upper Fayetteville Shale member is marked by open circulation, as revealed by its molluskdominated benthic fauna, and marks the end of the highstand systems tract and the beginning of a regression (and progradation) that gave rise to the deposition of the overlying Pitkin Limestone under shallow shelf conditions (Handford, 1996 and Meek, 1997).

In the upper part of the Fayetteville Shale, dark micritic limestones are interbedded with thin calcareous shale in a rhythmic pattern. They consist of a fossil hash composed primarily of crinozoan fragments and may be classified as packstones and grainstones. They appear to have been deposited as single storm events that washed detritus off of the Pitkin Limestone carbonate platform that was prograding as the Chesterian Sea regressed (Meek, 1997). The subsequent regression resulted in the progradation and aggradation on the Pitkin Limestone to end the Fayetteville transgressive/regressive cycle (Handford, 1996 and Meek, 1997).

In general the changes in U:Th ratio and TOC across the Fayetteville Shale at Marshal shows two shoaling upward patterns. The older cycle terminates with the flooding associated with the upper Fayetteville shale; the youngest culminating with the onset of Pitkin deposition

CHAPTER V

5.1 Summary

The gamma spectrometry and geochemical investigation of the Mississippian (Chesterian) Fayetteville and Imo shales in the type area has provided new insights into black shale environment of deposition and sediment source. The following were inferred from the gamma spectrometry and geochemical analyses of the study area.

The Marshall outcrop is divided into three main units: The black lower Fayetteville Shale, rhythmic upper Fayetteville Shale and the oolitic-bioclastic Pitkin Limestone. The black lower Fayetteville shale is predominantly made up of organically rich, fossiliferous black shale and laterally continuous micritic limestone beds. The black shale is a hot shale with 234 gamma API value and average TOC content of about 4 wt.%. The rhythmic upper Fayetteville shale consist predominantly alternating succession of limestone and black-dark gray shale. The black-dark gray shale is organically rich, fossiliferous and pyritic. It is a hot shale with API concentration of 264 and average TOC content of about 4.5 wt.% .

There is a close relationship in the organic richness and gamma ray concentration of the Fayetteville shale at Marshall. The Fayetteville Shale at Marshall is a relatively low clay content shale with illite as the dominant minerals. The Fayetteville shale at Marshall is deposited in relatively deep marine environment under anoxic condition. This is evident by higher value of uranium content compared to that of thorium and higher authigenic uranium compared to detrital uranium.

The changes in U:Th ratio and TOC across the Fayetteville Shale demonstrate that it contains two shoaling-upward sequences: the lower one terminating at the base of the highly radioactive upper Fayetteville Shale; the upper one culminating with the onset of Pitkin deposition.

The gamma spectrometry survey of the organically rich Fayetteville Shale at Spring Valley reveals that thorium concentration closely related to TOC with low values in Hindsville Limestone and higher values in the Fayetteville Shale. However, within the Fayetteville Shale, thorium concentration remains relatively flat and TOC varies between 1-7 wt.%. In contrast, a positive relationship is evident between uranium and TOC that is not considering the thorium concentration. As a result, uranium can be used as a proxy to predict the TOC content and source in the Fayetteville shale. High thorium concentrations towards the top of the outcrop are interpreted as an indication of increasing terigenous input and a strong indication for an oxic/suboxic environment. Within the black Fayetteville Shale unit, the uranium content decreases up section, while the thorium content increases signifying terrestrial input. It is evident from the gamma spectrometry analysis of this Fayetteville shale that it is deposited in a proximal position on the basin margin.

The Imo Shale at Peyton Creek is subdivided into four units using lithology and total gamma-ray. The Imo Shale is relatively clay rich, fossiliferous, radioactive and organically rich with average TOC content of 3.0 wt.%. The Imo contains black shale that transitions upward to gray shale, which is succeeded by sandstone and dark gray shale with thin dark limestone beds. The spectral analysis of the Imo Shale shows that terrigenous input and the detrital uranium component were prominent. This is interpreted as indicating more lithogenic materials and a detrital source. The black shale has relatively high total gamma-ray (>160 API units) values even though the detrital uranium component calculates higher than the authigenic one. U, Th, TOC and gamma-ray decrease upward from the basal black shale to the sandstone. Above the sandstone, as a result of dilution by terrigenous sediments, TOC and U concentrations decreases and gamma-ray correlates to Th rather than U. Across the Imo, TOC and U positively correlate, suggesting a marine source for organic carbon. The results indicate that API gamma-ray responds to U and Th and consequently may not be a reliable indicator of TOC concentration. However, U correlates positively with TOC across all units and is viewed as a reliable tool for estimating their gas-sourcing potential.

5.2 Future work/Recommendation

- With high TOC in Imo and Fayetteville shales, they can be considered as hydrocarbon potential source rocks. However, all other parameters such as rock eval analysis and victrinite reflectance need to be done in order to evaluate the hydrocarbon potential of the Fayetteville and Imo shales.
- Detailed biostratigraphic analysis using conodont will help construct a detailed biostratigraphic framework and internal stratigraphy of the formations
- Fractures and infilling cements (calcite) need to be adequately studied and understood to help in the exploration purposes especially horizontal drilling.
- Spectral gamma ray coupled with other logs such as spontaneous potential (SP), resistivity, density and neutron logs will help in identifying the hydrocarbon rich zones.
- Comparing the Fayetteville and Imo shale in the surface and in the sub-surface through core and outcrop data

- Determination of maximum thickness of the Imo sequence by a clear definition of its upper contacts. As such, more work need to be done in this area to determine its maximum thickness and upper limit.
- Subsurface mapping in order to determine their thickness as well as extent.

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APPPENDICES

1 Appendix A

Table 3: Gamma ray values of the Marshall Outcrop, Arkansas showing the concentration of potassium (K) in %, uranium (U) in ppm and thorium (Th) in ppm, total gamma in API (America Petroleum Institute), U/Th, and authigenic and detrital uranium. FT= Fayetteville and PK= Pitkin samples

Sample Name	K(%)	U(ppm)	TH(ppm)	8U	4^{TH}	16K	API	U/Th Ratio	Authigenic Uranium	Detrital Uranium
PK5	-0.10	0.80	0.20	6.40	0.80	-1.60	5.60	4.00	0.73	0.07
PK4	0.20	1.50	3.80	12.00	15.20	3.20	30.40	0.39	0.23	1.27
PK3	0.60	2.50	4.40	20.00	17.60	9.60	47.20	0.57	1.03	1.47
PK2	0.40	3.10	4.50	24.80	18.00	6.40	49.20	0.69	1.60	1.50
PK1	0.50	2.10	5.20	16.80	20.80	8.00	45.60	0.40	0.37	1.73
FT138	0.60	2.20	5.30	17.60	21.20	9.60	48.40	0.42	0.43	1.77
FT137	0.40	3.20	4.30	25.60	17.20	6.40	49.20	0.74	1.77	1.43
FT136	0.40	3.00	4.30	24.00	17.20	6.40	47.60	0.70	1.57	1.43
FT135	0.60	3.70	5.40	29.60	21.60	9.60	60.80	0.69	1.90	1.80
FT134	0.80	4.50	6.00	36.00	24.00	12.80	72.80	0.75	2.50	2.00
FT133	0.80	3.00	6.80	24.00	27.20	12.80	64.00	0.44	0.73	2.27
FT132	0.90	5.40	6.10	43.20	24.40	14.40	82.00	0.89	3.37	2.03
FT131	1.00	2.90	6.10	23.20	24.40	16.00	63.60	0.48	0.87	2.03
FT130	1.30	4.70	8.50	37.60	34.00	20.80	92.40	0.55	1.87	2.83
FT129	1.00	3.90	7.70	31.20	30.80	16.00	78.00	0.51	1.33	2.57
FT128	0.90	3.40	6.90	27.20	27.60	14.40	69.20	0.49	1.10	2.30
FT127	1.00	3.60	7.50	28.80	30.00	16.00	74.80	0.48	1.10	2.50

FT126	1.00	2.70	5.80	21.60	23.20	16.00	60.80	0.47	0.77	1.93
FT125	0.90	4.70	6.30	37.60	25.20	14.40	77.20	0.75	2.60	2.10
FT124	1.00	3.10	6.50	24.80	26.00	16.00	66.80	0.48	0.93	2.17
FT123	1.40	4.70	7.80	37.60	31.20	22.40	91.20	0.60	2.10	2.60
FT122	0.80	3.60	4.70	28.80	18.80	12.80	60.40	0.77	2.03	1.57
FT121	1.20	5.20	6.90	41.60	27.60	19.20	88.40	0.75	2.90	2.30
FT120	0.90	5.30	5.50	42.40	22.00	14.40	78.80	0.96	3.47	1.83
FT119	0.80	3.20	5.10	25.60	20.40	12.80	58.80	0.63	1.50	1.70
FT118	1.10	4.80	6.60	38.40	26.40	17.60	82.40	0.73	2.60	2.20
FT117	1.20	4.50	6.50	36.00	26.00	19.20	81.20	0.69	2.33	2.17
FT116	0.80	3.10	5.20	24.80	20.80	12.80	58.40	0.60	1.37	1.73
FT115	0.90	3.50	5.00	28.00	20.00	14.40	62.40	0.70	1.83	1.67
FT114	1.00	4.90	6.00	39.20	24.00	16.00	79.20	0.82	2.90	2.00
FT113	1.30	4.30	7.70	34.40	30.80	20.80	86.00	0.56	1.73	2.57
FT112	0.90	3.70	7.00	29.60	28.00	14.40	72.00	0.53	1.37	2.33
FT111	1.10	4.60	7.20	36.80	28.80	17.60	83.20	0.64	2.20	2.40
FT110	0.80	4.80	5.20	38.40	20.80	12.80	72.00	0.92	3.07	1.73
FT109	1.20	6.20	6.90	49.60	27.60	19.20	96.40	0.90	3.90	2.30
FT108	0.70	5.00	5.50	40.00	22.00	11.20	73.20	0.91	3.17	1.83
FT107	1.20	6.60	5.70	52.80	22.80	19.20	94.80	1.16	4.70	1.90
FT106	1.20	6.60	6.80	52.80	27.20	19.20	99.20	0.97	4.33	2.27
FT105	1.20	6.30	6.00	50.40	24.00	19.20	93.60	1.05	4.30	2.00
FT104	1.40	6.90	8.70	55.20	34.80	22.40	112.40	0.79	4.00	2.90
FT103	0.50	2.80	3.60	22.40	14.40	8.00	44.80	0.78	1.60	1.20
FT102	0.50	2.50	4.70	20.00	18.80	8.00	46.80	0.53	0.93	1.57
FT101	0.80	3.60	6.40	28.80	25.60	12.80	67.20	0.56	1.47	2.13
FT100	1.70	4.90	7.50	39.20	30.00	27.20	96.40	0.65	2.40	2.50

FT99	1.20	3.20	7.20	25.60	28.80	19.20	73.60	0.44	0.80	2.40
FT98	1.90	4.50	9.60	36.00	38.40	30.40	104.80	0.47	1.30	3.20
FT97	1.60	6.20	7.30	49.60	29.20	25.60	104.40	0.85	3.77	2.43
FT96	1.20	4.30	7.40	34.40	29.60	19.20	83.20	0.58	1.83	2.47
FT95	1.40	5.30	6.10	42.40	24.40	22.40	89.20	0.87	3.27	2.03
FT94	1.70	4.80	9.00	38.40	36.00	27.20	101.60	0.53	1.80	3.00
FT93	2.10	7.70	7.50	61.60	30.00	33.60	125.20	1.03	5.20	2.50
FT92	2.20	7.90	11.20	63.20	44.80	35.20	143.20	0.71	4.17	3.73
FT91	2.20	7.60	10.00	60.80	40.00	35.20	136.00	0.76	4.27	3.33
FT90	2.20	6.80	7.40	54.40	29.60	35.20	119.20	0.92	4.33	2.47
FT89	1.80	9.20	10.40	73.60	41.60	28.80	144.00	0.88	5.73	3.47
FT88	2.10	13.20	11.30	105.60	45.20	33.60	184.40	1.17	9.43	3.77
FT87	1.80	16.00	13.00	128.00	52.00	28.80	208.80	1.23	11.67	4.33
FT86	1.90	21.50	15.30	172.00	61.20	30.40	263.60	1.41	16.40	5.10
FT85	1.50	21.60	11.70	172.80	46.80	24.00	243.60	1.85	17.70	3.90
FT84	2.50	11.40	10.00	91.20	40.00	40.00	171.20	1.14	8.07	3.33
FT83	2.00	11.70	8.10	93.60	32.40	32.00	158.00	1.44	9.00	2.70
FT82	1.90	10.90	9.50	87.20	38.00	30.40	155.60	1.15	7.73	3.17
FT81	2.10	9.80	11.50	78.40	46.00	33.60	158.00	0.85	5.97	3.83
FT80	1.30	10.00	8.90	80.00	35.60	20.80	136.40	1.12	7.03	2.97
FT79	1.30	9.60	7.60	76.80	30.40	20.80	128.00	1.26	7.07	2.53
FT78	2.30	9.90	9.30	79.20	37.20	36.80	153.20	1.06	6.80	3.10
FT77	2.50	11.20	12.10	89.60	48.40	40.00	178.00	0.93	7.17	4.03
FT76	1.90	12.40	11.10	99.20	44.40	30.40	174.00	1.12	8.70	3.70
FT75	1.70	16.40	9.60	131.20	38.40	27.20	196.80	1.71	13.20	3.20
FT74	1.40	12.70	8.50	101.60	34.00	22.40	158.00	1.49	9.87	2.83
FT73	1.40	11.00	7.70	88.00	30.80	22.40	141.20	1.43	8.43	2.57

FT72	2.00	15.00	9.50	120.00	38.00	32.00	190.00	1.58	11.83	3.17
FT71	1.70	16.80	9.40	134.40	37.60	27.20	199.20	1.79	13.67	3.13
FT70	2.20	18.60	12.70	148.80	50.80	35.20	234.80	1.46	14.37	4.23
FT69	2.00	17.20	12.50	137.60	50.00	32.00	219.60	1.38	13.03	4.17
FT68	2.20	14.70	13.00	117.60	52.00	35.20	204.80	1.13	10.37	4.33
FT67	2.00	10.70	10.30	85.60	41.20	32.00	158.80	1.04	7.27	3.43
FT66	0.30	3.90	3.80	31.20	15.20	4.80	51.20	1.03	2.63	1.27
FT65	1.10	6.90	7.40	55.20	29.60	17.60	102.40	0.93	4.43	2.47
FT64	1.10	7.10	6.80	56.80	27.20	17.60	101.60	1.04	4.83	2.27
FT63	1.30	10.70	9.30	85.60	37.20	20.80	143.60	1.15	7.60	3.10
FT62	0.40	5.00	3.00	40.00	12.00	6.40	58.40	1.67	4.00	1.00
FT61	0.30	5.40	2.60	43.20	10.40	4.80	58.40	2.08	4.53	0.87
FT60	0.70	5.70	3.50	45.60	14.00	11.20	70.80	1.63	4.53	1.17
FT59	0.50	5.60	3.20	44.80	12.80	8.00	65.60	1.75	4.53	1.07
FT58	0.50	5.00	2.70	40.00	10.80	8.00	58.80	1.85	4.10	0.90
FT57	0.60	5.20	3.50	41.60	14.00	9.60	65.20	1.49	4.03	1.17
FT56	0.30	6.50	3.30	52.00	13.20	4.80	70.00	1.97	5.40	1.10
FT55	0.50	6.50	3.50	52.00	14.00	8.00	74.00	1.86	5.33	1.17
FT54	0.60	5.60	3.10	44.80	12.40	9.60	66.80	1.81	4.57	1.03
FT53	0.70	4.40	3.70	35.20	14.80	11.20	61.20	1.19	3.17	1.23
FT52	0.60	6.20	7.20	49.60	28.80	9.60	88.00	0.86	3.80	2.40
FT51	1.00	6.40	7.50	51.20	30.00	16.00	97.20	0.85	3.90	2.50
FT50	1.80	9.80	10.90	78.40	43.60	28.80	150.80	0.90	6.17	3.63
FT49	1.20	7.30	6.40	58.40	25.60	19.20	103.20	1.14	5.17	2.13
FT48	1.30	8.10	7.40	64.80	29.60	20.80	115.20	1.09	5.63	2.47
FT47	0.80	6.50	6.40	52.00	25.60	12.80	90.40	1.02	4.37	2.13
FT46	1.50	5.60	11.60	44.80	46.40	24.00	115.20	0.48	1.73	3.87

FT45	1.90	5.60	11.60	44.80	46.40	30.40	121.60	0.48	1.73	3.87
FT44	1.70	5.70	10.30	45.60	41.20	27.20	114.00	0.55	2.27	3.43
FT43	2.10	6.20	9.60	49.60	38.40	33.60	121.60	0.65	3.00	3.20
FT42	1.50	6.10	9.90	48.80	39.60	24.00	112.40	0.62	2.80	3.30
FT41	1.70	4.40	8.30	35.20	33.20	27.20	95.60	0.53	1.63	2.77
FT40	1.50	5.30	6.10	42.40	24.40	24.00	90.80	0.87	3.27	2.03
FT39	2.00	6.30	10.60	50.40	42.40	32.00	124.80	0.59	2.77	3.53
FT38	1.80	5.70	11.20	45.60	44.80	28.80	119.20	0.51	1.97	3.73
FT37	1.80	6.00	11.80	48.00	47.20	28.80	124.00	0.51	2.07	3.93
FT36	1.30	5.70	8.50	45.60	34.00	20.80	100.40	0.67	2.87	2.83
FT35	1.90	5.40	9.30	43.20	37.20	30.40	110.80	0.58	2.30	3.10
FT34	1.50	4.50	9.90	36.00	39.60	24.00	99.60	0.45	1.20	3.30
FT33	1.60	4.60	8.80	36.80	35.20	25.60	97.60	0.52	1.67	2.93
FT32	1.10	6.60	6.60	52.80	26.40	17.60	96.80	1.00	4.40	2.20
FT31	1.40	6.10	9.40	48.80	37.60	22.40	108.80	0.65	2.97	3.13
FT30	1.10	5.10	8.30	40.80	33.20	17.60	91.60	0.61	2.33	2.77
FT29	1.50	6.10	7.70	48.80	30.80	24.00	103.60	0.79	3.53	2.57
FT28	1.70	5.30	9.50	42.40	38.00	27.20	107.60	0.56	2.13	3.17
FT27	1.70	6.30	10.60	50.40	42.40	27.20	120.00	0.59	2.77	3.53
FT26	1.60	6.00	9.20	48.00	36.80	25.60	110.40	0.65	2.93	3.07
FT25	1.80	6.10	7.80	48.80	31.20	28.80	108.80	0.78	3.50	2.60
FT24	1.30	6.70	9.50	53.60	38.00	20.80	112.40	0.71	3.53	3.17
FT23	1.30	5.80	7.70	46.40	30.80	20.80	98.00	0.75	3.23	2.57
FT22	1.60	7.60	8.50	60.80	34.00	25.60	120.40	0.89	4.77	2.83
FT21	1.50	4.50	6.50	36.00	26.00	24.00	86.00	0.69	2.33	2.17
FT20	1.20	6.30	7.80	50.40	31.20	19.20	100.80	0.81	3.70	2.60
FT19	1.80	7.80	9.80	62.40	39.20	28.80	130.40	0.80	4.53	3.27

FT 18	1.80	9.60	8.90	76.80	35.60	28.80	141.20	1.08	6.63	2.97
FT17	2.30	9.80	9.60	78.40	38.40	36.80	153.60	1.02	6.60	3.20
FT16	2.80	15.20	16.80	121.60	67.20	44.80	233.60	0.90	9.60	5.60
FT15	2.30	17.80	11.00	142.40	44.00	36.80	223.20	1.62	14.13	3.67
FT14	2.20	9.50	13.10	76.00	52.40	35.20	163.60	0.73	5.13	4.37
FT13	1.80	9.50	10.90	76.00	43.60	28.80	148.40	0.87	5.87	3.63
FT12	1.80	8.40	10.90	67.20	43.60	28.80	139.60	0.77	4.77	3.63
FT11	1.60	9.00	11.60	72.00	46.40	25.60	144.00	0.78	5.13	3.87
FT10	1.90	7.30	9.80	58.40	39.20	30.40	128.00	0.74	4.03	3.27
FT9	1.70	6.80	10.10	54.40	40.40	27.20	122.00	0.67	3.43	3.37
FT8	1.80	8.20	10.40	65.60	41.60	28.80	136.00	0.79	4.73	3.47
FT7	1.90	6.00	12.60	48.00	50.40	30.40	128.80	0.48	1.80	4.20
FT6	1.80	8.20	10.40	65.60	41.60	28.80	136.00	0.79	4.73	3.47
FT5	2.20	12.90	12.50	103.20	50.00	35.20	188.40	1.03	8.73	4.17
FT4	2.10	17.90	14.00	143.20	56.00	33.60	232.80	1.28	13.23	4.67
FT3	2.80	14.70	15.90	117.60	63.60	44.80	226.00	0.92	9.40	5.30
FT2	2.10	14.60	12.00	116.80	48.00	33.60	198.40	1.22	10.60	4.00
FT1	2.30	12.40	11.30	99.20	45.20	36.80	181.20	1.10	8.63	3.77
FT0	3.20	17.00	14.30	136.00	57.20	51.20	244.40	1.19	12.23	4.77

2 Appendix B

Table 4 Gamma ray values of the Spring Valley Outcrop, Arkansas showing the concentration of potassium (K) in %, uranium (U) in ppm and thorium (Th) in ppm, total gamma in API (America Petroleum Institute), U/Th, and authigenic and detrital uranium. SV= Hindsville Limestone, SF= Fayetteville shale samples

Sample Name	K (%)	U (PPM)	TH (PPM)	16K	8U	4TH	API	U/Th Ratio	Authigenic Uranium	Detrital Uranium
SF12	3.4	4.8	14.0	54.40	38.40	56.00	148.80	0.343	0.133	4.7
SF11	4.2	4.1	13.0	67.20	32.80	52.00	152.00	0.315	-0.233	4.3
SF10	3.3	2.9	14.1	52.80	23.20	56.40	132.40	0.206	-1.800	4.7
SF9	3.1	3.2	11.7	49.60	25.60	46.80	122.00	0.274	-0.700	3.9
SF8	3.9	2.8	13.3	62.40	22.40	53.20	138.00	0.211	-1.633	4.4
SF7	4.1	3.8	11.8	65.60	30.40	47.20	143.20	0.322	-0.133	3.9
SF6	3.4	4.4	13.9	54.40	35.20	55.60	145.20	0.317	-0.233	4.6
SF5	3.6	4.7	8.9	57.60	37.60	35.60	130.80	0.528	1.733	3.0
SF4	3.1	5.2	11.9	49.60	41.60	47.60	138.80	0.437	1.233	4.0
SF3	3.3	7.5	12.4	52.80	60.00	49.60	162.40	0.605	3.367	4.1
SF2	3.4	8.8	13.6	54.40	70.40	54.40	179.20	0.647	4.267	4.5
SF1	3.6	6.7	11.4	57.60	53.60	45.60	156.80	0.588	2.900	3.8
SF0	1.9	8.0	10.2	30.40	64.00	40.80	135.20	0.784	4.600	3.4
SV27	0.1	3.5	2.3	1.60	28.00	9.20	38.80	1.522	2.733	0.8
SV26	0.1	3.1	1.7	1.60	24.80	6.80	33.20	1.824	2.533	0.6
SV25	0.2	3.6	2.4	3.20	28.80	9.60	41.60	1.500	2.800	0.8
SV24	0.2	1.9	1.9	3.20	15.20	7.60	26.00	1.000	1.267	0.6
SV23	0.2	2.7	5.9	3.20	21.60	23.60	48.40	0.458	0.733	2.0
SV22	0.2	0.7	2.1	3.20	5.60	8.40	17.20	0.333	0.000	0.7
SV21	0.2	0.8	2.3	3.20	6.40	9.20	18.80	0.348	0.033	0.8

SV20	0.5	2.5	5.3	8.00	20.00	21.20	49.20	0.472	0.733	1.8
SV19	0.2	2.3	2.1	3.20	18.40	8.40	30.00	1.095	1.600	0.7
SV18	0.3	2.2	2.0	4.80	17.60	8.00	30.40	1.100	1.533	0.7
SV17	0.1	2.0	0.9	1.60	16.00	3.60	21.20	2.222	1.700	0.3
SV16	0.1	2.7	1.2	1.60	21.60	4.80	28.00	2.250	2.300	0.4
SV15	0.1	3.6	1.6	1.60	28.80	6.40	36.80	2.250	3.067	0.5
SV14	0.3	3.2	2.3	4.80	25.60	9.20	39.60	1.391	2.433	0.8
SV13	0.1	2.0	3.6	1.60	16.00	14.40	32.00	0.556	0.800	1.2
SV12	0.2	1.2	1.6	3.20	9.60	6.40	19.20	0.750	0.667	0.5
SV11	0.2	0.1	3.7	3.20	0.80	14.80	18.80	0.027	-1.133	1.2
SV10	0.1	0.8	2.8	1.60	6.40	11.20	19.20	0.286	-0.133	0.9
SV9	0.6	1.0	5.4	9.60	8.00	21.60	39.20	0.185	-0.800	1.8
SV8	0.3	2.0	3.3	4.80	16.00	13.20	34.00	0.606	0.900	1.1
SV7	0.5	2.1	3.9	8.00	16.80	15.60	40.40	0.538	0.800	1.3
SV6	0.3	0.4	4.4	4.80	3.20	17.60	25.60	0.091	-1.067	1.5
SV5	0.2	0.8	3.7	3.20	6.40	14.80	24.40	0.216	-0.433	1.2
SV4	0.1	1.4	4.0	1.60	11.20	16.00	28.80	0.350	0.067	1.3
SV3	0.3	0.0	4.3	4.80	0.00	17.20	22.00	0.000	-1.433	1.4
SV2	0.4	1.3	4.5	6.40	10.40	18.00	34.80	0.289	-0.200	1.5
SV1	0.3	0.9	4.0	4.80	7.20	16.00	28.00	0.225	-0.433	1.3
SV 0	0.4	1.0	3.8	6.40	8.00	15.20	29.60	0.263	-0.267	1.3

3 Appendix C

Table 5 Gamma ray values of the Peyton Creek Outcrop, Arkansas showing the concentration of potassium (K) in %, uranium (U) in ppm and thorium (Th) in ppm, total gamma in API (America Petroleum Institute), U/Th, and authigenic and detrital uranium. PK= Pitkin Limestone and IM= Imo Formation samples.

SAMPLE NAME	K (%)	U (PPM)	TH (PPM)	16K	8U	4TH	API	U/Th Ratio	Authigenic Uranium	Detrital Uranium
PK0	0.4	2.2	12.0	6.40	17.60	48.00	72.00	0.183	-1.800	4.000
PK1	0.7	1.0	11.6	11.20	8.00	46.40	65.60	0.086	-2.867	3.867
PK2	0.2	1.0	6.3	3.20	8.00	25.20	36.40	0.159	-1.100	2.100
PK3	0.3	1.7	6.4	4.80	13.60	25.60	44.00	0.266	-0.433	2.133
PK4	0.6	4.6	18.3	9.60	36.80	73.20	119.60	0.251	-1.500	6.100
PK5	0.3	1.6	5.3	4.80	12.80	21.20	38.80	0.302	-0.167	1.767
PK6	0.3	0.6	7.6	4.80	4.80	30.40	40.00	0.079	-1.933	2.533
PK7	0.1	0.3	6.2	1.60	2.40	24.80	28.80	0.048	-1.767	2.067
PK8	0.2	2.0	6.2	3.20	16.00	24.80	44.00	0.323	-0.067	2.067
PK9	0.1	2.0	5.0	1.60	16.00	20.00	37.60	0.400	0.333	1.667
PK10	0.2	0.2	7.5	3.20	1.60	30.00	34.80	0.027	-2.300	2.500
PK11	0.2	0.4	4.1	3.20	3.20	16.40	22.80	0.098	-0.967	1.367
IM0	0.9	4.4	13.6	14.40	35.20	54.40	104.00	0.324	-0.133	4.533
IM1	1.1	5.0	13.1	17.60	40.00	52.40	110.00	0.382	0.633	4.367
IM2	1.4	6.9	12.6	22.40	55.20	50.40	128.00	0.548	2.700	4.200
IM3	1.7	8.4	14.3	27.20	67.20	57.20	151.60	0.587	3.633	4.767

IM4	1.5	8.0	13.4	24.00	64.00	53.60	141.60	0.597	3.533	4.467
IM5	1.4	8.6	17.6	22.40	68.80	70.40	161.60	0.489	2.733	5.867
IM6	1.5	8.2	16.4	24.00	65.60	65.60	155.20	0.500	2.733	5.467
IM7	1.0	9.9	16.1	16.00	79.20	64.40	159.60	0.615	4.533	5.367
IM8	1.6	8.3	13.2	25.60	66.40	52.80	144.80	0.629	3.900	4.400
IM9	1.3	7.2	18.1	20.80	57.60	72.40	150.80	0.398	1.167	6.033
IM10	1.0	3.9	18.3	16.00	31.20	73.20	120.40	0.213	-2.200	6.100
IM11	1.3	2.6	14.9	20.80	20.80	59.60	101.20	0.174	-2.367	4.967
IM12	1.1	3.1	15.7	17.60	24.80	62.80	105.20	0.197	-2.133	5.233
IM13	0.8	3.8	12.1	12.80	30.40	48.40	91.60	0.314	-0.233	4.033
IM14	0.8	3.1	14.3	12.80	24.80	57.20	94.80	0.217	-1.667	4.767
IM15	0.8	2.4	11.9	12.80	19.20	47.60	79.60	0.202	-1.567	3.967
IM16	0.8	1.7	15.5	12.80	13.60	62.00	88.40	0.110	-3.467	5.167
IM17	0.7	2.0	15.0	11.20	16.00	60.00	87.20	0.133	-3.000	5.000
IM18	0.6	2.3	13.9	9.60	18.40	55.60	83.60	0.165	-2.333	4.633
IM19	0.7	1.3	12.4	11.20	10.40	49.60	71.20	0.105	-2.833	4.133
IM20	0.7	1.3	11.5	11.20	10.40	46.00	67.60	0.113	-2.533	3.833
IM21	0.7	1.7	11.0	11.20	13.60	44.00	68.80	0.155	-1.967	3.667
IM22	0.6	3.0	10.8	9.60	24.00	43.20	76.80	0.278	-0.600	3.600
IM23	0.6	1.6	9.8	9.60	12.80	39.20	61.60	0.163	-1.667	3.267
IM24	0.9	1.5	8.7	14.40	12.00	34.80	61.20	0.172	-1.400	2.900
IM25	0.6	3.3	17.7	9.60	26.40	70.80	106.80	0.186	-2.600	5.900
IM26	0.5	1.6	17.5	8.00	12.80	70.00	90.80	0.091	-4.233	5.833

IM27	0.5	2.0	18.0	8.00	16.00	72.00	96.00	0.111	-4.000	6.000
IM28	0.9	2.6	20.1	14.40	20.80	80.40	115.60	0.129	-4.100	6.700
IM29	0.2	2.0	9.8	3.20	16.00	39.20	58.40	0.204	-1.267	3.267
IM30	0.1	1.1	6.9	1.60	8.80	27.60	38.00	0.159	-1.200	2.300
IM31	0.2	1.5	4.1	3.20	12.00	16.40	31.60	0.366	0.133	1.367
IM32	0.2	1.0	5.1	3.20	8.00	20.40	31.60	0.196	-0.700	1.700
IM33	0.3	0.7	4.5	4.80	5.60	18.00	28.40	0.156	-0.800	1.500
IM34	0.2	0.7	4.4	3.20	5.60	17.60	26.40	0.159	-0.767	1.467
IM35	0.0	1.6	3.5	0.00	12.80	14.00	26.80	0.457	0.433	1.167
IM36	0.1	0.6	2.7	1.60	4.80	10.80	17.20	0.222	-0.300	0.900
IM37	0.5	1.6	12.4	8.00	12.80	49.60	70.40	0.129	-2.533	4.133
IM38	0.4	1.8	7.2	6.40	14.40	28.80	49.60	0.250	-0.600	2.400
IM39	0.3	1.2	4.6	4.80	9.60	18.40	32.80	0.261	-0.333	1.533
IM40	0.3	1.4	5.5	4.80	11.20	22.00	38.00	0.255	-0.433	1.833
IM41	0.2	1.6	2.7	3.20	12.80	10.80	26.80	0.593	0.700	0.900
IM42	0.3	1.9	6.4	4.80	15.20	25.60	45.60	0.297	-0.233	2.133
IM43	0.3	0.9	6.0	4.80	7.20	24.00	36.00	0.150	-1.100	2.000
IM44	0.1	1.7	4.5	1.60	13.60	18.00	33.20	0.378	0.200	1.500
IM45	0.5	1.7	9.1	8.00	13.60	36.40	58.00	0.187	-1.333	3.033
IM46	0.3	1.4	7.5	4.80	11.20	30.00	46.00	0.187	-1.100	2.500
IM47	0.3	1.0	6.5	4.80	8.00	26.00	38.80	0.154	-1.167	2.167
IM48	0.2	0.9	5.0	3.20	7.20	20.00	30.40	0.180	-0.767	1.667
IM49	0.3	1.3	4.5	4.80	10.40	18.00	33.20	0.289	-0.200	1.500

IM50	0.1	1.2	6.4	1.60	9.60	25.60	36.80	0.188	-0.933	2.133
IM51	1.6	2.5	21.2	25.60	20.00	84.80	130.40	0.118	-4.567	7.067
IM52	1.5	3.5	19.2	24.00	28.00	76.80	128.80	0.182	-2.900	6.400
IM53	1.8	2.1	20.7	28.80	16.80	82.80	128.40	0.101	-4.800	6.900
IM54	1.7	1.3	2.1	27.20	10.40	8.36	45.96	0.622	0.603	0.697
IM55	1.5	1.7	6.8	24.00	13.60	27.20	64.80	0.250	-0.567	2.267
IM56	1.6	1.6	15.6	25.60	12.80	62.40	100.80	0.103	-3.600	5.200
IM57	1.4	1.9	14.4	22.40	15.20	57.60	95.20	0.132	-2.900	4.800
IM58	2.0	1.3	16.6	32.00	10.40	66.40	108.80	0.078	-4.233	5.533
IM59	2.1	2.8	17.4	33.60	22.40	69.60	125.60	0.161	-3.000	5.800
IM60	2.1	2.7	18.8	33.60	21.60	75.20	130.40	0.144	-3.567	6.267
IM61	1.9	1.9	16.4	30.40	15.20	65.60	111.20	0.116	-3.567	5.467
IM62	2.0	3.5	19.6	32.00	28.00	78.40	138.40	0.179	-3.033	6.533
IM63	2.0	2.8	20.1	32.00	22.40	80.40	134.80	0.139	-3.900	6.700
IM64	1.9	2.0	18.4	30.40	16.00	73.60	120.00	0.109	-4.133	6.133
IM65	2.1	2.7	19.4	33.60	21.60	77.60	132.80	0.139	-3.767	6.467
IM66	2.0	1.6	20.3	32.00	12.80	81.20	126.00	0.079	-5.167	6.767
IM67	1.7	1.0	20.1	27.20	8.00	80.40	115.60	0.050	-5.700	6.700
IM68	2.2	1.3	22.3	35.20	10.40	89.20	134.80	0.058	-6.133	7.433
IM69	1.6	2.6	18.2	25.60	20.80	72.80	119.20	0.143	-3.467	6.067
IM70	1.9	2.3	18.0	30.40	18.40	72.00	120.80	0.128	-3.700	6.000
IM71	2.1	1.1	18.5	33.60	8.80	74.00	116.40	0.059	-5.067	6.167
IM72	2.3	1.8	21.0	36.80	14.40	84.00	135.20	0.086	-5.200	7.000

IM73	2.2	2.4	22.4	35.20	19.20	89.60	144.00	0.107	-5.067	7.467
IM74	2.5	3.5	19.6	40.00	28.00	78.40	146.40	0.179	-3.033	6.533
IM75	2.7	3.1	21.8	43.20	24.80	87.20	155.20	0.142	-4.167	7.267
IM76	2.2	2.6	14.8	35.20	20.80	59.20	115.20	0.176	-2.333	4.933
IM77	2.3	3.4	17.9	36.80	27.20	71.60	135.60	0.190	-2.567	5.967
IM78	2.6	3.3	17.7	41.60	26.40	70.80	138.80	0.186	-2.600	5.900
IM79	2.3	3.7	15.9	36.80	29.60	63.60	130.00	0.233	-1.600	5.300
IM80	2.4	3.9	17.0	38.40	31.20	68.00	137.60	0.229	-1.767	5.667
IM81	1.9	2.9	16.7	30.40	23.20	66.80	120.40	0.174	-2.667	5.567
IM82	1.2	2.8	12.8	19.20	22.40	51.20	92.80	0.219	-1.467	4.267
IM83	2.1	3.9	17.8	33.60	31.20	71.20	136.00	0.219	-2.033	5.933
IM84	2.6	2.4	18.4	41.60	19.20	73.60	134.40	0.130	-3.733	6.133
IM85	2.3	4.7	19.3	36.80	37.60	77.20	151.60	0.244	-1.733	6.433
IM86	2.1	2.9	18.2	33.60	23.20	72.80	129.60	0.159	-3.167	6.067
IM87	2.3	3.5	19.9	36.80	28.00	79.60	144.40	0.176	-3.133	6.633
IM88	2.2	2.3	21.4	35.20	18.40	85.60	139.20	0.107	-4.833	7.133
IM89	2.4	4.3	17.5	38.40	34.40	70.00	142.80	0.246	-1.533	5.833
IM90	2.5	2.1	22.6	40.00	16.80	90.40	147.20	0.093	-5.433	7.533
IM91	2.1	3.4	16.8	33.60	27.20	67.20	128.00	0.202	-2.200	5.600
IM92	2.3	2.4	19.3	36.80	19.20	77.20	133.20	0.124	-4.033	6.433
IM93	2.6	2.4	19.6	41.60	19.20	78.40	139.20	0.122	-4.133	6.533
IM94	1.6	1.7	17.2	25.60	13.60	68.80	108.00	0.099	-4.033	5.733
IM95	1.5	2.9	19.3	24.00	23.20	77.20	124.40	0.150	-3.533	6.433

IM96	1.1	1.7	13.9	17.60	13.60	55.60	86.80	0.122	-2.933	4.633
IM97	0.9	2.8	14.5	14.40	22.40	58.00	94.80	0.193	-2.033	4.833
IM98	0.6	3.0	12.2	9.60	24.00	48.80	82.40	0.246	-1.067	4.067
IM99	1.6	2.6	19.4	25.60	20.80	77.60	124.00	0.134	-3.867	6.467
IM100	2.5	1.8	21.3	40.00	14.40	85.20	139.60	0.085	-5.300	7.100
IM101	2.3	1.4	16.3	36.80	11.20	65.20	113.20	0.086	-4.033	5.433
IM102	2.0	2.3	15.4	32.00	18.40	61.60	112.00	0.149	-2.833	5.133
IM103	2.4	3.1	14.2	38.40	24.80	56.80	120.00	0.218	-1.633	4.733
IM104	2.7	2.2	21.3	43.20	17.60	85.20	146.00	0.103	-4.900	7.100
IM105	2.5	2.6	17.4	40.00	20.80	69.60	130.40	0.149	-3.200	5.800
IM106	2.7	2.3	14.7	43.20	18.40	58.80	120.40	0.156	-2.600	4.900
IM107	2.6	2.7	14.8	41.60	21.60	59.20	122.40	0.182	-2.233	4.933
IM108	2.4	3.3	17.9	38.40	26.40	71.60	136.40	0.184	-2.667	5.967
IM109	2.8	1.4	16.2	44.80	11.20	64.80	120.80	0.086	-4.000	5.400
IM110	2.4	2.5	17.9	38.40	20.00	71.60	130.00	0.140	-3.467	5.967
IM111	2.6	1.5	19.4	41.60	12.00	77.60	131.20	0.077	-4.967	6.467
IM112	2.3	2.9	17.2	36.80	23.20	68.80	128.80	0.169	-2.833	5.733
IM113	2.6	1.6	18.9	41.60	12.80	75.60	130.00	0.085	-4.700	6.300
IM114	2.6	2.0	20.9	41.60	16.00	83.60	141.20	0.096	-4.967	6.967
IM115	2.4	3.2	18.1	38.40	25.60	72.40	136.40	0.177	-2.833	6.033
IM116	1.7	2.0	16.2	27.20	16.00	64.80	108.00	0.123	-3.400	5.400
IM117	1.1	0.5	10.7	17.60	4.00	42.80	64.40	0.047	-3.067	3.567
IM118	1.7	2.6	15.9	27.20	20.80	63.60	111.60	0.164	-2.700	5.300

IM119	1.7	2.7	16.1	27.20	21.60	64.40	113.20	0.168	-2.667	5.367
IM120	1.3	1.6	17.5	20.80	12.80	70.00	103.60	0.091	-4.233	5.833
IM121	2.1	3.9	19.1	33.60	31.20	76.40	141.20	0.204	-2.467	6.367
IM122	2.8	2.7	20.4	44.80	21.60	81.60	148.00	0.132	-4.100	6.800
IM123	2.7	2.4	19.8	43.20	19.20	79.20	141.60	0.121	-4.200	6.600

4 Appendix D

Table 6: Total organic carbon (TOC) values of Marshall outcrop Arkansas. Note: FT= Fayetteville, PK= Pitkin and the 0 values of TOC represents areas that samples were not collected.

Sample Name	Total Carbon (wt.%)	Total Inorganic Carbon (wt.%)	Total Organic Carbon (wt.%)
PTK	12.9351	12.9901	0.0550
FT142	10.8631	11.5890	0.7259
FT141	0.0000	0.0000	0.0000
FT140	0.0000	0.0000	0.0000
FT139	0.0000	0.0000	0.0000
FT138	0.0000	0.0000	0.0000
FT137	0.0000	0.0000	0.0000
FT136	0.0000	0.0000	0.0000
FT135	3.3670	3.4988	0.1318
FT134	0.0000	0.0000	0.0000
FT133	0.0000	0.0000	0.0000
FT132	4.1681	4.9394	0.7713

FT131	0.0000	0.0000	0.0000
FT130	0.0000	0.0000	0.0000
FT129	4.1851	5.4402	1.2551
FT128	10.0962	10.6359	0.5397
FT127	0.0000	0.0000	0.0000
FT126	0.0000	0.0000	0.0000
FT125	4.2359	5.6287	1.3928
FT124	0.0000	0.0000	0.0000
FT123	0.0000	0.0000	0.0000
FT122	0.0000	0.0000	0.0000
FT121	0.0000	0.0000	0.0000
FT120	3.5122	4.7653	1.2531
FT119	0.0000	0.0000	0.0000
FT118	0.0000	0.0000	0.0000
FT117	0.0000	0.0000	0.0000
FT116	0.0000	0.0000	0.0000
FT115	0.0000	0.0000	0.0000
FT114	0.0000	0.0000	0.0000
FT113	0.0000	0.0000	0.0000
FT112	0.0000	0.0000	0.0000
FT111	0.0000	0.0000	0.0000
FT110	0.0000	0.0000	0.0000
FT109	0.0000	0.0000	0.0000
FT108	0.0000	0.0000	0.0000
FT107	0.0000	0.0000	0.0000
FT106	0.0000	0.0000	0.0000
FT105	0.0000	0.0000	0.0000

FT104	5.3671	6.1018	0.7347
FT103	0.0000	0.0000	0.0000
FT102	0.0000	0.0000	0.0000
FT101	0.0000	0.0000	0.0000
FT100	0.0000	0.0000	0.0000
FT99	0.0000	0.0000	0.0000
FT98	4.3686	5.6942	1.3256
FT97	4.4553	5.8187	1.3634
FT96	7.0239	7.6177	0.5938
FT95	0.0000	0.0000	0.0000
FT94	3.5092	5.1860	1.6768
FT93	3.4811	5.3913	1.9102
FT92	1.8893	5.5009	3.6116
FT91	1.4431	5.0212	3.5781
FT90	1.0573	5.3346	4.2773
FT89	1.3300	5.6801	4.3501
FT88	0.2577	4.5998	4.3421
FT87	0.5808	5.2123	4.6315
FT86	1.0606	7.4996	6.4390
FT85	3.2977	7.0160	3.7183
FT84	0.7415	2.1002	1.3587
FT83	4.2304	7.6558	3.4254
FT82	1.9875	5.7977	3.8102
FT81	0.9596	4.3046	3.3450
FT80	2.5783	5.0646	2.4863
FT79	0.0000	0.0000	0.0000
FT78	5.8523	7.3659	1.5136

FT77	1.3939	4.2271	2.8332
FT76	2.5560	5.0708	2.5148
FT75	4.3495	6.2874	1.9379
FT74	5.8256	6.9308	1.1052
FT73	9.4485	10.0463	0.5978
FT72	2.4914	5.6589	3.1675
FT71	1.7062	5.3656	3.6594
FT70	3.6008	6.1715	2.5707
FT69	2.6319	5.5880	2.9561
FT 68	1.8628	4.4818	2.6190
FT67	1.7072	4.0787	2.3715
FT66	0.0000	0.0000	0.0000
FT65	0.0000	0.0000	0.0000
FT64	0.0000	0.0000	0.0000
FT63	3.2511	4.9814	1.7303
FT62	0.0000	0.0000	0.0000
FT61	0.0000	0.0000	0.0000
FT60	0.0000	0.0000	0.0000
FT59	0.0000	0.0000	0.0000
FT58	0.0000	0.0000	0.0000
FT57	0.0000	0.0000	0.0000
FT56	0.0000	0.0000	0.0000
FT55	0.0000	0.0000	0.0000
FT54	0.0000	0.0000	0.0000
FT53	0.0000	0.0000	0.0000
FT52	0.0000	0.0000	0.0000
FT51	0.0000	0.0000	0.0000

FT50	2.1153	3.7255	1.6102
FT49	0.0000	0.0000	0.0000
FT48	0.0000	0.0000	0.0000
FT47	0.0000	0.0000	0.0000
FT46	0.0000	0.0000	0.0000
FT45	0.0000	0.0000	0.0000
FT44	0.0000	0.0000	0.0000
FT43	0.0000	0.0000	0.0000
FT42	0.0000	0.0000	0.0000
FT41	0.0000	0.0000	0.0000
FT40	0.0000	0.0000	0.0000
FT39	4.0729	5.2540	1.1811
FT38	4.1801	5.0496	0.8695
FT37	4.1527	5.2306	1.0779
FT36	0.0000	0.0000	0.0000
FT35	3.8754	5.0590	1.1836
FT34	0.0000	0.0000	0.0000
FT33	0.0000	0.0000	0.0000
FT32	0.0000	0.0000	0.0000
FT31	0.0000	0.0000	0.0000
FT30	0.0000	0.0000	0.0000
FT29	0.0000	0.0000	0.0000
FT28	0.0000	0.0000	0.0000
FT27	0.0000	0.0000	0.0000
FT26	0.0000	0.0000	0.0000
FT25	0.0000	0.0000	0.0000
FT24	0.0000	0.0000	0.0000

FT23	0.0000	0.0000	0.0000
FT22	0.0000	0.0000	0.0000
FT21	6.0093	7.2780	1.2687
FT20	9.4045	9.7694	0.3649
FT19	3.5593	5.1372	1.5779
FT18	3.6992	6.4708	2.7716
FT17	3.0723	6.2951	3.2228
FT16	0.5347	4.1625	3.6278
FT15	0.4451	4.1162	3.6711
FT14	0.8128	3.1816	2.3688
FT13	0.0019	4.5847	4.5828
FT12	0.0044	5.2838	5.2794
FT11	0.0055	4.5779	4.5724
FT10	0.0118	4.1578	4.1460
FT9	0.0154	5.2529	5.2375
FT8	0.0034	4.1732	4.1698
FT7	0.0406	4.0716	4.0310
FT6	0.0505	5.0635	5.0130
FT5	0.0030	4.6041	4.6011
FT4	0.1352	3.3363	3.2011
FT3	0.0207	4.9023	4.8816
FT2	0.0002	4.1579	4.1577
FT1	0.0030	4.8491	4.8461
FT0	0.0024	5.5681	5.5657

5 Appendix E

Table 7: Total organic carbon (TOC) values of Spring Valley, Arkansas. Note: SV= Hindsville, SF= Fayetteville and the 0 values of TOC represents areas that samples were not collected.

Sample Name	Total Carbon (wt.%)	Total Inorganic Carbon (wt.%)	Total Organic Carbon (wt.%)
SF12	3.9747	0.0000	3.9747
SF11	1.5490	0.0003	1.5487
SF10	1.3849	0.0000	1.3849
SF9	1.8357	0.0000	1.8357
SF8	1.6678	0.0000	1.6678
SF7	1.4582	0.0016	1.4566
SF6	3.6577	0.0010	3.6567
SF5	3.2036	0.0003	3.2033
SF4	4.8954	0.0004	4.8950
SF3	4.8853	0.0026	4.8827
SF2	6.9521	0.0015	6.9506
SF1	3.7573	0.0014	3.7559
SF0	7.0709	0.0033	7.0676
SV27	0.0000	0.0000	0.0000
SV26	0.0000	0.0000	0.0000
SV25	0.0000	0.0000	0.0000
SV24	0.0000	0.0000	0.0000
SV23	0.0000	0.0000	0.0000
SV22	6.5146	5.9321	0.5825
SV21	0.0000	0.0000	0.0000

SV20	0.0000	0.0000	0.0000
SV19	0.0000	0.0000	0.0000
SV18	0.0000	0.0000	0.0000
SV17	0.0000	0.0000	0.0000
SV16	0.0000	0.0000	0.0000
SV15	0.0000	0.0000	0.0000
SV14	0.0000	0.0000	0.0000
SV13	0.0000	0.0000	0.0000
SV12	0.0000	0.0000	0.0000
SV11	0.0000	0.0000	0.0000
SV10	0.0000	0.0000	0.0000
SV9	0.0000	0.0000	0.0000
SV8	0.0000	0.0000	0.0000
SV7	11.2267	11.1273	0.0994
SV6	0.0000	0.0000	0.0000
SV5	0.0000	0.0000	0.0000
SV4	0.0000	0.0000	0.0000
SV3	0.0000	0.0000	0.0000
SV2	1.0500	0.7263	0.3237
SV1	11.9717	11.8526	0.1191
SV0	0.0000	0.0000	0.0000

6 Appendix F

Table 8: Total organic carbon (TOC) values of Peyton Creek, Arkansas. Note: PK= Pitkin Formation and IM= Imo Formation values. The 0 values of TOC represents areas that samples were not collected.

Sample Name	Total Carbon (wt.%)	Total Inorganic Carbon (wt.%)	Total Organic Carbon (wt.%)
PK0	6.5540	5.4218	1.1322
PK1	4.5910	3.2857	1.3053
PK2	0.0000	0.0000	0.0000
PK3	10.9860	10.9704	0.0156
PK4	5.9775	3.6837	2.2938
PK5	0.0000	0.0000	0.0000
PK6	0.0000	0.0000	0.0000
PK7	0.0000	0.0000	0.0000
PK8	0.0000	0.0000	0.0000
PK9	0.0000	0.0000	0.0000
PK10	0.0000	0.0000	0.0000
PK11	0.0000	0.0000	0.0000
IM0	5.5901	3.7352	1.8549
IM1	5.7599	4.5017	1.2582
IM2	6.8371	5.6826	1.1545
IM3	3.7911	0.1298	3.6613
IM4	4.0679	0.5794	3.4885
IM5	4.8002	0.8724	3.9278
IM6	4.6457	0.3239	4.3218

IM7	3.9824	0.2755	3.7069
IM8	4.7451	0.3707	4.3744
IM9	3.0620	0.0316	3.0304
IM10	4.8362	3.8578	0.9784
IM11	4.7967	3.9082	0.8885
IM12	5.0040	4.6796	0.3244
IM13	5.3408	4.5677	0.7731
IM14	4.9722	3.9644	1.0078
IM15	5.7703	4.7626	1.0077
IM16	5.1286	4.7853	0.3433
IM17	6.1281	5.2854	0.8427
IM18	6.4751	5.6799	0.7952
IM19	7.1797	6.3752	0.8045
IM20	7.1597	6.3675	0.7922
IM21	7.2187	6.4396	0.7791
IM22	7.0254	5.8670	1.1584
IM23	7.3779	6.6495	0.7284
IM24	6.8203	6.2481	0.5722
IM25	0.0000	0.0000	0.0000
IM26	0.0000	0.0000	0.0000
IM27	0.0000	0.0000	0.0000
IM28	0.0000	0.0000	0.0000
IM29	0.3465	0.1058	0.2407
IM30	0.0000	0.0000	0.0000
IM31	0.0000	0.0000	0.0000
IM32	0.0000	0.0000	0.0000

IM33	0.0000	0.0000	0.0000
IM34	0.0000	0.0000	0.0000
IM35	0.0000	0.0000	0.0000
IM36	0.0000	0.0000	0.0000
IM37	0.0000	0.0000	0.0000
IM38	0.0000	0.0000	0.0000
IM39	0.0000	0.0000	0.0000
IM40	0.0000	0.0000	0.0000
IM41	0.0000	0.0000	0.0000
IM42	0.0000	0.0000	0.0000
IM43	0.0000	0.0000	0.0000
IM44	0.0000	0.0000	0.0000
IM45	0.0000	0.0000	0.0000
IM46	0.0000	0.0000	0.0000
IM47	0.0000	0.0000	0.0000
IM48	0.0000	0.0000	0.0000
IM49	0.0000	0.0000	0.0000
IM50	0.0000	0.0000	0.0000
IM51	0.0000	0.0000	0.0000
IM52	0.0000	0.0000	0.0000
IM53	0.0000	0.0000	0.0000
IM54	1.8564	0.4649	1.3915
IM55	2.5191	1.6199	0.8992
IM56	0.0000	0.0000	0.0000
IM57	0.0000	0.0000	0.0000
IM58	0.0000	0.0000	0.0000

IM59	1.6903	0.0068	1.6835
IM60	0.0000	0.0000	0.0000
IM61	0.0000	0.0000	0.0000
IM62	0.0000	0.0000	0.0000
IM63	0.0000	0.0000	0.0000
IM64	0.0000	0.0000	0.0000
IM65	0.0000	0.0000	0.0000
IM66	0.0000	0.0000	0.0000
IM67	1.5790	0.0022	1.5768
IM68	0.0000	0.0000	0.0000
IM69	0.0000	0.0000	0.0000
IM70	0.0000	0.0000	0.0000
IM71	0.0000	0.0000	0.0000
IM72	0.0000	0.0000	0.0000
IM73	1.5979	0.0006	1.5973
IM74	1.2201	0.2252	0.9949
IM75	0.0000	0.0000	0.0000
IM76	0.0000	0.0000	0.0000
IM77	0.0000	0.0000	0.0000
IM78	0.0000	0.0000	0.0000
IM79	0.0000	0.0000	0.0000
IM80	0.0000	0.0000	0.0000
IM81	0.0000	0.0000	0.0000
IM82	0.0000	0.0000	0.0000
IM83	0.0000	0.0000	0.0000
IM84	0.0000	0.0000	0.0000

IM85	1.4447	0.2610	1.1837
IM86	0.0000	0.0000	0.0000
IM87	0.0000	0.0000	0.0000
IM88	0.0000	0.0000	0.0000
IM89	0.0000	0.0000	0.0000
IM90	0.0000	0.0000	0.0000
IM91	1.0748	0.0522	1.0226
IM92	0.0000	0.0000	0.0000
IM93	0.0000	0.0000	0.0000
IM94	0.0000	0.0000	0.0000
IM95	0.0000	0.0000	0.0000
IM96	0.0000	0.0000	0.0000
IM97	0.0000	0.0000	0.0000
IM98	0.0000	0.0000	0.0000
IM99	0.0000	0.0000	0.0000
IM100	1.6676	0.0019	1.6657
IM101	0.0000	0.0000	0.0000
IM102	0.0000	0.0000	0.0000
IM103	0.0000	0.0000	0.0000
IM104	0.9844	0.2165	0.7679
IM105	0.0000	0.0000	0.0000
IM106	0.0000	0.0000	0.0000
IM107	0.0000	0.0000	0.0000
IM108	1.1962	0.3484	0.8478
IM109	0.0000	0.0000	0.0000
IM110	0.0000	0.0000	0.0000

IM111	0.0000	0.0000	0.0000
IM112	0.9163	0.0021	0.9142
IM113	0.0000	0.0000	0.0000
IM114	0.0000	0.0000	0.0000
IM115	0.0000	0.0000	0.0000
IM116	0.0000	0.0000	0.0000
IM117	0.2417	0.0029	0.2388
IM118	0.0000	0.0000	0.0000
IM119	1.0227	0.0010	1.0217
IM120	0.0000	0.0000	0.0000
IM121	0.0000	0.0000	0.0000
IM122	0.0000	0.0000	0.0000
IM123	0.0000	0.0000	0.0000

VITA

Adetola Onaadepo Alase

Candidate for the Degree of

Master of Science

Thesis: GAMMA SPECTROMETRY AND GEOCHEMICAL INVESTIGATION OF THE MISSISSIPPIAN (CHESTERIAN) FAYETTEVILLE SHALE AND IMO SHALE, ARKOMA BASIN, ARKANSAS

Major Field: GEOLOGY

Biographical:

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Completed the requirements for the Master of Science in Geology at Oklahoma State University, Stillwater, Oklahoma in May, 2011. Completed the requirements for the Bachelor of Science in Geology at University of Ilorin, Ilorin, Nigeria in December, 2005

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Name: Adetola Alase Date of Degree: July, 2012

Institution: Oklahoma State University Location: Stillwater, Oklahoma

Title of Study: GAMMA SPECTROMETRY AND GEOCHEMICAL
INVESTIGATION OF THE MISSISSIPPIAN (CHESTERIAN)
FAYETTEVILLE SHALE AND IMO SHALE, ARKOMA BASIN, ARKANSAS

Pages in Study: 138 Candidate for the Degree of Master of Science

Major Field: Geology

Scope and Method of Study: The primary goal of this study was to integrate gamma-ray spectrometry, geochemistry and lithofacies distributions to interpret sediment source and depositional settings of the Fayetteville Shale and The Imo Shale in northern Arkansas.

Findings and Conclusions: For this Study, more than 250 gamma-ray spectrometry measurements were collected from the Mississippian (Chesterian) Hindsville, Fayetteville, Pitkin and Imo formations, northern Arkansas and analyzed to provide insight into radionuclide buildup and concentration of organic matter in these important natural-gas-bearing rocks. The black lower Fayetteville shale is organically rich, fossiliferous and contains laterally continuous micritic limestone beds. The black shale is radioactive and has an average TOC content of 4 wt.%. The rhythmic upper Fayetteville shale is an alternating succession of limestone and black to dark-gray shale that is organically rich, fossiliferous, pyritic, radioactive and has an average TOC content of 4.5 wt.%. The Fayetteville Shale at Marshall is relatively low-clay content and interpreted as relatively deeper-marine and anoxic as evidenced by a higher uranium content compared to thorium. The changes in U:Th ratio and TOC across the Fayetteville Shale demonstrate that it contains two shoaling-upward sequences: the lower one terminating at the base of the highly radioactive upper Fayetteville Shale; the upper one culminating with the onset of Pitkin deposition. The Imo Shale at Peyton Creek is subdivided into four units using lithology and total gamma-ray. The Imo Shale is relatively clay rich, fossiliferous, radioactive and organically rich with average TOC content of 3.0 wt.%. The Imo contains black shale that transitions upward to gray shale, which is succeeded by sandstone and dark gray shale with thin dark limestone beds. U, Th, TOC and gamma-ray decrease upward from the basal black shale to the sandstone. Above the sandstone, as a result of dilution by terrigenous sediments, TOC and U concentrations decreases and gamma-ray correlates to Th rather than U. Across the Imo, TOC and U positively correlate, suggesting a marine source for organic carbon. The results indicate that API gamma-ray responds to U and Th and consequently may not be a reliable indicator of TOC concentration. However, U correlates positively with TOC across all units and is viewed as a reliable tool for estimating their gas-sourcing potential.

ADVISER'S APPROVAL: Dr. Darwin Boardman