SPECTROMETRY AND GEOCHEMICAL INVESTIGATION OF SELECTED OUTCROPS OF THE CHATTANOOGA SHALE IN THE OZARK REGION OF NORTH AMERICA

By

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SPECTROMETRY AND GEOCHEMICAL

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CHAPTER I

INTRODUCTION

1.0 Preamble

The Upper Devonian-Mississippian Chattanooga Shale is extensive and of varying thickness in many parts of North America (Duncan, 1983; de Witt et al., 1993; Lambert, 1992). In North America, the name Chattanooga Shale has been used for some black shale exposures both in the Appalachian and Ozark region (Purdue and Miser, 1968; Cram, 1930; De Witt, 1981; Over, 2007). In the Appalachian region, Hayes (1891) originated the name Chattanooga from shales present on Cameron Hill in a town called Chattanooga in Tennessee. In the Ozarks, Taff (1905) applied the name "Chattanooga" to black shales exposed in Tahlequah, Oklahoma. In northern Arkansas and Missouri areas of the Ozark region, the name "Eureka" and "Noel" were given respectively to similar exposed black shales (Branner; 1891; Adams et al., 1904). To date, most attention has been on Chattanooga Shale in the Appalachian region while little attention has been devoted to its counterpart in the Ozark region. Previous studies have indicated that the lithological composition of the Chattanooga Shale varies from locality to locality (Huffman and George, 1960; Lambert 1992; Schieber, 1994a).

Of importance, Over (2007) in his biostratigraphical characterization of the Chattanooga Shale in the Appalachian Basin stated that the Appalachian Chattanooga Shale "are not necessary contiguous" with the "Chattanooga" in the Ozarks despite their lithological similarity and time equivalence. Boardman (2009 personal communication) believed that the "Chattanooga Shales" in the Ozark region are the shallow water facies of the Woodford Shale and that a new name should be proposed for the shale.

In the event of looking for a new name for the "Chattanooga Shale" in the Ozark region numerous geological studies have to be done. These works include but are not limited to biostratigrahical study, total carbon analysis, total gamma ray measurement, hydrogen index, metal extraction and clay mineralogy. This thesis aims at focusing at the total organic carbon concentration, gamma ray measurement and clay mineralogy of some selected outcrops of the "Chattanooga shale" in the Ozarks.

1.1 Objective

The aim of this project is to contribute to the proposed name changing of the "Chattanooga Shale" in the Ozark region. This thesis will determine the gamma ray concentration and total organic carbon content (TOC) of the Chattanooga Shale in the Ozark region. The result of the TOC concentration and total gamma ray will be used to test the hypothesis which states that an increase in gamma ray value often leads to an increase in the amount of total organic carbon. Clay type analysis will be carried out to determine the clay mineralogy of the Chattanooga Shale.

To achieve this, detailed spectral gamma ray measurements were carried out in the field and samples were collected for total organic carbon (TOC) and clay type analysis.

1.2 Importance of gamma ray

The importance of gamma ray measurements cannot be over emphasized in black shale studies. This is because it is a reliable tool that measures individual radionuclide elements present in black shales. These radionuclide elements include uranium (U), thorium (Th) and potassium (K). The units of measurement of radionuclide elements are ppm, ppm, and % respectively. In the petroleum industry, most black shales with high gamma ray values have been noted for their hydrocarbon enrichment. The Mississippian Devonian Shales in the United State and Silurian Shales in North Africa and Arabia are very good examples. Shale with high gamma values is known as radioactive or hot shale. Luning et al., (2000) defined black shales as 'hot' shales when the gamma ray values exceed 200 API. Stocks and Lawrence, (1990) are of the opinion that an increase in gamma ray often results into a corresponding increase in total organic carbon concentration.

1.3 Importance of total organic carbon concentration

In order for a sedimentary basin to be considered a good petroleum system, high total organic carbon content along with other properties such as the presence of source and reservoir rocks, traps and seals, and economically viable formation thickness must be present within the system. The total organic carbon content of shale is a measure of the amount of organic material present in the shale. Organic materials are sourced from the remains of dead phytoplankton (plant) and zooplankton (animals). The presence of high concentration of organic material in shales makes them black and often source rocks for hydrocarbon. Shales that are not rich organically are often lighter in color than the organically rich ones.

1.4 Location of study area

A total of five outcrops of the Chattanooga Shale in the Ozark region were examined for the purpose of this project. These outcrops are located in Missouri, Arkansas and Oklahoma (Fig. 1). The first outcrop is located in Jane in the southwestern part of Missouri in McDonald County. It is an outcrop exposed as a result of road cut on the newly constructed U.S. Highway 71. It is located 0.4 km from the intersection of U.S Highway 71 and 90 (Fig. 2). The Jane outcrop is characterized by three distinct layers, which can easily be classified visually into lower, middle and upper units. The upper unit is characterized by alternating light and dark colored bands whose width ranges between 0.2 and 0.4 meters thick. This outcrop provides an incomplete section of the Chattanooga Shale because the underlying unit is not exposed.

Figure 1: Location map of Arkansas, Oklahoma and Missouri.

Figure 2: Location map of sample site in McDonald County, Southeastern Missouri.

The second outcrop surveyed for this project is located in Bella Vista Arkansas in northwestern Benton County, Arkansas (Fig. 3). The distance of this outcrop from the Jane outcrop in Missouri is 16 km. This outcrop is located west of U.S Highway 71. This outcrop was selected for this project because of its extensiveness. Duncan (1970) did his master's research on the geochemical properties of the outcrop. This outcrop represents an incomplete section of the Chattanooga Shale.

The third outcrop explored is located near Tahlequah, Oklahoma in Cherokee County (Fig. 4). This outcrop is referred to in this project as "Hanging rock" a name adopted because of the orientation of the overlying Compton Limestone that rests uncomformably on the shale. The Hanging rock is located opposite the Illinois River.

The fourth outcrop examined is the Eagles Bluff outcrop in Cherokee County of Northeastern Oklahoma (Fig. 4). The name “Eagles Bluff” has been adopted for this outcrop because of its proximity to the Eagles Bluff settlement. This outcrop has been selected because it represents a complete section of the Chattanooga Shale. The Eagles Bluff is also located opposite the Illinois River. The fifth and last outcrop selected for this project is also located in Cherokee County near Tahlequah Oklahoma (Fig. 4). It is known as “No Head Hollow” because of its proximity to the No Hollow Head public access area. It is located along the Illinois River.

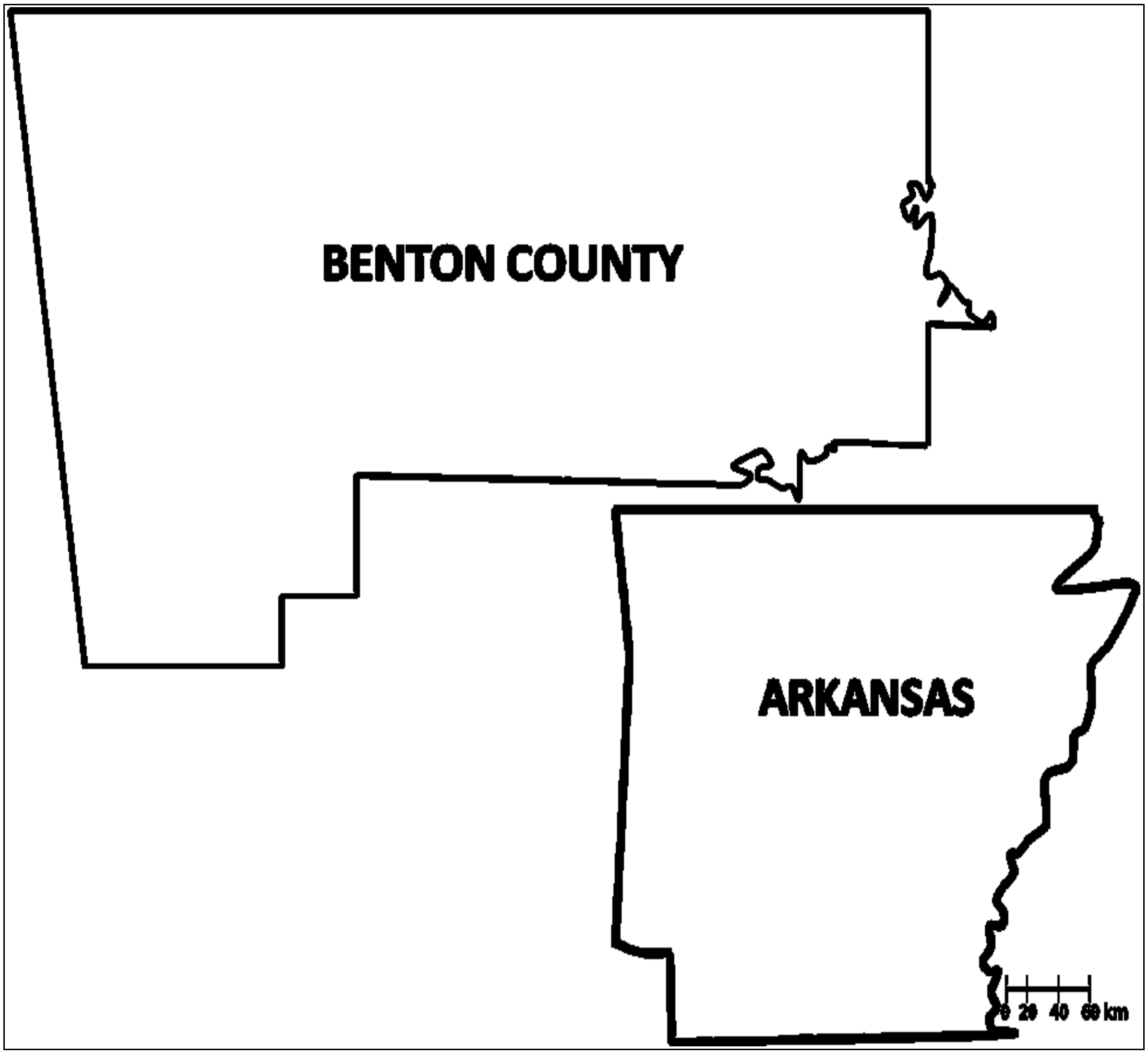

Figure 3: Location map of study area in Benton County, northwestern, Oklahoma.

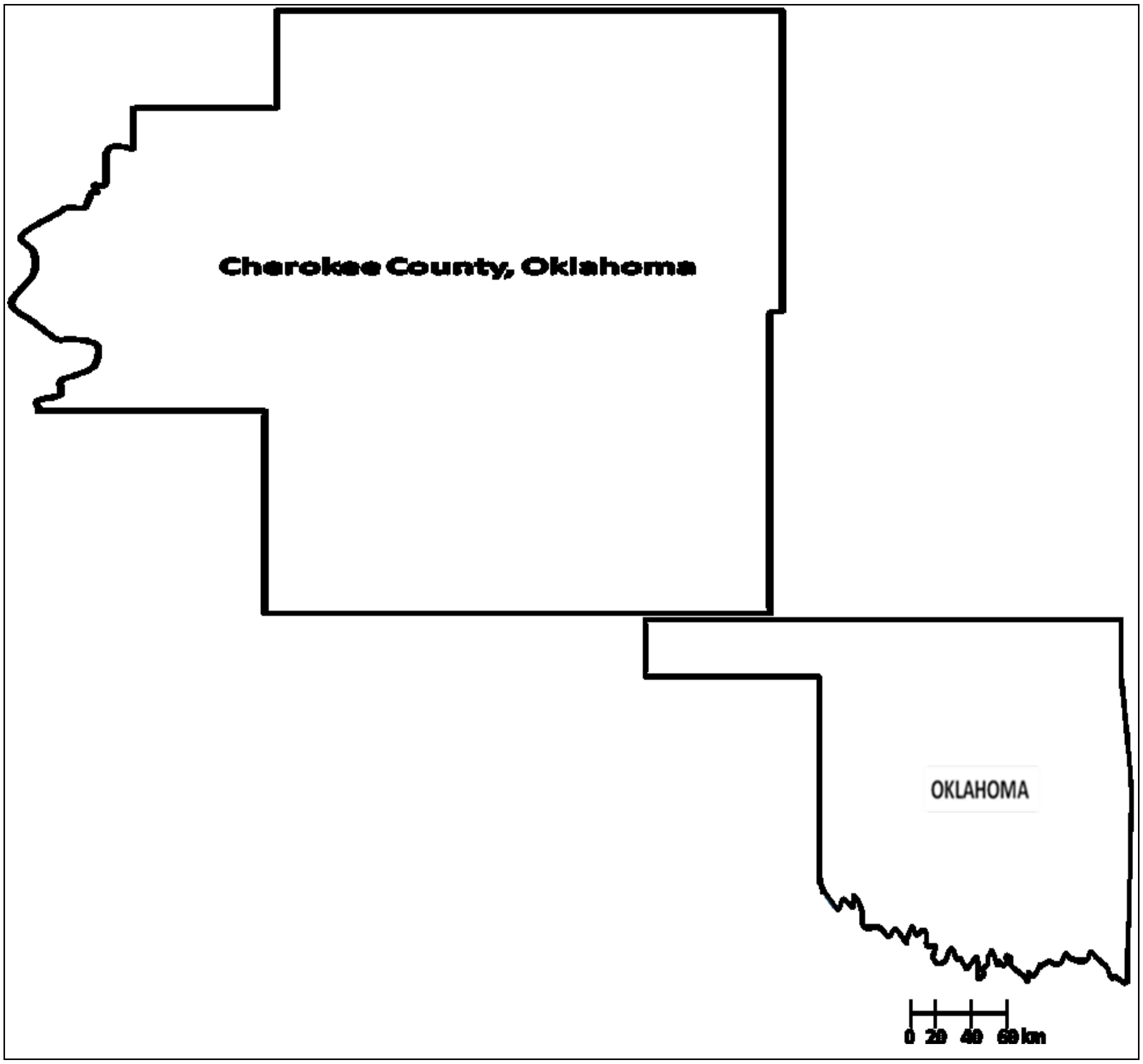

Figure 4: Location map of sampled sites in Cherokee County, Northeastern Oklahoma.

1.5 Geologic Setting

The study areas in this project are located on the southern flank of the Ozark Dome (Fig.5). The Ozark Dome is located in the southern half of Missouri, north central and northwest Arkansas, northeast Oklahoma and southeast Kansas. The Ozark dome is a structural dome that is flanked east ward by steeply dipping rock units. The Ozark dome is a broad, circular area of Paleozoic strata that are predominantly limestone with a core of Precambrian basement rocks. The Precambrian basement rocks are exposed around St. Francis Mountain in Missouri. Mapes (1968) described the dome as 'erosive' which means that units decrease in age away from the center. Mapes (1968) observed that strata immediately north of Arkansas- Missouri border dip gently southward sequel to the influence of the Ozark dome. However, the orientation of the dip decreases southward onto the north Arkansas structural platform (Chinn and Konig, 1973). The structural deformation of the Ozark dome is minimal in southwestern part of Missouri. The intense deformation has been linked to two major events which include; deformation as a result of limestone dissolution at depth, and stress associated with the Ouachita Orogeny (Quinn, 1963; Chin & Knonig, 1973). Quinn (1963) believed that the limestone dissolution is of Pleistocene or Holocene age. The successions of rocks in the Ozark Dome consists of approximately 609 meters thick (2000 feet) of Cambrian through Pennsylvanian age sedimentary rocks that are formed by regression and transgression of the epieric seas (Caplan, 1960). Chinn and Konig (1973) described northwest Arkansas and northeast Oklahoma as part of what is known as the "northern Arkansas Structural Platform". Three broad erosional plateaus were recognized within the Ozark dome which includes the Salem, Springfield and the Boston Plateaus (Croneis, 1930; Manger et al., 1988). The Salem plateau is the oldest and exists along the northern Arkansas Structural Platform and northward into Missouri. The Salem is composed of Ordovician aged carbonate rocks at elevations of between 76.2 meters and 381 meters (Croneis, 1930). The Springfield Plateau is located northwest of north Arkansas Structural Platform. The Springfield is characterized by Lower Mississippian rocks of the St. Joe Group. The Boston Plateau is the highest and located along the southern half of the north Arkansas Structural Platform. The Boston Plateau is overlain by shale and sandstone of the Atoka Formation (Kelly, 1997).

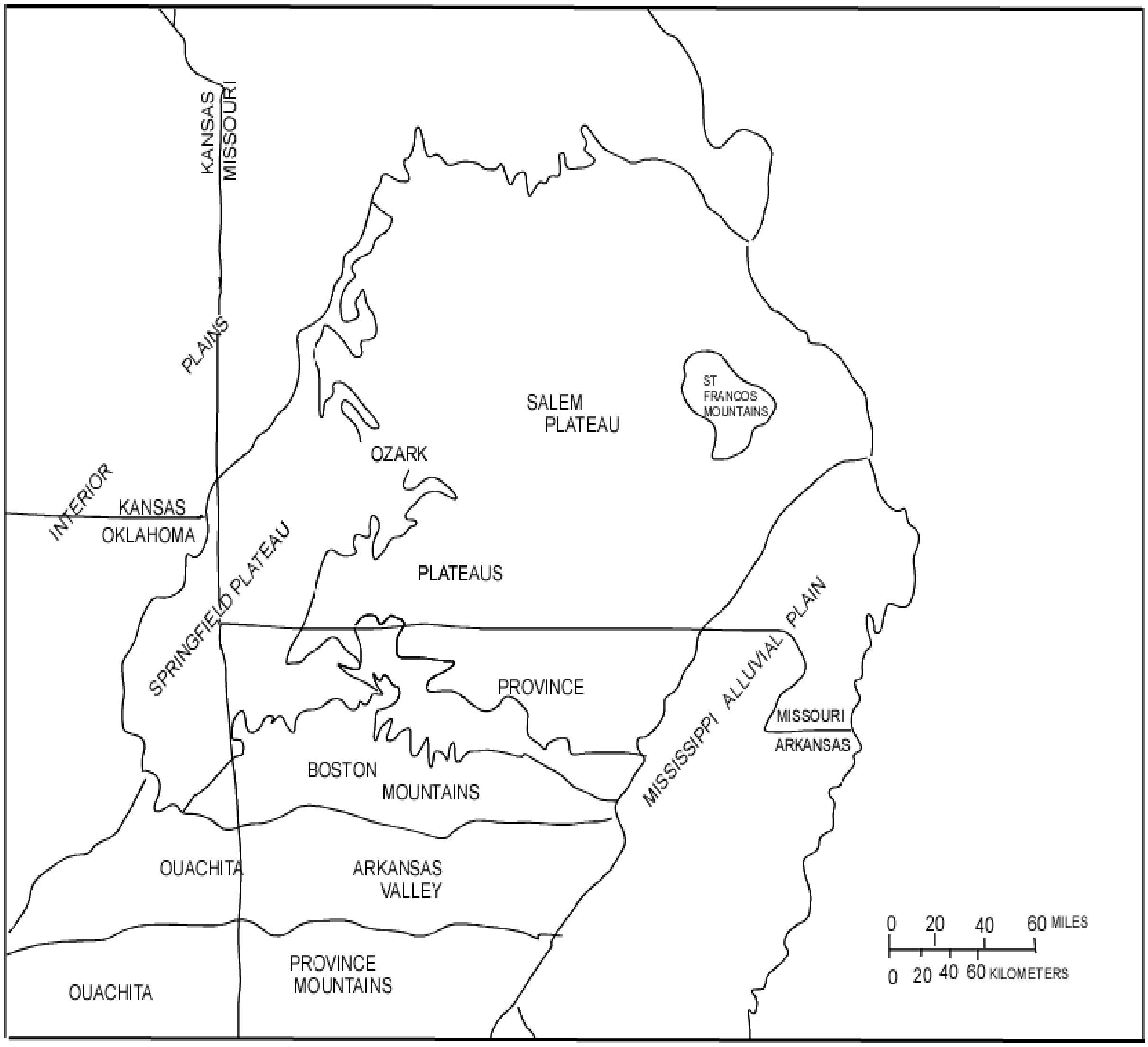

Figure 5: Map of the Ozark Plateau of the Mid- Continent (Modified on 4/30/09 from http://pubs.usgs.gov/sir/2008/5023/pdf/09tennyson.pdf).

1.6 Stratigraphic Relationship

The Chattanooga Shale has been divided into two members namely, the main upper Chattanooga black shale and the underlying Sylamore basal sandstone member (Duncan, 1983) (Fig.6). The Chattanooga Shale is bounded by surface of unconformities (Duncan, 1983). The basal Sylamore Sandstone overlies uncomformably the St. Clair, Frisco and Sallisaw Formations in the southern part of Marble County in Oklahoma

(Huffman and George, 1960). In northwest Arkansas, the basal Sylamore Sandstone Member is underlain by the Clifty Formation or Powell Formation (Duncan, 1983). The Sylamore Sandstone is of varied thickness and well exposed in many areas in northeastern Oklahoma. A thickness of about 5.4 meters had been recorded in Sec.29, T.14N; R.24E (Huffman and George, 1960). The basal sandstone is lithologically characterized by dark grey to sandy black shale and grayish blue phosphatic and calcareous rich sandstone. The Sylamore is usually friable, but locally it is extremely quartzitic and hard (Huffman and George, 1960). It is analogous to the Misener Sandstone in the subsurface of Kansas and Oklahoma and with the Hardin Sandstone of Tennessee (Huffman and George, 1960; Newell, 2001).

The Chattanooga Shale is widely distributed in Appalachian and Ozark region of the United State and parts of Mexico and Canada (Duncan, 1983). The Chattanooga Shale is organically rich black fissile shale that is well jointed and weathers perfectly into thin flakes. The shale conformably overlies the Sylamore Sandstone wherever it is well developed (Fig.6). However, in the absence of the basal sandstone due to erosion or non-deposition, the Chattanooga Shale lies uncomformably on beds ranging from Early Ordovician to Devonian (Huffman and George, 1960). The Chattanooga Shale Member is overlain by the Bachelor Shale (Fig. 6). In the explored area, the Bachelor Shale is the Devonian-Mississippian boundary wherever it occurs, while the Chattanooga Shale serves as the boundary wherever the Bachelor is absent probably due to erosion or non-deposition. The Bachelor Shale has an average thickness ranging from 0.1 to 0.2 meters. It is mostly greenish to grayish in color. The Bachelor Shale is overlain conformably by the St. Joe Group of the Kinderhookian Stages.

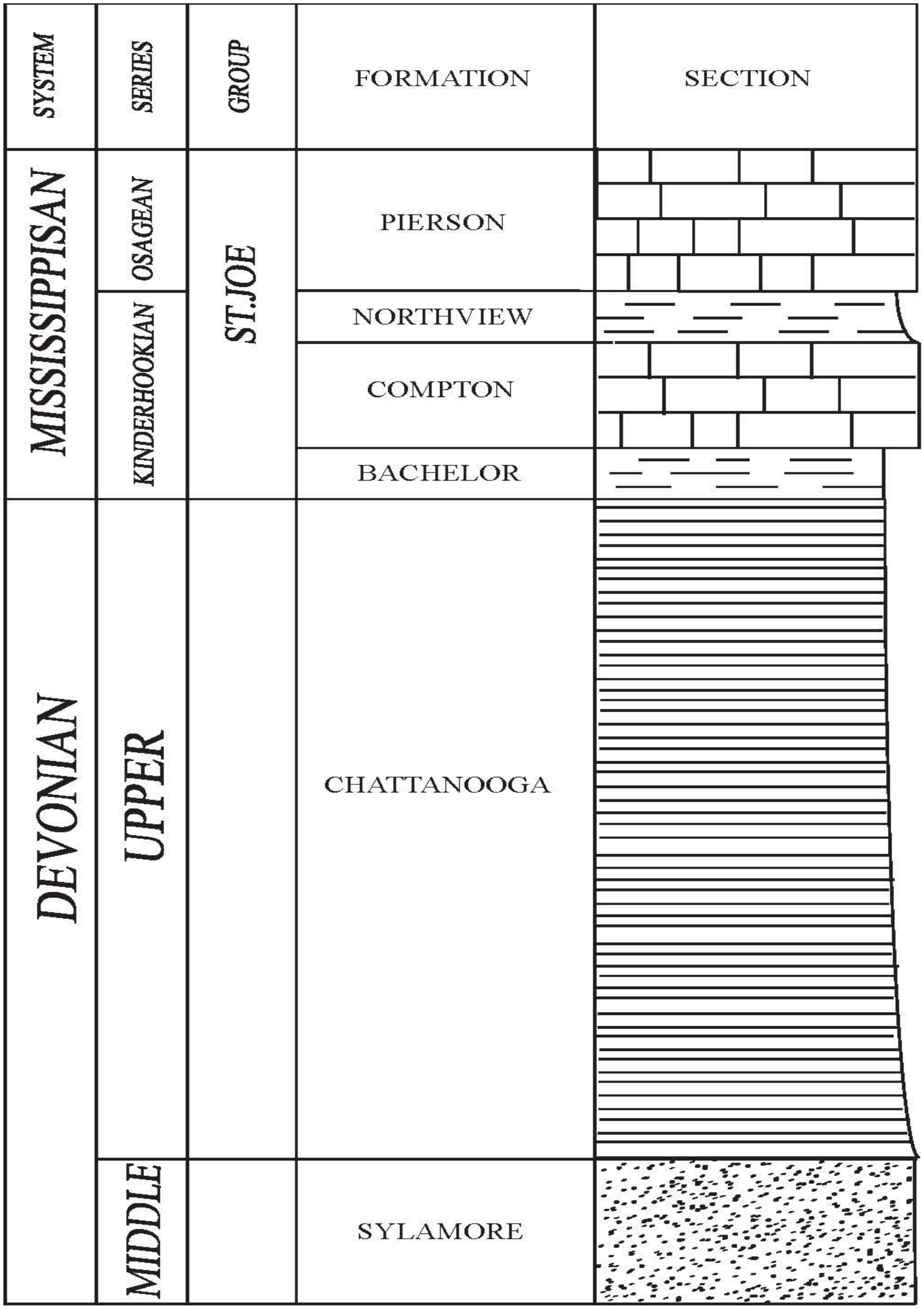

Figure 6 : Generalized stratigraphic section of the Chattanooga Shale in the Ozark region (Modified from Duncan, 1983).

1.7 Depositional Settings

The depositional environment of the Chattanooga Shale member has generated a lot of controversy since the 19th century both in the Appalachian and Ozark region. The controversy was based on the depth of deposition of the shale. Twenhofel (1939) was of the opinion that individual black shale formations should be interpreted based on their characteristics and that the idea of generalized interpretation should be discouraged because of the complexities that surround the deposition of black shale. In Tennessee and Kentucky, some researchers believed that the Chattanooga Shale was a deposit of shallow water environment under oxic condition (Schieber, 1994a), while others believed that it was deposited in a deep water environment (Potter et al., 1982; Ettensohn, 1985). Conant and Swanson (1961) also interpreted the depositional origin of the Chattanooga Shale as of shallow water. Schieber (1994a) corroborated the findings of Conant and Swanson (1961) by concluding that the Chattanooga Shale in central Tennessee is of a shallow water origin under oxic condition after observing large scale subtle bioturbation as well as storm deposits at the base of the shale. The investigation of the Chattanooga Shale in central Tennessee by Schieber (1994a) also suggests that the individual interpretation of black shale might be a good idea. He stated that "despite the subtle differences in lithology and sedimentary features that exist between the Chattanooga Shale of central Tennessee, and its lateral equivalents in eastern Tennessee and eastern Kentucky and Ohio, conclusions from central Tennessee should not be used as a proxy to these areas without critically re-examining them". In the Ozark region, many hypotheses have been made about the depositional processes of the Chattanooga Shale.

For instance, Conant and Swanson (1961) are of the opinion that the shale is of shallow water origin while Potter et al., (1982) and Ettensohn (1985) thought that the Chattanooga Shale is a deposit of deep water environments. Also, Hurst (2008), in his spectrometry study of the Chattanooga Shale specified that it was deposited under anoxic conditions and never indicated the water depth.

1.8 Extent and Thickness

The Chattanooga Shale is exposed throughout the eastern half of the United States and some parts of Mexico and Canada (Duncan, 1983; de Witt et al., 1993; Lambert, 1992). The thickness of the Chattanooga Shale and its equivalent ranges between 0 and 107 meters (Kelly, 1997) (Fig. 7). The thickness of the Chattanooga Shale is highest in northeastern Oklahoma (Kelly, 1997). Formerly known as Noel Shale in southwestern Missouri, Chattanooga Shale exposures have been recorded around Jackson Quarry Mountains and in 'intervening Payne Hollow' (Huffman, 1960). The Chattanooga Shale is equally exposed around stream deep cuts such as the Illinois River, the Tenkiller Lake along the Qualls Dome, and along the eroded crest of an anticlinal uplift close to Fort Gibson (Huffman, 1960). Bass (1936) equally recorded Chattanooga outcrops on Illinois River in Adair and Cherokee Counties, Oklahoma. He also noted some exposures around Spring and Spavinaw Creeks in Mayes and Delaware Counties. The Chattanooga Shale was equally observed almost continuously along the Illinois River channel in Tahlequah Oklahoma.

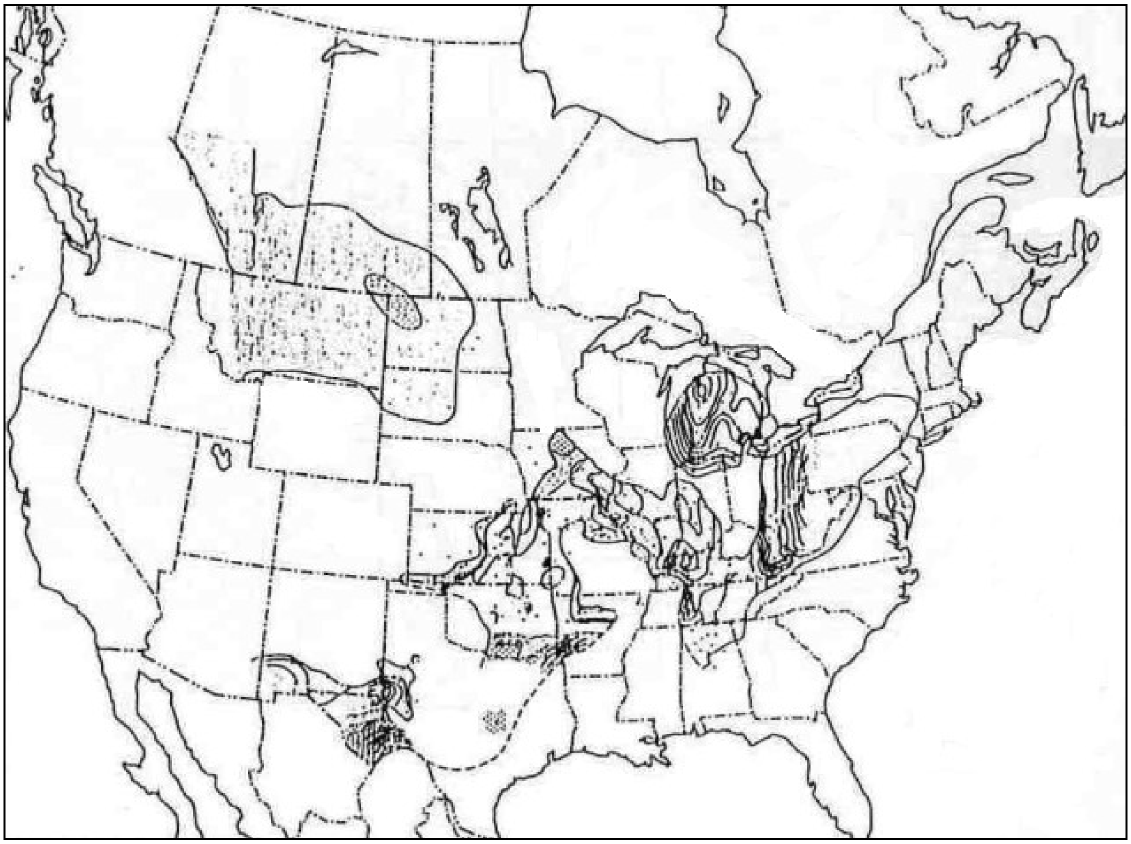

Figure 7: Map showing the thickness and extent of the Chattanooga Shale in North America (Adopted from Kelly, 1997).

CHAPTER II

REVIEW OF LITERATURE

2.0 Definition

The "Black Shales" near Chattanooga town in Tennessee were first christened "Chattanooga Shale" by Hayes (1891) according to Huffman and George (1960). Branner (1891) named stratigraphically equivalent black shale members in northern Arkansas "Eureka" and the name "Noel" was adopted for the black shale exposed near Noel, McDonald County, in southwestern Missouri (Adams et al., 1904). Taff (1905) adopted the name Chattanooga Shale for similar black shales members exposed near Tahlequah in northeastern Oklahoma. Ver Wiebe (1946) refereed to the Chattanooga Shale in Kansas as the "Kinderhook Shale" a name that was generally in use until 1956. The term "Kinderhook Shale" was recorded to have been based on the assumption that the Chattanooga was Mississippian in age (Lee, 1956). The name Chattanooga was accepted both in the Appalachians and the Ozark region of United States (Purdue and Miser, 1916; Ireland, 1930; Cram, 1930; Leatherock and Bass, 1936; Huffman, 1958, Landis, 1962). However, Over (2007) is of the opinion that the Chattanooga Shale in the Ozark region is not contiguous with the Chattanooga Shale in the Appalachian.

The Chattanooga Shale has been divided into two members; the basal Sylamore Sandstone Member and the Chattanooga Shale member. The Sylamore Member underlies the Chattanooga Shale and marks the beginning of the Upper Devonian transgression (Kelly, 1994). The name Sylamore was given to the Sylamore Sandstone Member of the Chattanooga Shale by Penrose (1891). The Sylamore Sandstone was described as “brown, yellow or gray sandstone, often containing green or black shale like layers.

Grabau (1906) examined the provenance of the Chattanooga Shale in Arkansas and Missouri and concluded that they were similar to the ones in Tennessee. He believed that the Chattanooga Shale is a trangressive basal deposit of an advancing sea and that the rock’s fine grained characteristics could only be attributed to the mixture of residual soil that is enriched in clay and carbonaceous material.

Crouse (1925a) presented the economic viability of Devonian Shales in two separate reports. Crouse (1925a), noted that the concentration of silver and gold in the Devonian Shales were not of economic importance because of their very low abundance.

Thiessen (1925) while looking at the depositional process of the Chattanooga Shale believed that the shale was deposited in shallow water environment under a very quite condition. He buttressed his claims that the Chattanooga Shale was deposited in an area that has once been covered by swamps or marshes.

Twenhofel (1939) was of the opinion that the preservation of organic matter is a function of anoxic bottom water condition. He believed the absence of oxygen will inhibit organic matter from been consumed by oxidation and organisms.

Stockdale (1939) also corroborated the theory of Grabau (1906) by referring to the Chattanooga Shale of Kentucky and Tennessee as a transgressive basal shore deposit.

Rich (1948) refuted the transgressive, basal, shore deposit proposition of Grabau (1906) and Twenhofel (1939) and proposed that the Chattanooga Shale was a deposit of deep water environment. He based his claims on the presence of organic materials, thin bedded phosphatic nodules, thin siliceous calcareous beds previously thought as volcanic ash and absence in diameters of wave action at the base of the Chattanooga.

Keulegan and Krumbein (1949) designed a model using physics and geology principles to complement the shallow water origin of the Chattanooga Shale.

Rich (1951) further claimed that black shales are generally deposits of deep water environments. Rich (1953) described deposition of black shales and their usual underlying accompanied sandstones using a paleogeographical model. He was of the opinion that sandstone deposition is often accompanied with a basal lag, a phenomenon that he believed always gave room for toxic water conditions which serve as a premise for the deposition of black shales.

Breger and Duel (1955) stated that the uranium content of the Chattanooga Shale exist “as a colloidal phase distributed through the matrix of organic material”. They carried out a petrograhpic study of the Chattanooga Shale by looking at thin sections. Breger and Duel (1955) concluded that most of the “uranium is present in the organic matter content as fine disseminations and that no relationship exists between the pyrite in the organic matter and uranium”.

Brown (1956) examined the uranium content of the Chattanooga Shale. He attributed the unusual enrichment of uranium in the shale to slow processes of deposition and non-oxidizing condition in the Chattanooga Sea. Brown (1956) stated that Chattanooga Shale is different from other uranium enriched shales because of its low phosphate and oil content. He showed that similarities exist between the blackness of the shale and its uranium content and stated that the portion of the shale enriched in phosphate contains lesser amount of uranium compared to the black facies (Duncan, 1983).

Hass (1956) used fossils (conodonts) to determine the biostratigraphy of Chattanooga Shale with reference to data on Chattanooga Shales from the Appalachian region of the United States.

Duel (1957) proposed different models for the occurrence of the Chattanooga Uranium content. These are not limited to but include this: (a) existence of the uranium as a "colloidal phase dispersed through the organic matrix, (b) disassociation of the uranium from the organic matter and the mineral matter.

Glover (1959) studied the stratigraphy and uranium content of the Chattanooga shale in the Appalachian region of the United State. He attributed both irregular deposition conditions and abundant supply of phosphate rich black shale as factors responsible for the low uranium content. Glover (1959) supported the shallow water theory for the deposition of the Chattanooga. Glover (1959) believed that the presence of gray shale in the Chattanooga is as a result of unusual rapid supply of inorganic material into the sediment pile. Glover (1959) noted higher amount of clay and less organic matter in the gray beds compared to the black shales. He further believed that rapid deposition accounted for the black and grey sedimentary imprints present is some of the Chattanooga outcrops.

Conant and Swanson (1961) divided the Chattanooga Shale in the Appalachian Basin into three members. These members include the Hardin Sandstone, the

Dowelltown Member and the Gassaway Member. They interpreted the depositional origin of the Chattanooga Shale as shallow water and claimed that the disappearance of storm waves at the base of the shale was due to unusual shoreline, gentle bottom slope and scattered island. Conant and Swanson (1961) believed that grey shales are formed either under highly oxidized conditions or extremely reducing conditions. Conant and Swanson equally believed that rapid sedimentation could lead to a dilution of the sediment pile thereby resulting in the formation of grey shale.

Landis (1962) explored the Chattanooga Shale of northern Arkansas in the Ozark region and proposed that the trangressive concept of the Chattanooga in this region can be related to that of the Chattanooga Shale in Tennessee in the Appalachian region. He was of the opinion that the Syalamore Sandstone which is the basal unit of the Chattanooga is "probably a transgressive deposit of the advancing Late Devonian Early Mississippian Sea". Landis (1962) also believed that the Chattanooga Shale of both regions had been subjected to the same depositional conditions.

Reaugh and McLaughlin (1975) examined palynomorphs from the Tennessee region of the Appalachian and inferred that the anoxic conditions supported by various authors as the condition of deposition of the Chattanooga should not be applied to other units within the basin. They based their claims on the presence of "normal marine micro plankton and burrowed beds".

Provo (1976) described the Devonian-Mississippian black shales in North America and throughout the world. Provo (1976) explained that black shale "could form as distal facies of turbidites associated with the Catskill Delta or occur on craton far from marginal margins". He was of the opinion that all black shales formed in the United State were sequel to two tectonic events. Provo agreed with Twenhofel (1939) and believed that black shale's deposition is influenced by the rapid supply of organic matter, water stratification and that organically rich mud is not a function of depth. Provo (1977) claimed that oxygen level is a major factor in the deposition of organically rich mud and not compulsorily water depth. Provo (1977) was of the opinion that black shales are usually characterized by high uranium values than the light colored organically poor shale.

Griffith (1978) having considered the sedimentologic and stratigraphic processes of the New Albany Shale of north central Kentucky concluded that the Shale was deposited in a continuous 'deepening environment'. Depths ranging between 30 meter and 152 meter were proposed for the shale deposition of the shale.

Renton et al. (1979) were of the opinion that degradation of plant materials could set in at PH values between 4.5 and 6 due to bacterial activities. They believed that this degradation is only confined to swamps where moderate to high PH exists. Renton et al., stated that the formation of black shale could result when peat deposit is subjected to either periodic or constant supply of seawater with moderate PH.

Ettensohn and Barron (1980) examined the impact of tectonism in the formation of Devonian black shales. Ettensohn and Barron believed that "Black Shale Sea" was confined to the east and south by the Acadian Mountains, to the north by the craton and to the west by Trans-Continental Arch. They explained that the "Marathon region of Texas and the Ouachita region" were responsible for the opening of the ocean. They stated that transgression of "Black Shale Sea" is best explained in terms of tectonics. Ettensohn and Barron (1980) believed that the occurrence of increasing subduction and collision of the continental margins during the late Devonian period was responsible for increase in sea floor spreading.

Duncan (1983) examined the geochemistry of the Chattanooga Shale in northwestern Arkansas. Duncan research was based on the metal composition and organic carbon content of the Chattanooga Shale. He used atomic absorption method to extract 13 different elements from the shale. Duncan (1983) observed that the deposition of the Chattanooga Shale in northern Arkansas was accompanied much by detrital influxes unlike other Devonian black shales. He believed that geochemical variation in the shale is much more obvious than stratigraphic variation and that the greater variation in the geochemical data is influenced by "resistate vs. clay deposition". Duncan (1983) stated that the lower concentrations of organic carbon as well as trace metals in the Chattanooga Shale indicated that reducing conditions was a prominent factor during the deposition of Chattanooga Shale in northern Arkansas.

Lambert (1992) used gamma ray as a proxy to predict the internal stratigraphy of the Chattanooga Shale in Kansas and Oklahoma. Lambert (1992) divided the Chattanooga Shale in Kansas into two namely the uppermost Shale unit and the underlying more radioactive shale. Lambert (1992) reported gamma ray values ranging between 120 and 160 API units for the uppermost shale in southern Kansas and values ranging between 80 and 110 API units for the shale in northern Kansas. Subsequently, he reported values ranging from 110 to 140 API units for the uppermost shale interval in the north and values ranging from 180 to 320 API units for the most underlying radioactive interval.

Lambert (1993) examined the internal stratigraphy and organic facies of the Chattanooga (Woodford Shale) in Oklahoma and Kansas. Lambert (1993) divided the Chattanooga into several members which include the basal Misener Sandstone, and the lower, middle and upper shale members. He concluded that the middle unit of the shale is the most important part of the shale. He believed that the middle unit is the most radioactive, and that it was deposited during the period of maximum transgression because of the mode of distribution of the organic material within the shale body. Lambert (1993) also assumed that the middle unit is the most thermally matured for the generation of oil.

Schieber (1994) in his detailed study of the internal structures, bioturbation and erosional surfaces that characterized the Chattanooga Shale of central Tennessee concluded that the Chattanooga Shale was deposited in a shallow water environment as proposed by Conant and Swanson (1961). He stated that his conclusion from the Chattanooga Shale from central Tennessee should not be applied to its lateral equivalent in eastern Tennessee and eastern Kentucky and Ohio despite the relationship between them.

Kelly (1997) examined the biostratigraphic assemblage of the Chattanooga Shale in north western Arkansas and northeastern Oklahoma. Kelly (1997) discovered conodonts from the bedding planes of the Chattanooga Shale in this region. He attributed the presence of the conodonts to significant erosional unconformity in areas where green-gray calcareous Shales overlies the black Chattanooga Shale. Kelly (1997) was the first to report the presence of abundant conodont from the Chattanooga Shale in Arkansas. He identified the conodont specie within the Chattanooga Shale as *Palmatolepis* and identified *Siphonodella cooperi* in the overlying greenish colored Bachelor Shale.

Newell (2001) studied the facies and petrophysical characteristics of the Chattanooga Shale and Misener Sandstones in central Kansas. Newell (2001) noted high gamma ray content in the Chattanooga Shale of the McPherson Valley. He believed that the gamma ray content could make the Chattanooga a potential source rock in the area. He stated that the deposition of the Misener Sandstone must have been associated with that of the Chattanooga Shale. Newell (2001) considered the Misener Sandstone as series of paralic and estuarine-fluvial sand bodies that are typical of successive stillstands during a sea-level rise.

In the biostratigraphic study of the Chattanooga Shale in the Appalachian basin, Over (2007) identified varieties of fossils within the Chattanooga Shale. He stated that the presence of fossils within the Chattanooga has brought about a global correlation of the formation. Over (2007) stated that the fossils belong to the high Givetian, Frasnian and Famennian periods.

Hurst (2008) examined the gamma ray characteristics of some selected outcrops of the Chattanooga Shale in the Ozark and Appalachian region. Hurst tested the effectiveness of using individual radioelement components of total gamma ray as a proxy for sediment source during deposition. He was of the opinion that shales with higher uranium content indicate more marine environments while shales with higher thorium and potassium ratios are product of terrestrially derived siliciclastic material.

CHAPTER III

METHODOLOGY

3.0 Field Techniques

During the fall and spring of 2008 and 2009 respectively, five outcrops of the Chattanooga Shale in the Ozark region were surveyed for gamma ray and sampled for geochemical analysis. Samples and measurements were taken at one foot interval and at every lithological change across the selected outcrops. For the purpose of this study, a total of 138 samples were collected and analyzed.

3.1 Gamma Ray Measurement

The purpose of the gamma ray measurement was to determine the distribution of individual radioelement within the Chattanooga Shale. The outcrops were surveyed using a SAIC GR-320 ENVISPEC gamma ray spectrometer. The gamma ray spectrometer is designed to measure individual radionuclide component of uranium (U), thorium (Th) and potassium (K) present in sediments as well as total radiation emitted by this radionuclide. The SAIC GR-320 ENVISPEC consists of a handy detector, a cable and a square box shaped processor. The handy detector is a ruggedly designed device that is mounted against rock surfaces to measure any form of radiation emitted by the rock. The cable is designed to send signals obtained from the rock through the detector to the processor which doubles as the storing device. The processor is designed to store, interpret and break gamma ray data into individual radionuclide. The surface area of the handy detector is about 11 inches wide. The SAIC GR-320 ENVISPEC is a cost effective and easy to use device that does every measurement in 60 second. All measurements were taken at 1 foot interval and documented. The mode of gamma ray survey of all the outcrops is described as follows;

(1) Measurement of the Jane Missouri Chattanooga Shale began at the base. The measurement was extended into the conformable overlying Bachelor Shale and the Compton Limestone (Fig. 8).

(2) At Bella Vista, the gamma ray measurements of the Chattanooga Shale started at the base Chattanooga Shale and extended to the overlying Bachelor Shale and Compton Limestone (Fig.9).

(3) At the Hanging Rock outcrop near Tahlequah Oklahoma, the survey was restricted mainly to the shale body. Measurements could not be taken from the overlying succession because of inaccessibility (Fig.10).

(4) The Chattanooga Shale at the Eagles Bluff represents a complete section of the Chattanooga Shale as a result measurements were taken from the underlying unit as well as the overlying Bachelor Shale (Fig. 11).

(5) At the No Head Hollow outcrop, gamma surveys were taken from the Chattanooga Shale and the overlying Bachelor Shale (Fig. 12).

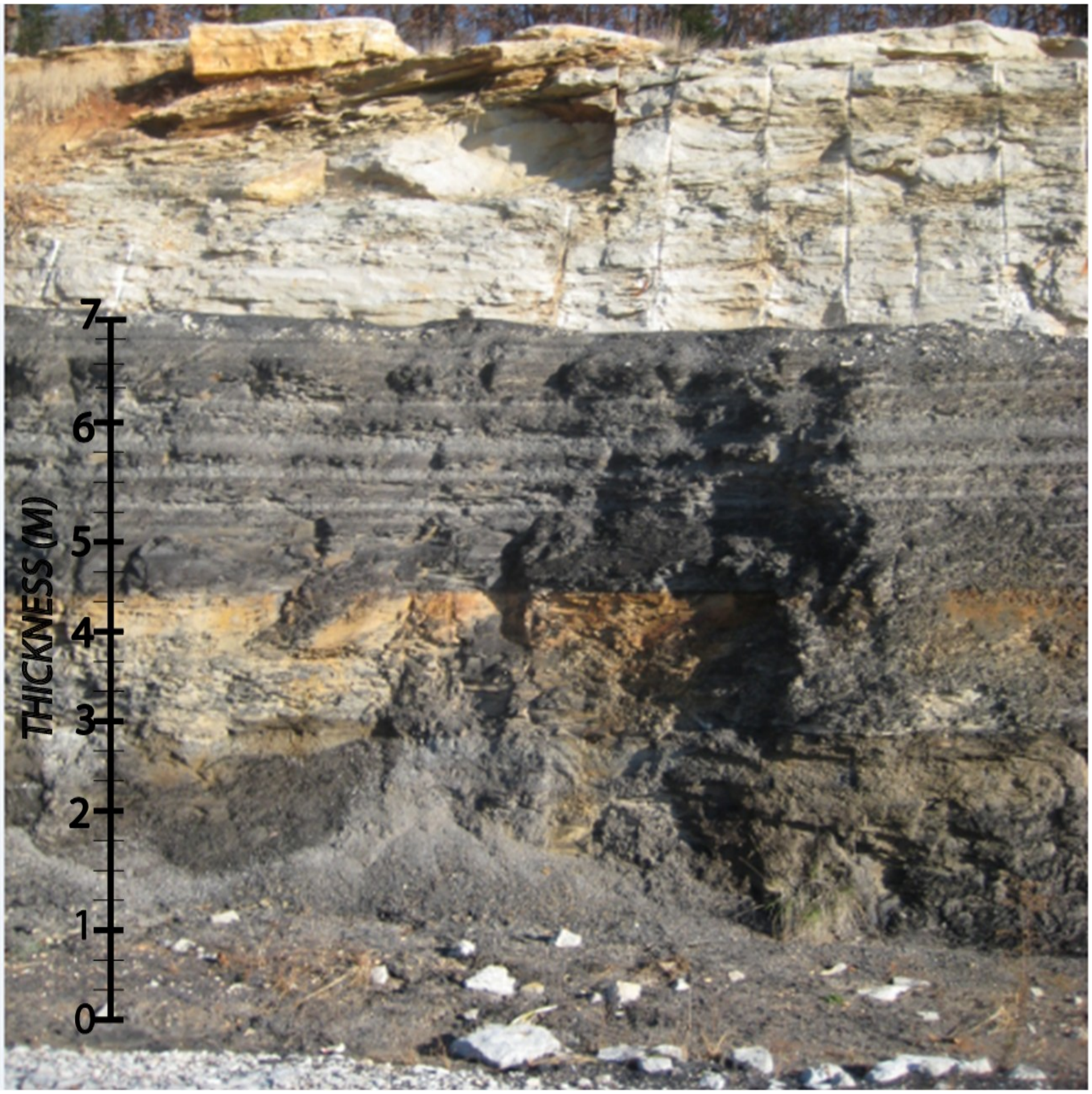

Figure 8: Jane Missouri outcrop showing the Chattanooga Shale and the overlying Compton Limestone.

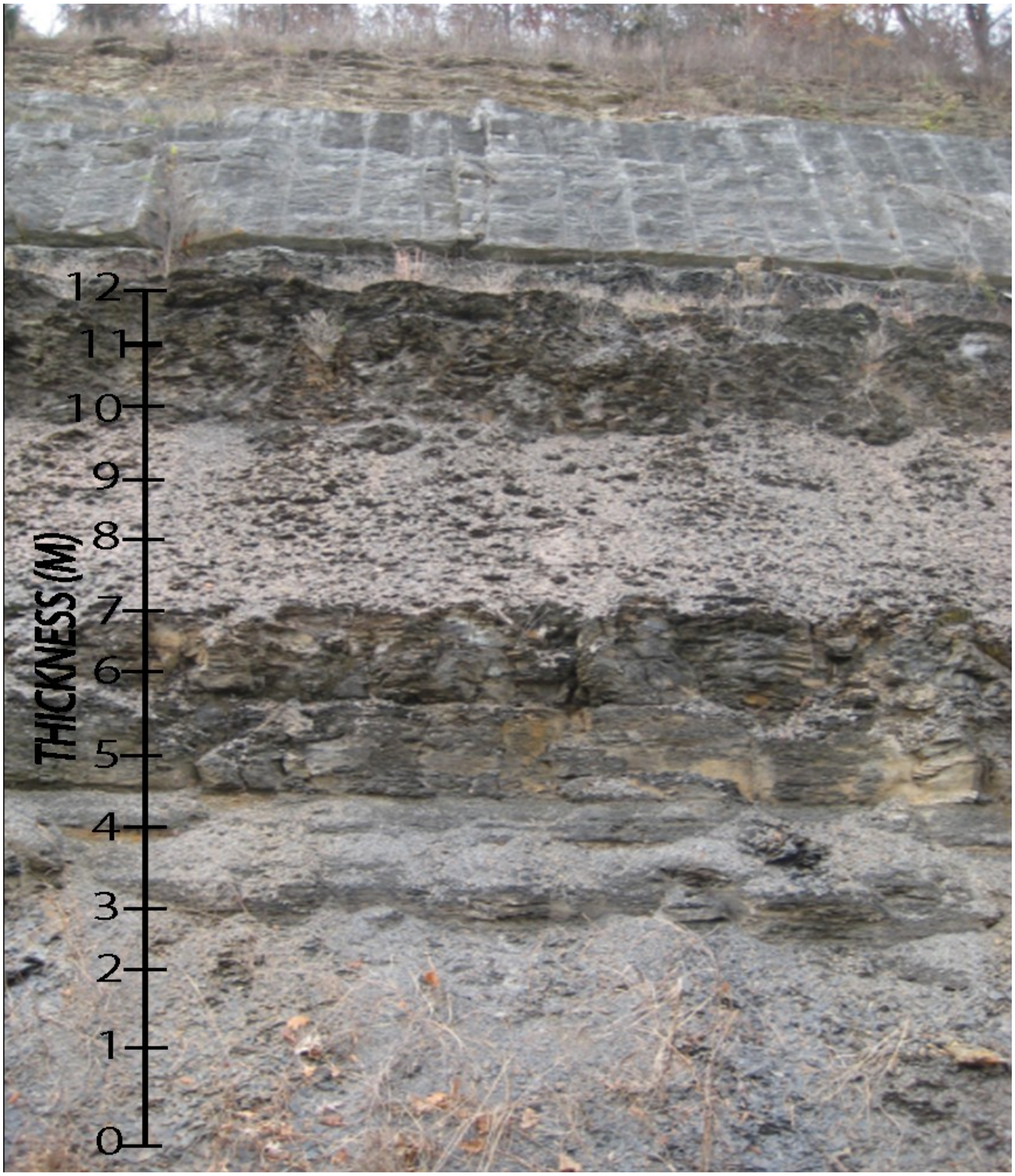

Figure 9: Picture of the Bella Vista Arkansas outcrop on US highway 71 In Benton County Arkansas.

Figure 10: Picture of the Hanging Wall Rock located in Tahlequah Oklahoma.

Figure 11: Picture of the Chattanooga Shale at Eagles Bluff, Oklahoma. Note the blocky and platy nature of the shale.

Figure 12: Picture of the Chattanooga Shale at the No Head Hollow near Tahlequah Oklahoma.

3.2 Significance of gamma ray

Gamma ray is a measurement of the natural radioactivity of a rock (Aksoy et al., 2004). Gamma ray survey can be carried out in the subsurface or at the surface. Gamma ray measurements provide information about changes in the natural radioactivity that emanates from uranium, thorium and potassium. Since the concentrations of these natural occurring radioelement varies in rocks, measurement of gamma ray helps in lithologic identification as well as stratigraphic correlation. Gamma ray provides excellent information in identifying different rock types. Aksoy et al (2004) stated that shales are easily differentiated from sandstones because of the low potassium content of sandstone when compared to shale. In well bore, gamma ray is used to calculate shale volume and generally provides information about the shaliness of a formation.

The major sources of gamma ray include individual radionuclide such as Uranium (U), Potassium (K), and Thorium (Th). These radionuclides give information about redox conditions which give room for the development of uranium in euxinic marine environment. The presence of uranium in shales could either be detrital or authigenic (Luning, 2003). Taylor (1965) and Wedepohl (1991) considered "average non-bituminous shale containing about 4 ppm uranium as of detrital origin". An increase in the amount of uranium in sediments is a function of the reduction and precipitation of authigenic uranium, which is an important factor in many oxygen-depleted systems (Luning, 2003). Thorium and potassium are the most abundant source of radioactivity in sediment and they are mainly indicative of detrital origin. Thorium concentrations have equally been reported in authigenic phosphates (Kidder, 1985). Arthur and Sageman (1994) stated that potassium is abundant in micas, feldspars and illitic clays.

3.3 Laboratory Techniques

The total carbon content of all the measured samples was determined using a CM5014 CO_2 coulometer. The concentration of the total inorganic carbon (TIC) was determined using a CM5130 acidification module. The total organic carbon (TOC) concentration was determined by measuring total carbon (TC) and subtracting it from the measured total inorganic carbon (TOC = TC – TIC). The CM5014 CO_2 coulometer is manufactured by UIC Inc, Illinois United State. The Coulometer is a machine that is designed to provide accurate determination of carbon in any CO_2 containing gas stream. The machine is equally manufactured to detect carbon values within the range of 0.01ug to 100 mg. The main component of the coulometer includes a cell assembly that is designed as an electron carrier within the system. For the determination of the total carbon, all samples were prepared by crushing them into fine powder using electric motor crusher. The crushed samples were weighed in a small ceramic 'boat' and placed via a tube into a furnace chamber. The furnace chamber is a component of the CM5014 CO_2 coulometer which operates at the temperature of 950^0C. The time spent analyzing each sample is a function of the organic richness of the sample. The average time recorded during the course of the analysis ranges between 10 and 25 minutes. The time spent on the organically rich black samples is lesser than the organically lean lighter colored samples.

The CM 5130 acidification module is also manufactured by UIC Inc. It is designed to trap inorganic carbon from sediments. The CM 5130 module is built to trap all forms of inorganic carbon from acidified sediment when subjected to heat reaction. The machine is designed to analyze both solid and liquid samples. The determination of the total inorganic carbon samples was also done using crushed samples. In this case, the crushed samples were placed in a test tube, attached to a clamp, and inserted in a furnace. 5ml per chloric acid was injected from a dispenser unto the sample, and left until the end point is determined for any present total inorganic carbon. The light grayed samples are said to have higher values of total inorganic carbon and also react quickly to total inorganic carbon test compared to the darker ones. An average of 20 minutes was spent on each sample.

3.4 Clay Mineralogy

The clay composition of the Chattanooga Shale was determined using a x-ray diffraction technique. The x-ray machine utilized was a Philips PW 3710. For the purpose of this project, both bulk and extracted clay analysis were run. The bulk analysis is a measure of the total mineralogical constituents of a rock. This include all minerals associated with the formation of rocks as well as all present clay minerals such as illite, glauconite, montmorillonite, chlorite and mixed layer clays. In general, examples of bulk minerals include calcite, quartz, and dolomite. The extracted clay analysis is a measure of just the clay minerals present in a rock as opposed to the bulk analysis. Examples of clay minerals include but are not limited to the above examples. The procedures employed before the samples were subjected to x-ray analysis include sample preparation and analytical procedures.

SAMPLE PRPARATION FOR THE BULK SAMPLES: All samples were disintegrated and crushed into powdery form using a ceramic mortar and pestle and a motor crusher. The ceramic mortar and pestle were first used to disintegrate the samples into smaller pieces before subjected to the motor crusher. The crushed samples were then put on a metal slide and placed in the x-ray chamber for analysis. Each sample takes approximately 25 minutes to run.

SAMPLE PREPARATION FOR THE EXTRACTED SAMPLES: 20g of the crushed samples were poured and filled with sodium acetate (NaOac) in a centrifuge tube, stir well, placed in a water filled container and heated at 80^0Cfor 30 minute. The purpose of the addition of the sodium acetate is to remove of all the rock forming minerals such as calcite. Next, the sodium acetate was washed from the samples and centrifuged at 1500 rpm for 5 minutes. The centrifuging allowed all the solids to settle at the bottom of the tube and the clay size particles to suspend. The suspended clay particles were then extracted using a pipette and deposited on a glass slide mounted on a hot plate in order to dry the clay particles. Next the slides were put in a glycometer in order to allow for the detection of the expandable clays. The glycomated slides were then x-rayed.

ANALYTICAL PROCEDURES: the x-ray analyses of the extracted clays and bulk samples were carried out using Philip PW 3710. The x-ray machine is designed to make use of a 45 Kv and 40 mA radiation source for its operation. The x-ray machine is connected to Xpert Data Collector software that reads and interprets the entire signal sends out by the machine. The bulk and extracted clay slides are put in the x-ray chamber and analyzed by the machine at an angle of $2\text{-}30^0$ 2θ at a scan rate of approximately 25 minutes.

CHAPTER IV

FINDINGS

4.0 Results

This chapter discusses the relationship between the total organic carbon content and total gamma ray characteristics as well as clay mineralogy of the Chattanooga Shales in the area of study.

4.1 Jane Missouri

The Chattanooga Shale outcrop in Jane, Missouri is located along US Highway 71 in Missouri. The total thickness of the outcrop was measured to be 6.4 meters thick (21 feet) and divided into three distinctive units based on visual observation and gamma ray characteristics (fig.13). The outcrop is deposited on the southwestern edge of the Ozark Uplift and composed of thick units of Devonian to Mississippian rocks (Fig. 5) (Fig. 14). The stratigraphy of the exposed section consists of the massive Mississippian Compton Limestone, the Lower Mississippian Bachelor Shale and the Upper Devonian Chattanooga Shale (Fig.13). The characteristic of each individual unit within the Chattanooga Shale is described as follows.

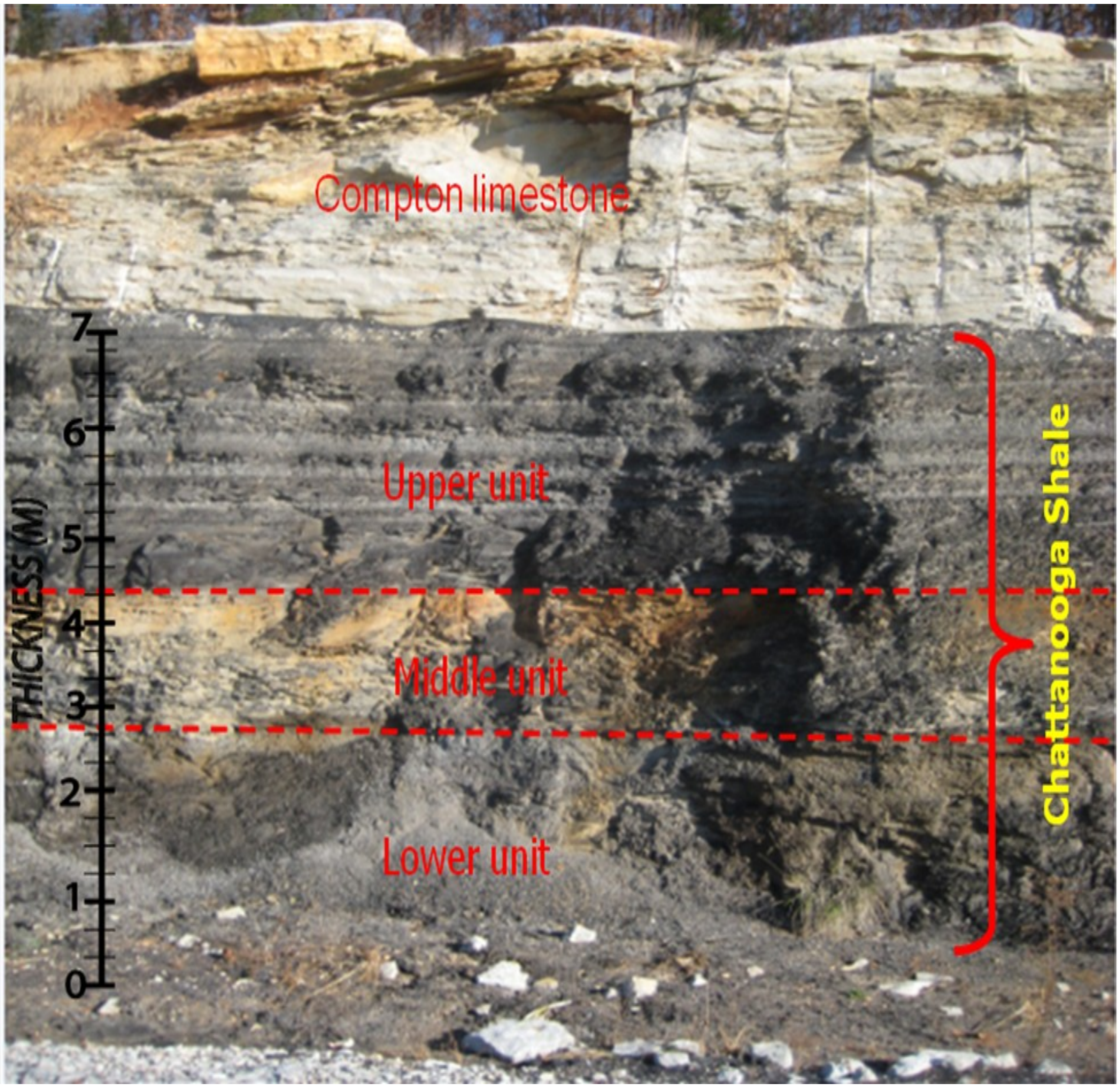

Figure 13: Photograph of the Jane Missouri outcrop showing the three distinctive units within outcrop.

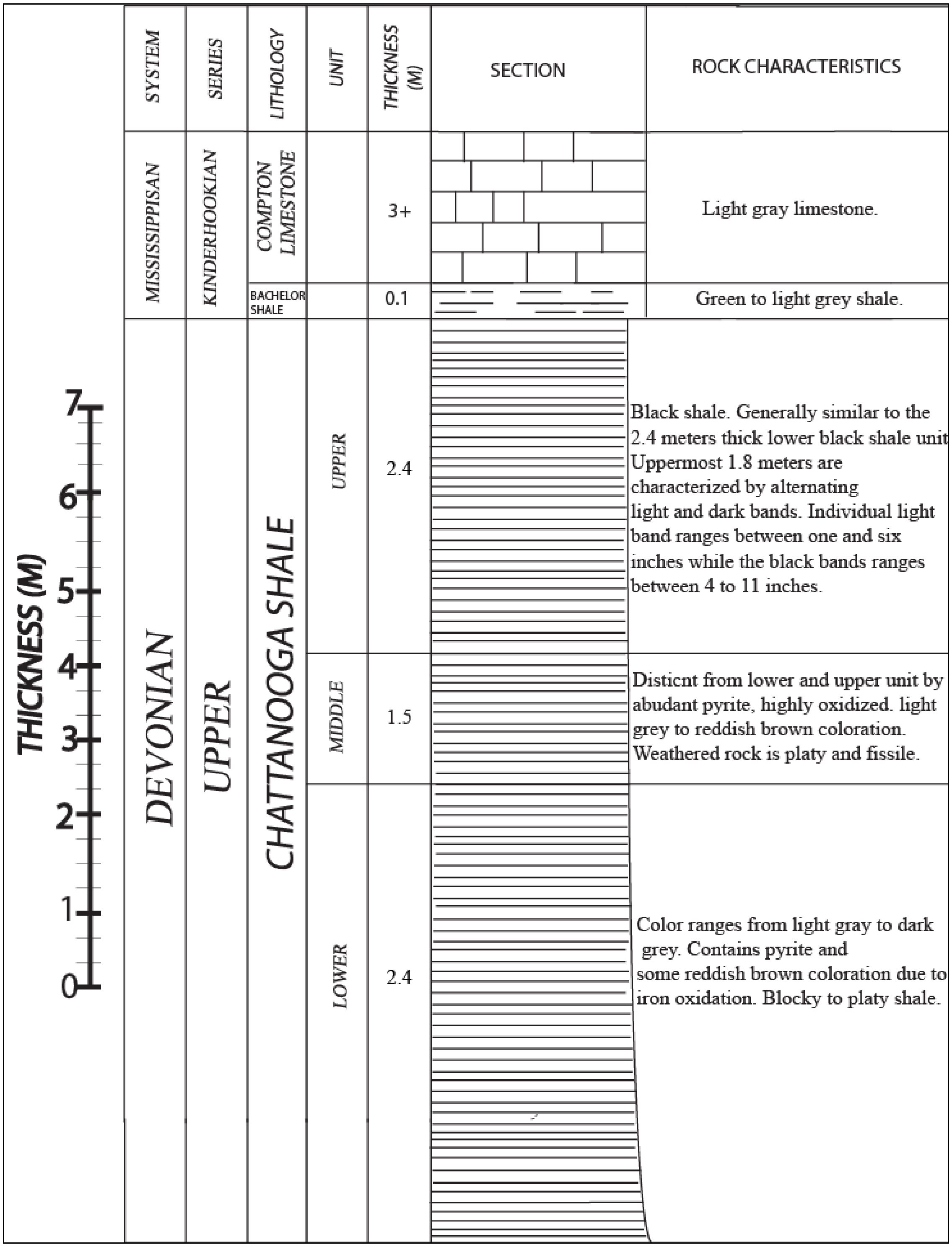

Figure 14: Stratigraphic section of Jane Missouri outcrop showing the relative thickness of each unit.

4.1.1 LOWER UNIT

The Lower Unit is 2.4 meters thick (8 feet) and composed of mainly dark gray to black massive blocky shale (Fig. 13). This lowermost blocky shale unit is characterized with vertical fractures which make it easier for the shale to break into straight thin and thick slabs along bedding planes whenever pressure was being applied during sample collection. The sharp transition of this unit into the middle unit is marked by an obvious change in coloration.

4.1.2 MIDDLE UNIT

The middle unit is 1.5 meters thick (5 feet) and also composed of massive blocky shale. Generally, the entire middle unit distinguished from both the lowermost and the uppermost unit because of its unusual enrichment in pyrite. This unit is massive with very little evidence of weathering. However, weathered surface tends to be fissile and or platy with reddish brown coloration. Just like the lowermost unit, this unit is also characterized with vertical fractures. This unit has the highest values of gamma readings with the uranium content taking the lead when compared to the upper and lower units (fig. 15).

4.1.3 UPPER UNIT

The uppermost unit is also 2.4 meters thick (8 feet) and has almost the same characteristics with the lowermost unit. The uppermost 1.8 meters (6 feet) of this interval is characterized by distinct alternating light and dark bands. The thickness of the light bands ranges between and 1 and 6 inches while that of the black bands ranges from 4 to

11 inches. These alternating light and dark bands are believed to represent different periods of a depositional cycle as evident by the variation in the TOC and gamma ray content of each interval.

4.1.4 BACHELOR SHALE

The thickness of the Bachelor Shale ranges from 0.1 to 0.2 meters in the area of study. In Jane, the thickness of the Bachelor Shale is 0.1 meters and is composed of a muddy, greenish to light grayish shale. The Bachelor Shale is thought to serve as a transition between the Devonian Chattanooga Shale and the Upper Mississippian Compton limestone wherever it occurs. The contact is characterized by an abrupt change from muddy crumbly shale unit to a very massive limestone.

4.1.5 COMPTON LIMESTONE

The Compton is a massive light grey limestone. The limestone rests unconformably over the Bachelor Shale and characterized by abundant pyrite (fig. 14).

4.1.6 TOTAL ORGANIC CARBON (TOC) CONCENTRATION

The determination of total organic carbon content in black shales cannot be over emphasized. The amount of total organic carbon present in black shales determines its organic richness and contributes to its ability to generate hydrocarbon. The Chattanooga Shale in Jane Missouri can be described as organically rich black shale. The total concentration of organic carbon in this outcrop is equivalent with some of the lowermost hot Silurian Shales in North Africa and Arabia (table, 1). The TOC concentration in this outcrop varies significantly from one unit to the other (table 2). However, the overall average values of the total organic carbon content across the outcrop ranges from 0.2 wt% on the minimum to 4.48 wt% on the maximum with mean value of 1.94 wt%. The TOC concentration of the upper unit ranges from 0.2 wt% to 2.3 wt%. The middle unit was measured at 1.5 meters and has TOC values ranging from 1.8 wt% to 2.7 wt %. The TOC value of the lower unit ranges from 0.8 wt% to 2.6wt%. The middle unit has the highest value of TOC.

The total organic carbon concentration of Jane outcrop is the lowest of all the other five examined outcrops. The lower organic carbon content Chattanooga Shale in Jane is a key to understanding the position of the outcrop within the basin.

4.1.7 Gamma-Ray Characteristics

The Chattanooga Shale in Jane was measured using gamma ray spectrometer described in chapter three. A total of 25 measurements were taken vertically across the outcrop at one foot interval. Out of the 25 measurements, 21 were taken directly from the Chattanooga Shale, one from the Bachelor Shale and three measurements from the basal part of the Compton Limestone. The total gamma value across the outcrop varies significantly from one unit to another (fig. 15) (table, 2). In the lowermost unit, the distribution of radionuclide elements varies. This is because of the sudden increase in the value of the total gamma ray in the lowermost four feet of the unit (fig. 15). The concentration of thorium ranges from 15.9 to 21.0 ppm while that of uranium ranges from 5.5 to 10.1 ppm. The concentration of potassium is lowest in the lowermost unit with values ranging between 5.4 and 6.4%. The total gamma ray across the lower unit ranges from 194 to 254.4 API. The middle unit is the hottest part in the outcrop with gamma value ranging from 253 to 273 API. The concentration of thorium ranges from 17.4 on the minimum to

21.4 ppm on the maximum. The concentration of uranium ranges from 8.2 to 13.7 ppm while that of potassium ranges from 5.8 to 6.4 %.

The spectral concentration of individual radionuclides is lowest in the upper unit. The upper unit consists of intervals of both ‘hot’ and normal shale as the total gamma value ranges from 178 to 244 API. The concentration of thorium ranges from 14.5 to 18.9 ppm while that of uranium ranges from 5.9 to 11.1 ppm.

The overall concentration of individual radionuclide across the outcrop indicates that the Chattanooga shale is a ‘hot’ shale. Lunning et al., (2000) stated that shales are defined as ‘hot’ when they have gamma values of more than 200 API. The concentration of thorium is highest followed by uranium and potassium respectively (table, 3). The concentration of thorium ranges from 14.5 to 20.9 ppm with an average value of 19 ppm. The concentration of uranium ranges from 5.9 to 13.7 ppm with an average value of 8.0 ppm. The concentration of potassium is the lowest with values ranging from 4.6 to 6.4 %. The average total gamma ray value across the outcrop ranges from 178 to 273 API with a mean value of 226 API.

The gamma ray value of the Bachelor Shale is very low when compared to the Chattanooga Shale. The total gamma value of the shale is 172 API while the values of the individual radionuclides thorium, uranium, and potassium are 13.4 ppm, 4.6 ppm and 5.1 respectively.

The Compton Limestone clearly indicates that the carbonate rocks are generally less radioactive than the shales. Three gamma ray readings were collected in the lowermost part of Compton where it uncomformably overlies the Bachelor Shale. The gamma value of the limestone varies from 39.6 to 82.8 API units while the value of the individual radionuclide thorium ranges from 4.3 to 8.3ppm. The spectral reading of uranium ranges from 0.8 to 1.4 ppm and that of potassium ranges from 1.0 to 2.4%.

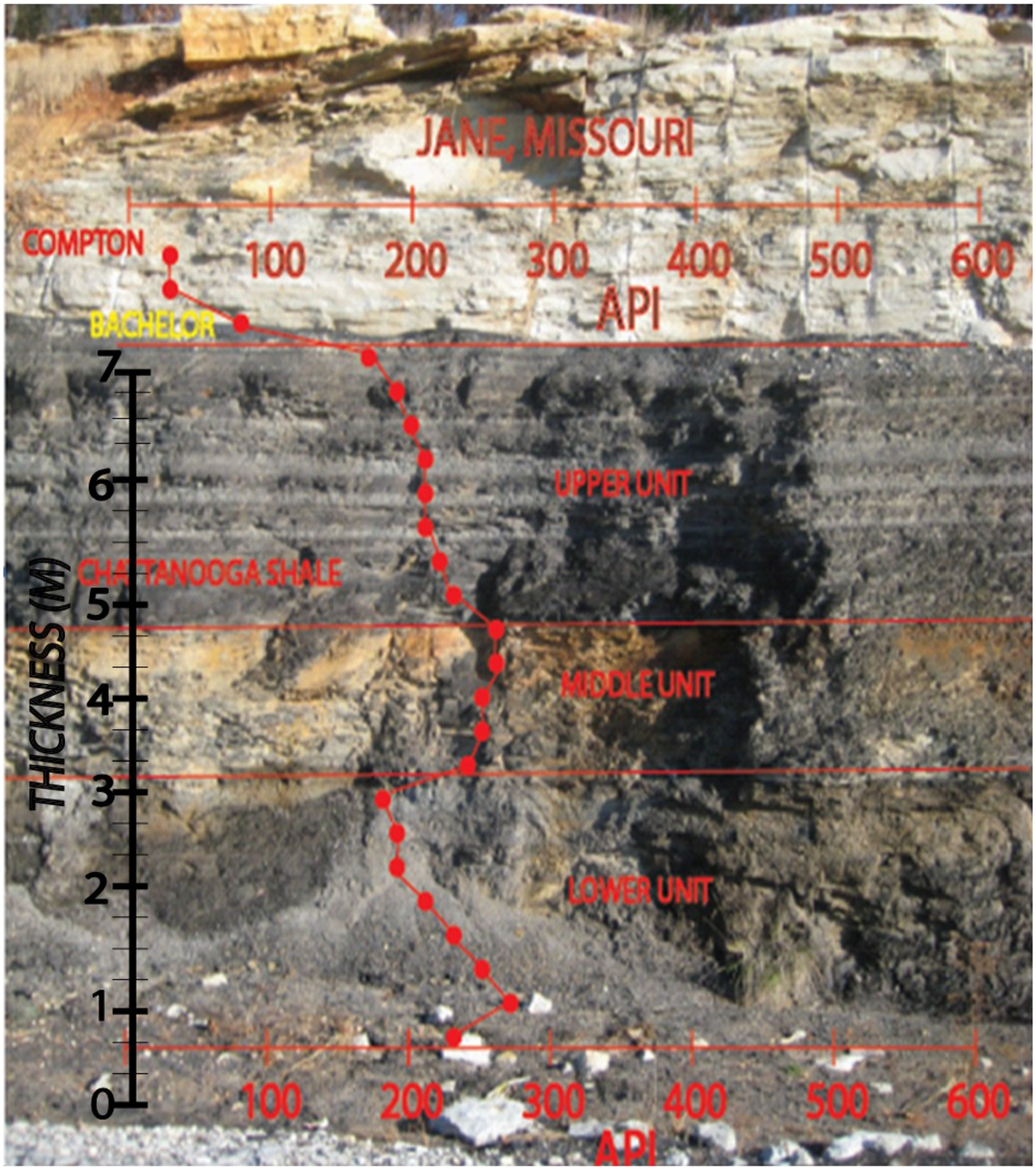

Figure 15: Photograph of the Jane Missouri outcrop showing the gamma ray characteristics across the outcrop.

Country	TOC (wt %)	Average Thickness (ft)	(R_o)	Basin Name	Gamma Ray (API)
Morocco	3-10	15	1.0-3.0	Tindoulf, Talda	_
Algeria	1-17	28	1.1-1.75	Sbaa, Mouydir, Mya	>200
Tunisia	1.5-20	55-180	_	_	_
Libya	1.28-16.7	25		Murzuq	>150
Egypt	_	600	_	Qattarah	_
Sudan	_	30-40	_	Djadi	_
Mauritania	<1	_	_	Taoudenni	_
Iran	1.0-4.3	_	_	Kuh-e-farghun	_
Iraq	0.96-9.94	40	_	Western Desert	_
Saudi Arabia	8	50-70	2.3-2.5	Qalibah, Qusaiba	>200
Jordan	0.4-11	1200	1.2	Risha, Sirhan	>200
Oman	_	220	_	_	>200
Qatar	0.5-7	_	_	_	_
Sardinia (Italy)	_	100	_	_	_
Maguma terrane (Nova Scotia)	_	800	_	_	_
Romania	0.06-4.48	700-2200	0.5-2.5	Meosian platform	_
USA	0.2-6.1	13-37	-	Ozark Platform	147-632

Table 1: Table showing the total organic concentration and gamma ray values of hot Silurian Shales in North Africa and Arabia (Luning et al, 2000).

SAMPLE #	Total carbon (wt %)	Total inorganic (wt %)	Total organic carbon (wt %)
MO 1	2.1	0	2.1
MO 2	1.4	0.4	1.0
MO 3	1.7	0.4	1.3
MO 4	1.1	0.9	0.2
MO 5	2.2	0	2.2
MO 6	1.7	0.6	1.1
MO 7	2.4	0.2	2.2
MO 8	2.7	0.3	2.4
MO 9	2.1	0	2.1
MO 10	3.0	0.2	2.7
MO 11	2.1	0.2	1.9
MO 12	2.2	0	2.2
MO 13	2.0	0	2.0
MO 14	1.5	0.4	1.1
MO 15	1.8	0.9	0.9
MO 16	2.1	0.2	1.9
MO 17	2.6	0.1	2.5
MO 18	2.9	0.2	2.7
MO 19	2.6	0	2.6
MO 20	2.7	0.3	2.4
MO 21	2.8	0.3	2.5

Table 2: Table showing the total organic carbon content of Jane Missouri Chattanooga Shale. Note: The value of the TOC is highest at the middle unit.

SAMPLE#	TH (ppm)	U (ppm)	K (%)	Total GAMMA (API)
MO 1	14.5	5.9	4.6	178.8
MO 2	17.1	6.8	4.9	201.2
MO 3	15.8	7.7	5.4	211.2
MO 4	16.5	8	5.4	216.4
MO 5	16.5	7.4	5.7	216.4
MO 6	15.5	7.7	5.8	216.4
MO 7	18.9	8.5	5.6	233.2
MO 8	16.6	11.1	5.6	244.8
MO 9	17.5	13.4	6	273.2
MO 10	17.4	13.7	5.8	272
MO 11	18.8	11	5.8	256
MO 12	18.5	10.8	6.5	264.4
MO 13	21.4	8.2	6.4	253.6
MO 14	15.9	5.5	5.4	194
MO 15	16.3	6.5	5.4	203.6
MO 16	16.7	5.1	5.7	198.8
MO 17	17.8	6.3	5.3	206.4
MO 18	18	10.1	5.7	244
MO 19	21	8.7	6.3	254.4
MO 20	20.9	9.2	6.4	176
MO 21	16.8	9.6	6	240

Table 3: Table showing the concentrations of thorium (Th) in ppm, uranium (U) in ppm, potassium (k) in % and total gamma ray in America Petroleum Institute (API) units, in the Jane Missouri outcrop.

4.1.8 Relationship between total carbon and gamma ray

The relationship between the total organic carbon and gamma-ray values within the Chattanooga Shale in Jane Missouri support the observation that increase in gamma values often correlate to increase in TOC (Fig. 16) Stable and close relationship between In Jane Missouri, the relationship between the TOC and gamma ray values indicate that the middle unit is relatively richer when compared to the lower and upper units. The highest gamma value of 272 and 273.2 API recorded in the middle unit corresponds to the highest values of TOC which is 2.1 wt% and 2.7 wt% respectively. The high ratio of thorium to uranium in the outcrop indicates that the outcrop is a distal water facie of the Chattanooga Shale deposited on the high shelf.

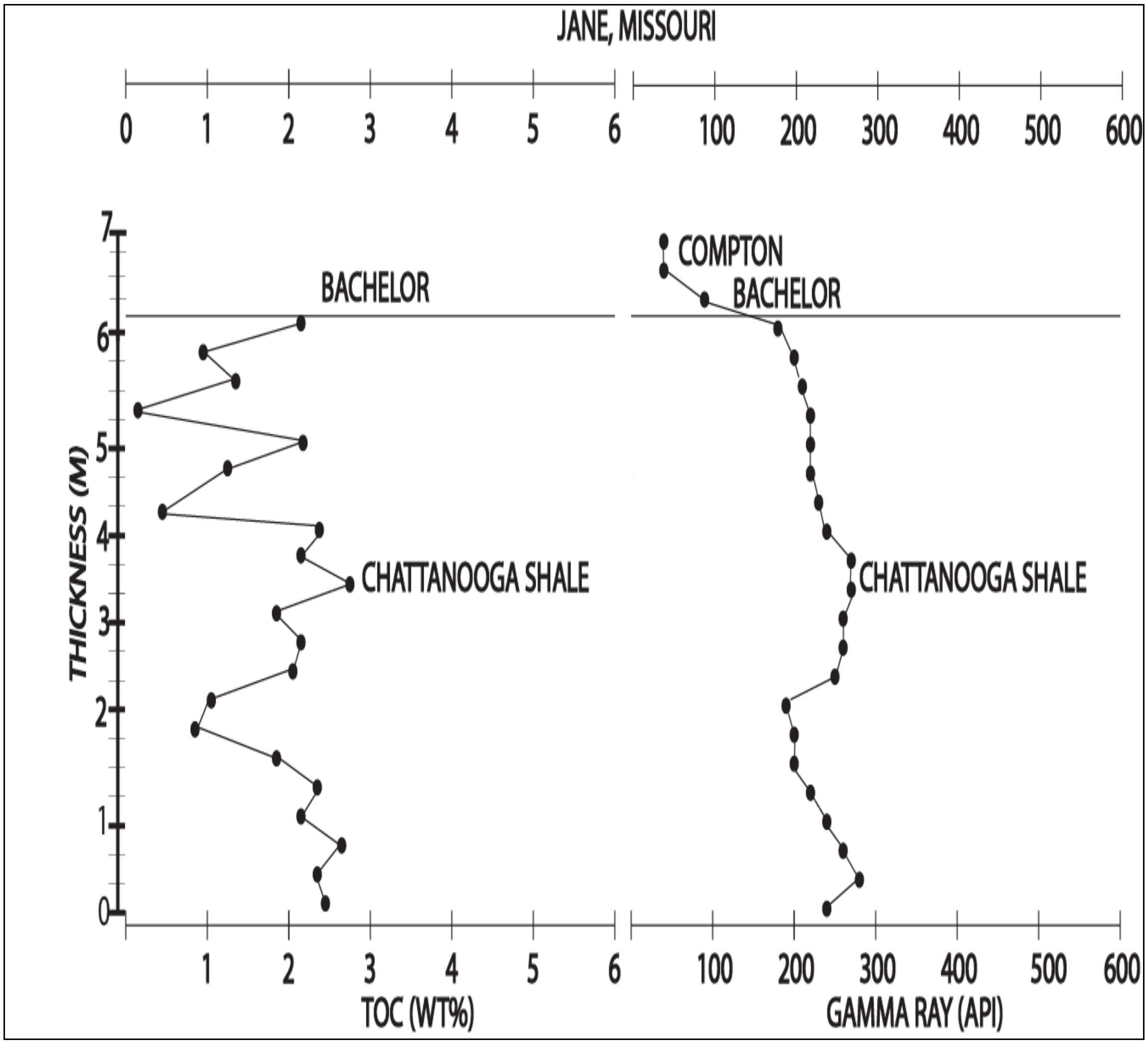

Figure 16: Graph showing the relationship between the gamma ray intensities and total organic carbon concentration of the Jane Missouri Chattanooga Shale.

4.2 Bella Vista Arkansas

The Chattanooga Shale outcrop in Bella Vista Arkansas has been described by Chinn and Kronig, (1973) as part of the northern Arkansas structural platform. The Chattanooga Shale at this location is 11.2 meters (37 feet). The stratigraphic composition of the Chattanooga Shale at Bella Vista, Arkansas includes exposures of the Bachelor Shale and Compton Limestone. The Bachelor Shale overlies the Chattanooga Shale, while the Compton Limestone overlies the Bachelor Shale at this location (fig. 17 & 18). The

Chattanooga Shale member in Bella Vista, Arkansas is characterized by a unique lithologic uniformity upon first examination. However, upon close and careful examination the outcrop is characterized by more than one feature. Some of the notable diagnostic features in the shale member include (a) alternating light and dark bands that are restricted to the uppermost unit, (b) massive beds with intercalating fissile beds of about 1 to 2 inches thick at the middle and basal part, (c) thick units of thin flaked weathered surface and (d) an oxidized layer in the blocky basal part.

The overall shale member can be described as light to dark grey, massive to fissile, crumbly carbonaceous pyritic shale. Duncan (1983) believed that the black coloration exhibited by the shale is due to a combination of finely disseminated pyrite and or present of organic rich materials. Fresh samples of the Chattanooga Shale emit petroleum odor when broken.

One diagnostic feature about the shale is that it weathers mainly into thin flakes of shale, which rarely go into clay. The weathered thin flakes remain dark both at the surface and upon digging; thus as the flakes are removed by erosion, fresh surfaces are being exposed. The massive beds have reddish-brown coloration as a result of oxidation of pyrite.

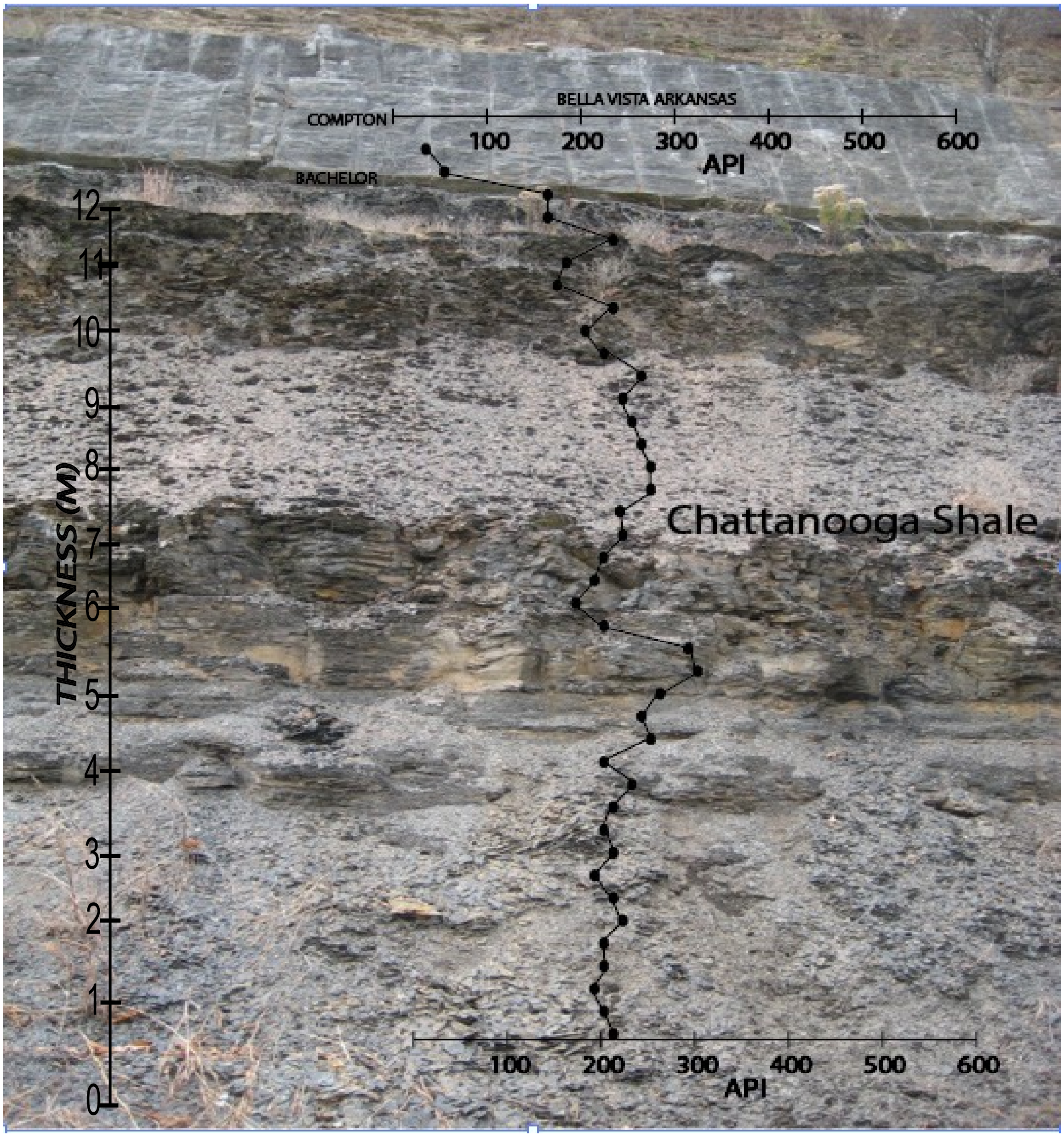

Figure 17: Photograph of the Chattanooga Shale in Bella Vista Arkansas showing gamma ray signature across the outcrop.

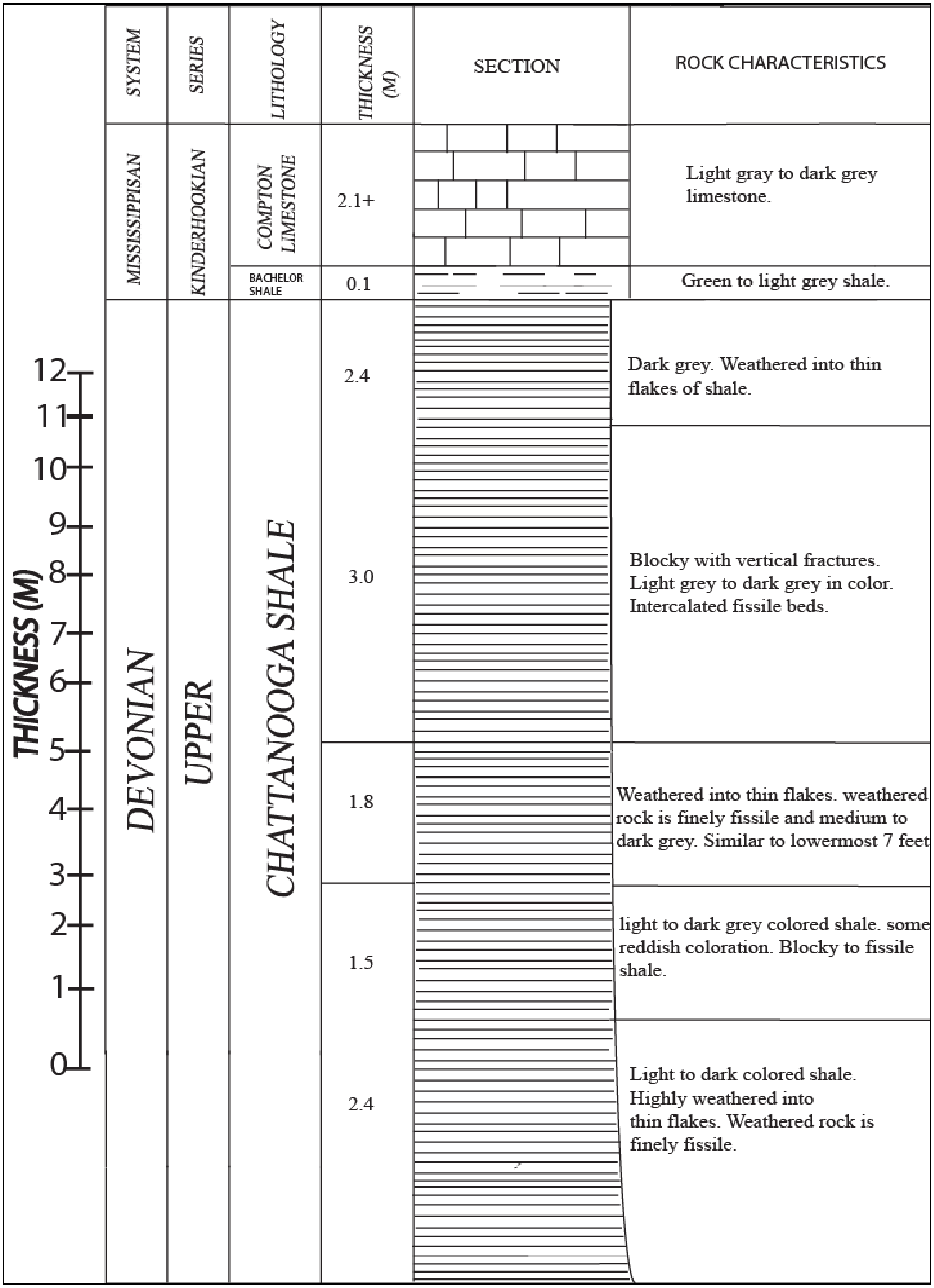

Figure 18: Stratigraphic section of the Chattanooga Shale at Bella Vista, Arkansas.

The diagnostics characteristics of the Chattanooga Shale in Bella Vista, Arkansas are described as follows.

4.2.1 Lower Unit

The lower unit of the Chattanooga Shale in Bella Vista is 3.9 meters (13 feet thick) and composed of crumbly to fissile, blocky shale (Figs. 17 & 18). The lowermost 2.4 meters (8 feet) of this unit is composed predominantly of weathered thin flakes of shale that are light to dark grey colored, while the remaining upper 1.5 meters (5 feet) is of the same color but consist of crumbly to fissile and blocky shale. Some reddish brown coloration was also noticed. The reddish brown coloration of the upper 1.5 meters (5 feet) is as a result of oxidation of pyrite.

4.2.2 Middle Unit

The middle unit is 1.8 meters thick (6 feet) and consists of finely fissile and some weathered thin flakes of shale. The weathered thin flakes are predominantly medium grey to dark grey and rarely degenerate into clays. Upon the erosion of the thin flakes, fresh black surface of the shale is exposed. Digging into fresh samples of the shale indicates the presence of thin fissile beds with fractures along their bedding planes.

4.2.3 Upper Unit

The upper unit is 5.4 meters thick (18 feet) and consists of weathered, blocky to fissile shale. The transition from the middle unit to the upper unit is marked by a distinct change in the weathering nature of the shale. The lowermost 3.0 meters (10 feet) of the upper unit is blocky and characterized by some vertical fractures. It is light grey to dark grey in color and consists of intercalated thin fissile shale beds. The uppermost 2.4 meters (8 feet) of the unit is predominantly dominated by weathered dark grey thin flakes of shale.

4.2.4 Bachelor Shale

The thickness of the Bachelor Shale is 0.1 meters thick (0.6 feet) and is composed of muddy, greenish to light grayish shale. Upon contact with water, the shale can be molded into any desired shape. The Bachelor Shale is also enriched in pyrite. The contact of the Bachelor Shale with the overlying Compton limestone is sharp and characterized by an abrupt transition from muddy crumbly shale unit to a very massive limestone.

4.2.5 Compton Limestone

The Compton Limestone is composed of light grey to dark grey limestone. The limestone is overlain unconformably on the Bachelor Shale. The Compton Limestone is also characterized by pyrite, but not as abundant as the ones observed at the Jane Missouri outcrop.

4.2.6 Total organic carbon (TOC) concentration

The total organic carbon content of Bella Vista Shale varies significantly from one unit to another. The shale is characterized by cycles of high and low total organic carbon concentration (fig. 19). The total organic carbon content across the shale ranges from 0.9 to 3.1 wt% (table, 4). The total organic carbon concentration of the upper unit ranges from 0.9 to 3.1 wt%. The mean value of the TOC concentration of the upper unit was calculated at 2.2 wt%. The TOC concentration of the middle unit ranges from 2.1 to 2.9 wt% while the mean value is 2.6 wt%. The middle unit is the thinnest of the three units and consists of the highest concentrations of organic matter. The TOC concentration of the lower unit ranges from 1.0 to 2.9 wt% and has a mean value of 2.0 wt%.

4.2.7 Gamma-Ray Concentration

The Chattanooga Shale in Bella Vista was also measured using gamma ray spectrometer. A total of 41 measurements were taken vertically across the outcrop at one foot intervals. Out of the 41 measurements, 37 were taken directly from the Chattanooga Shale, one from the Bachelor Shale and three measurements from the basal part of the Compton Limestone. The gamma signature of the Chattanooga Shale at this location also varies but to a considerable extent (fig.17 & 19). For instance, the middle unit has higher gamma ray intensities than both the lower and upper units. In general, the shale can be referred to as 'hot' shale as most of the intervals surveyed have gamma rays values greater than 200 API (table, 5). The gamma value of the lower unit ranges from 198 to 239 API while that of the middle unit ranges from 211 to 310 API. The gamma values of the upper unit is the lowest and ranges from 147 to 263 API. The relationship between the uranium and thorium indicates that the outcrop was deposited in close proximity to the shelf thus making the shale a shallow facies of the Chattanooga in the Ozark region.

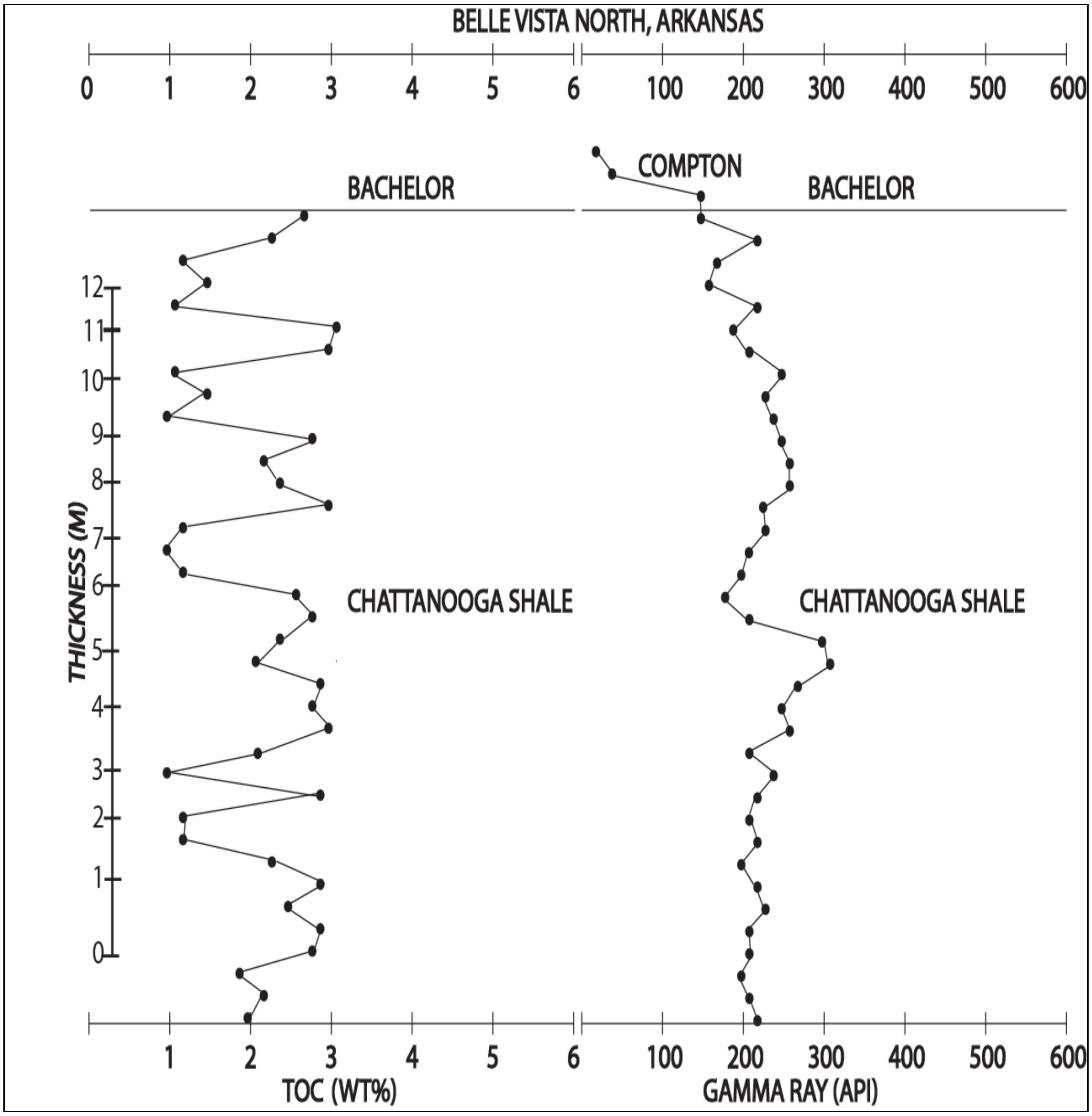

Figure 19: Graph showing the relationship between the gamma ray intensities and total organic carbon content of the Arkansas Bell Vista Chattanooga Shale.

SAMPLE #	Total carbon (wt %)	Total inorganic (wt %)	Total organic carbon (wt %)
AR 1	2.6	0	2.6
AR 2	2.3	0	2.3
AR 3	1.4	0.3	1.1
AR 4	1.5	0	1.5
AR 5	1.4	0.3	1.1
AR 6	3.1	0	3.1
AR 7	3.3	0.2	3.1
AR 8	1.3	0.2	1.1
AR 9	1.6	0.1	1.5
AR 10	1.3	0.3	1.0
AR 11	2.8	0	2.8
AR 12	2.3	0.2	2.1
AR 13	2.4	0	2.4
AR 14	3.0	0	3.0
AR 15	1.5	0.3	1.2
AR 16	1.3	0.3	1.0
AR 17	1.2	0	1.2
AR 18	2.6	0	2.6
AR 19	2.8	0	2.8
AR 20	2.6	0.2	2.4
AR 21	2.3	0.1	2.1
AR 22	2.9	0	2.9
AR 23	2.7	0	2.7
AR 24	2.9	0	2.9
AR 25	2.3	0.1	2.1
AR 26	1.2	0.2	1.0
AR 27	2.9	0	2.9
AR 28	1.2	0	1.2
AR 29	1.2	0	1.2
AR 30	2.6	0.3	2.3
AR 31	3.1	0.2	2.9
AR 32	2.4	0	2.4
AR 33	2.8	0	2.8
AR 34	2.7	0	2.7
AR 35	2.1	0.2	1.9
AR 36	2.1	0	2.1
AR 37	1.9	0	1.9

Table 4: Table showing the total organic carbon concentration of the Bella Vista Chattanooga Shale.

SAMPLE #	Th (ppm)	U (ppm)	K (%)	Total GAMMA (API)
AR 1	10.2	3.9	4.7	147.2
AR 2	19.4	6.6	5.7	221.6
AR 3	14.6	3.8	4.8	165.6
AR 4	16.1	3.3	4.4	161.2
AR 5	16.8	8	5.5	219.2
AR 6	12.8	7.1	5.2	191.2
AR 7	14.8	7.8	5.3	206.4
AR 8	17.5	11.3	5.6	250.0
AR 9	15.4	9.7	5.6	228.8
AR 10	18.1	9.1	6.0	241.2
AR 11	19.4	10.5	5.8	254.4
AR 12	23.1	8.8	6.3	263.6
AR 13	16.7	10.9	6.5	258.0
AR 14	16.8	7.9	6.3	231.2
AR 15	18.1	9.1	5.0	225.2
AR 16	13.9	8.8	5.2	209.2
AR 17	14.6	7.3	5.1	198.4
AR 18	14.0	5.7	4.9	180.0
AR 19	19.7	5.6	5.5	211.6
AR 20	17.6	16.2	6.4	302.4
AR 21	18.3	16.2	6.7	310.0
AR 22	19.7	12.2	6.1	274.0
AR 23	15.9	11.1	6.3	253.2
AR 24	17.0	11.1	6.2	256.0
AR 25	16.7	5.9	6.2	213.2
AR 26	21.1	7.7	5.8	238.8
AR 27	17.2	7.4	5.6	217.6
AR 28	16.1	6.7	5.8	210.8
AR 29	16.5	6.9	5.9	215.6
AR 30	15.5	5.4	5.8	198.0
AR 31	18.5	7.2	5.7	222.8
AR 32	15.1	9.8	6.0	234.8
AR 33	14.8	7.0	5.9	209.6
AR 34	16.1	6.9	5.9	214.0
AR 35	16.5	5.4	5.8	202.0
AR 36	15.5	7.2	5.7	210.8
AR 37	14.5	7.8	6.0	216.4

Table 5: Table showing the total gamma ray intensities of the Bella Vista Arkansas Chattanooga Shale.

4.2.8 Relationship between total carbon and gamma ray

The relationship between the total organic carbon and gamma ray contents of the Chattanooga Shale in Bella Vista indicate that the TOC increases as the gamma ray increases thus supporting the hypothesis that increase in gamma ray often indicates an increase in total organic carbon (fig. 19). The middle unit is the hottest and richest part of the entire Chattanooga Shale in Bella Vista. The highest gamma value in the unit is 310 API and the highest TOC value is 2.9 wt%. Though the upper and lower units consist of gamma values that are less than 200 API and TOC values that are as low as 0.9 wt%, the Chattanooga Shale in this location can be considered as organically rich shale. This is because of the overall relative higher values of both the TOC and gamma ray. The TOC content averages 2 %wt while the total gamma intensity averages 210 API.

4.3 NO Head Hollow, Oklahoma

No Head Hollow is located in Southeastern, Oklahoma. The Chattanooga Shale at this location was measured to be 11.2 meters thick (37 feet) and composed of five different lithologies of different ages (fig. 20). The five different units present in No Hollow Head include the Lower Ordovician Fite Dolomitic Limestone, Upper Ordovician Fernvale Limestone, Upper Devonian Chattanooga Shale, Lower Mississippian Bachelor Shale and the Upper Compton Limestone. This project only focuses on the Upper Devonian Chattanooga Shale. Upon first examination, the weathering nature of the Chattanooga Shale at this location makes it look exactly the same. However, close examination reveals subtle differences within the rock. The gamma ray signature of the outcrop was used to divide the outcrop into three units. The physical properties of each unit as well as the characteristics of the overlying units are described as follows.

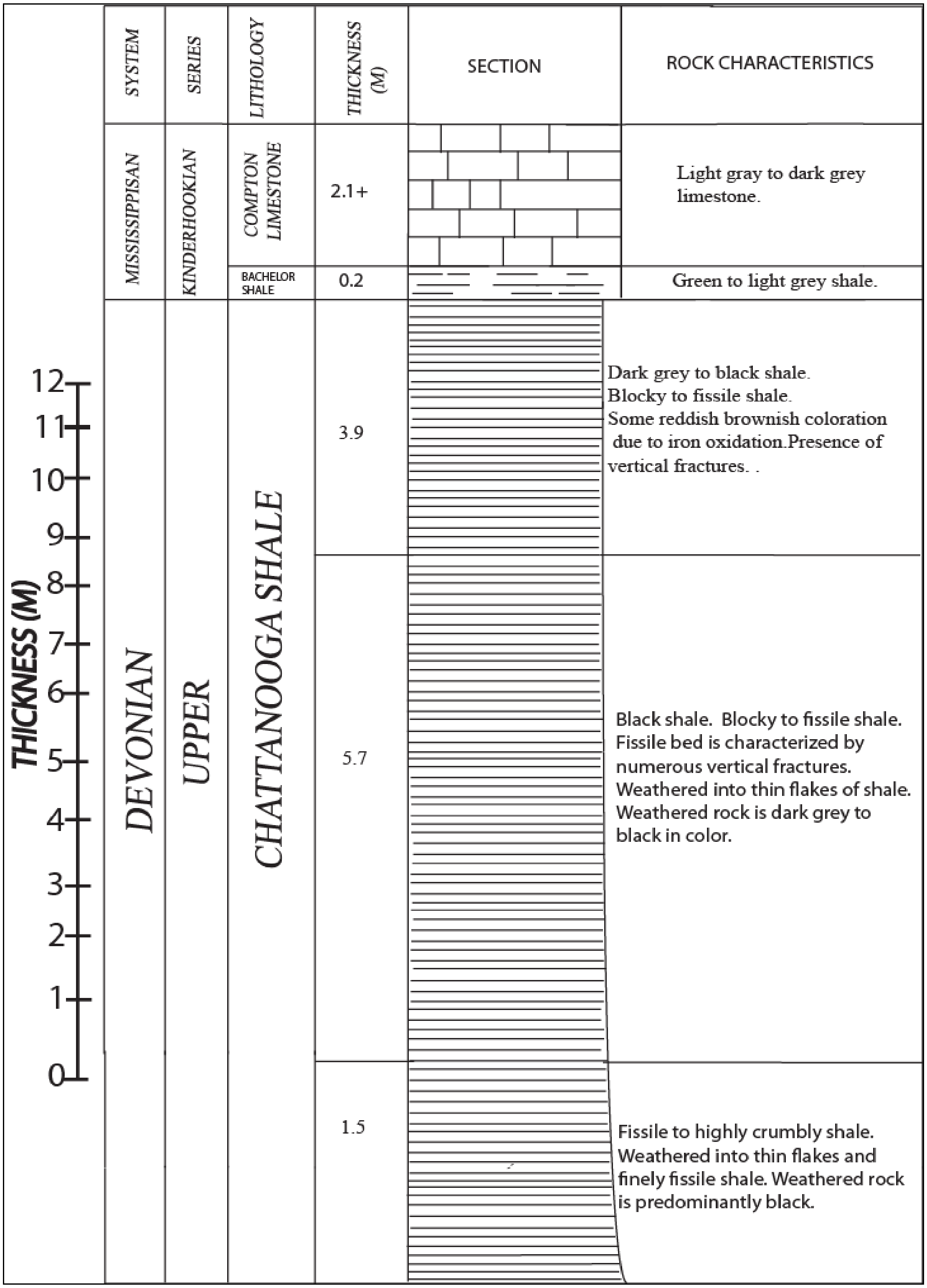

Figure 20: Stratigraphic section of the Chattanooga Shale outcrop at No Head Hollow near Tahlequah, Oklahoma.

4.3.1 Upper Unit

The upper unit is the only unit within the Chattanooga Shale at this location that has not been seriously affected by weathering. The upper unit is 3.9 meters thick (13 feet) and characterized by massive beds with intercalations of fissile beds (fig. 20 & 21). The lowermost 0.6 meters (2 feet) into this unit is characterized by weathered platy shales that are dark grey to black in coloration. The massive beds are restricted to the uppermost part of the unit and are characterized by some vertical fractures. The fractures within the unit are presumed to have facilitated the development of the lowermost weathered surface at the base of the unit.

4.3.2 Middle Unit

The middle unit is characterized by alternation of blocky and finely fissile shale. First visual examination of the outcrop suggests the middle unit is completely composed of weathered shale but close examination shows more subtle variation within the unit. The thickness of the middle unit is 5.7 meters thick (19 feet) based on gamma ray signature. The base of the middle unit is marked by a thinly blocky bed with vertical and horizontal fractures. The coloration between the weathered and the fresh surface is marked by subtle differences. The weathered surface is dark grey to black in color while the fresh surface is mostly black with some brown stains. The brown coloration is a result of the oxidation of pyrite in the unit.

4.3.3 Lower Unit

The lower unit is the thinnest part of the Chattanooga Shale in No Hollow Head. The total thickness of the unit is 1.5 meters thick (5 feet) and characterized predominantly by fissile and weathered shale. The lower unit contains vertical fractures that make it easily split upon contact. The lower unit is characterized with some silt size particles that are only evident upon very close observation of the outcrop.

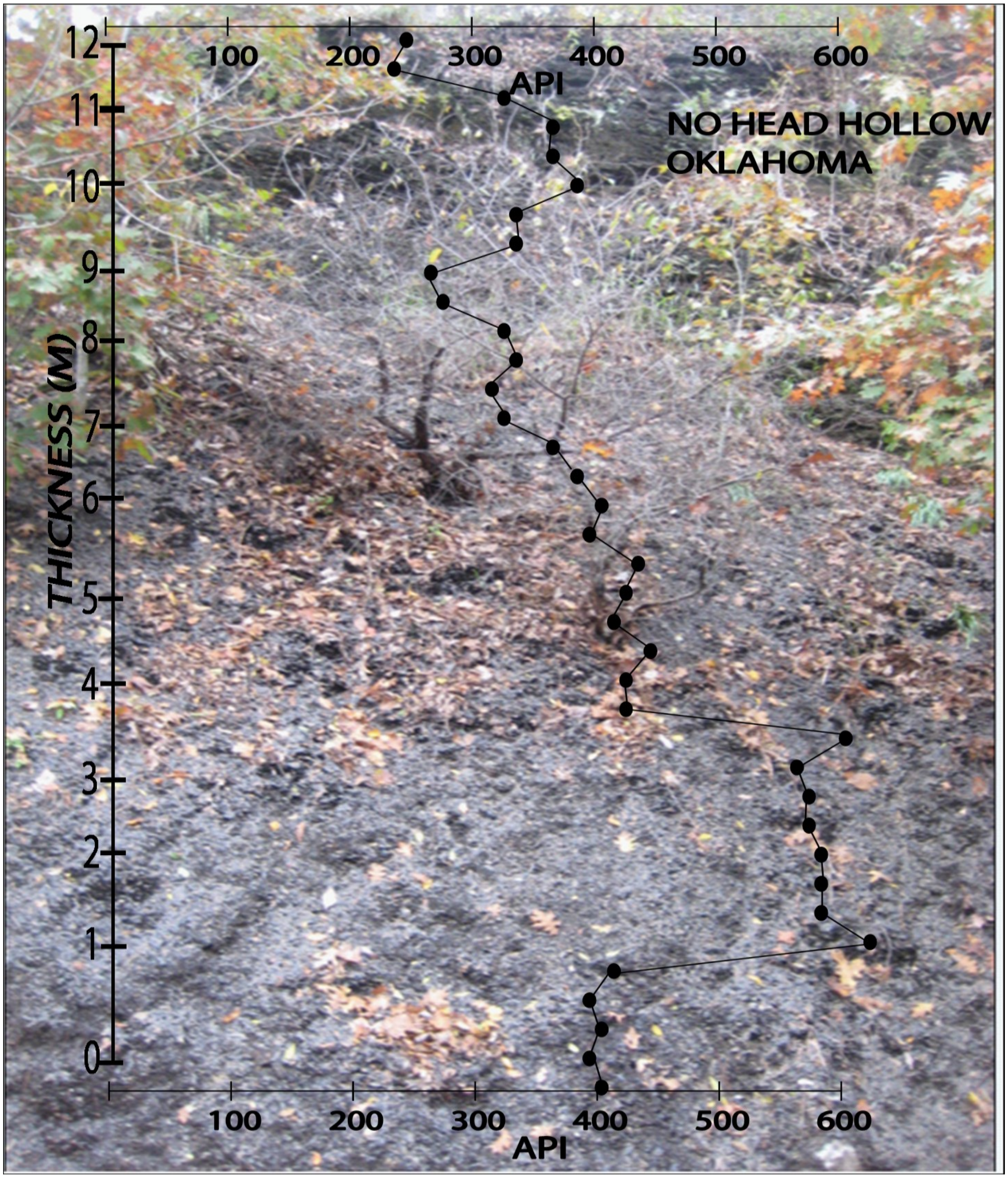

Figure 21: Photograph of the Chattanooga Shale at No Head Hollow Oklahoma showing the Upper and middle and lower units of the Chattanooga Shale.

4.3.4 Fite Limestone

The Fite Formation is a dolomitic limestone with dark gray coloration. It is the oldest formation in the outcrop and absent in Jane and Bella Vista. The Limestone is not as vuggy as the Fernvale Limestone (Hurst, 2008).

4.3.5 Fernvale Limestone

The Fernvale Formation in No Hollow Head is a massive light to dark gray limestone bed. The limestone appeared to have been deeply buried in the northern side of the outcrop as it was only exposed in close proximity to the river channel that flows through the back of the outcrop. The limestone consists of some visible fossils shells such as crinoids.

4.3.6 Bachelor Shale

The thickness of the Bachelor Shale here is thin as it measures 0.2 meters (8 inches) in thickness. The shale is very soft and greenish in color. It can easily be mold into any shape when adequately wet.

4.3.7 Compton Limestone

The average thickness of the Compton Limestone is over 2.1 meters thick (7 feet) and conformably overlies the Bachelor Shale. The Compton limestone is dark gray in color. The formation is devoid of pyrite unlike the outcrop at Jane and appears grain supported texturally.

4.3.8 Total Organic Carbon

The Chattanooga Shale in the No Head Hollow, Oklahoma is organically rich black shale with a total organic carbon content ranging between 3.6 and 6.1 wt% (table, 6) (fig. 22). The overall organic richness of the shale is similar to other known Devonian Mississippian black shales in United State (table, 7). The upper unit has values TOC ranging between 4.1 and 6.1 wt%. The mean value of the upper unit was calculated at 4.7 wt %. The middle unit, which is the thickest section of the three units, has TOC values ranging from 3.7 to 5.7 wt% with a mean value of 4.1 wt%. The lower unit is the thinnest unit and consists of TOC values ranging between 5.1 and 5.9 wt %, with mean value of 5.6 wt%. In general, the outcrop consists of organically rich material that is capable of generating hydrocarbons if adequately buried in the subsurface.

4.3.9 Total Gamma Ray Characteristics

The gamma ray characteristics of the Chattanooga Shale at the No Hollow Head were also measured using SAIC GR-320 ENVISPEC spectrometer. A total of 37 measurements were taken vertically across the outcrop at one foot intervals. All the measurements taken at this outcrop were restricted to the Chattanooga Shale alone. The Chattanooga Shale at No Hollow is a “hot” shale as the minimum gamma value was determined to be 234 API (table, 8) (fig. 22). Unlike the Chattanooga Shale in Jane Missouri and Bella Vista Arkansas, the uranium content of the No Hollow Head shale is higher than thorium, thus indicating that the shale was deposited in a deep open marine environment. The Chattanooga shale in No Head Hollow is thought to be a deeper facie of the Chattanooga Shale in the Ozark region. On average, the uranium content values are almost double that of the thorium for all measurements taken. The value of the uranium ranges from 13.9 to 59.2 ppm while that of thorium ranges from 11.3 to 18.0 ppm. The concentration of potassium ranges from 3.8 to 5.8 % while the total gamma value ranges from 391 to 414 API.

4.3.10 Relationship between TOC and Total gamma ray values

The relationship between TOC and total gamma ray values of the Chattanooga Shale in No Head Hollow support the hypothesis that an increase in gamma values signifies a corresponding increase in total organic carbon values (fig. 22). The average gamma value across the outcrop is 400 API while the average value of total organic value is 5 wt%. The gamma value across the outcrop signifies that the shale reaches a maximum value of over 600 API at the base of the middle unit (fig. 22).

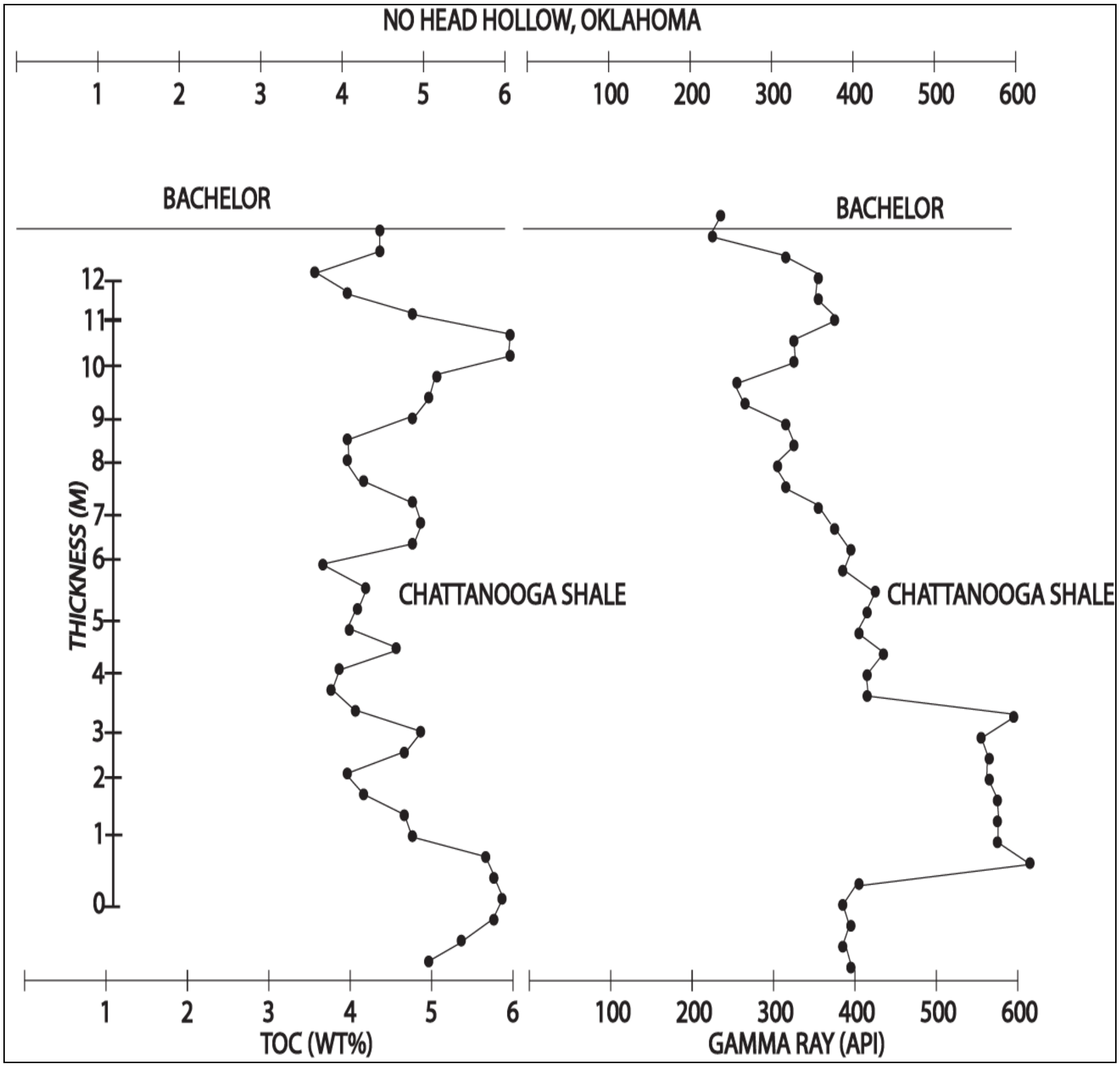

Figure 22: Graph showing the relationship between the gamma ray intensities and total organic carbon content of the Chattanooga Shale in No Head Hollow Oklahoma.

SAMPLE #	Total carbon (wt %)	Total inorganic (wt %)	Total organic carbon (wt %)
NH0 1	4.5	0	4.5
NH0 2	4.5	0	4.5
NH0 3	3.6	0	3.6
NH0 4	4.0	0	4.0
NH0 5	4.9	0	4.9
NH0 6	6.1	0	6.1
NH0 7	6.0	0	6.0
NH0 8	5.1	0	5.1
NH0 9	5.1	0	5.1
NH0 10	4.8	0	4.8
NH0 11	4.1	0	4.1
NH0 12	4.1	0	4.1
NH0 13	4.2	0	4.2
NH0 14	4.8	0	4.8
NH0 15	4.9	0	4.9
NH0 16	4.8	0	4.8
NH0 17	3.7	0	3.7
NH0 18	4.2	0	4.2
NH0 19	4.2	0	4.2
NH0 20	4.1	0	4.1
NH0 21	4.1	0	4.1
NH0 22	4.6	0	4.6
NH0 23	3.9	0	3.9
NH0 24	3.8	0	3.8
NH0 25	4.1	0	4.1
NH0 26	4.9	0	4.9
NH0 27	4.7	0	4.7
NH0 28	4.1	0	4.1
NH0 29	4.2	0	4.2
NH0 30	4.8	0	4.8
NH0 31	4.8	0	4.8
NH0 32	5.7	0	5.7
NH0 33	5.8	0	5.8
NH0 34	5.9	0	5.9
NH0 35	5.8	0	5.8
NH0 36	5.4	0	5.4
NH0 37	5.1	0	5.1

Table 6: Table showing the total organic carbon concentration of the Chattanooga Shale in No Head Hollow Oklahoma.

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	6	2.1-8	1-2
GIP, BCF/Section	20-50	40-120	150-250	70-150	25-65	70-90
Average TOC, wt%	3.5-8.1	3.1-10	3.1-5	2.1-10	4.0-9.5	4.48

Table 7: Table showing the total organic carbon concentration of some selected black shales in North America. (Data Source: Deutsche Bank/XTO Energy)

SAMPLE #	Th (ppm)	U (ppm)	K (%)	Total GAMMA (API)
NH0 1	13.1	13.4	4.7	234.8
NH0 2	11.6	23.2	5.2	315.2
NH0 3	14.3	29.1	4.4	360.4
NH0 4	13.2	28.5	5.1	362.4
NH0 5	15	30	5.1	381.6
NH0 6	13	24.9	5	331.2
NH0 7	13	25.6	4.3	325.6
NH0 8	11.6	19.1	4.1	264.8
NH0 9	11.3	19.3	4.6	273.2
NH0 10	13.6	20.8	5.9	315.2
NH0 11	13.3	25.1	4.7	329.2
NH0 12	13.1	23.1	4.7	312.4
NH0 13	11.6	23.2	5.2	315.2
NH0 14	12.8	29.1	4.6	357.6
NH0 15	13.7	30.3	4.7	372.4
NH0 16	13.9	31.6	5.7	399.6
NH0 17	14.1	30.8	5.1	384.4
NH0 18	14.1	29.9	5.9	390
NH0 19	14.1	34.8	5.8	427.6
NH0 20	14.1	34.8	5.6	424.4
NH0 21	14.5	34.2	5.1	413.2
NH0 22	14.7	36.7	5.2	435.6
NH0 23	14.1	36.8	5.6	440.4
NH0 24	11.3	37.2	4.6	416.4
NH0 25	15.4	56	5.5	597.6
NH0 26	15.6	50.6	5.6	556.8
NH0 27	15.8	51.2	5.8	565.6
NH0 28	16.8	51.6	5.4	566.4
NH0 29	17.9	52.5	5.8	584.4
NH0 30	18	50.9	6.3	580
NH0 31	14.6	52.1	6.3	576
NH0 32	14.6	59.2	5.8	624.8
NH0 33	14.3	34.2	5.2	414
NH0 34	14.5	30.1	6	394.8
NH0 35	14.1	31.9	5.8	404.4
NH0 36	13.1	34.8	3.8	391.6
NH0 37	12.9	35.3	4.4	404.4

Table 8: Table showing the total gamma ray intensities of the Chattanooga Shale in No Head Hollow Oklahoma. Note: The value of uranium is higher than that of thorium.

Eagles Bluff

The Eagles Bluff Shale is located opposite the Illinois River. Unlike other outcrops that were explored for this project, the Eagles Bluff Shale is composed of the complete section of the Chattanooga Shale because of the exposure of the underlying unit. The Chattanooga Shale which is the major concern of this project was measured to be 9.1 meters thick (30 feet). Apart from the Chattanooga Shale, other formations present at this location include; the Sylamore, Compton, Northview, and Pierson (Fig. 23). The lithology of the Sylamore Sandstone includes a dark grey medium to fine grained sandstone. The thickness of the Sylamore Sandstone could not be easily determined as it has been buried by sediments that were eroded from the upper units. Evidence from the exposed 1.2 meters (4 feet) of the Sylamore sandstone indicates that it is fine grained in texture and tan in coloration. The Chattanooga Shale at this location looks uniform upon first examination, however critical examination and digging shows some variations within the shale (Fig. 24). The Chattanooga Shale could only be divided into three units based on the gamma ray survey as individuals units could not be easily identified by visual observation unlike the Jane Missouri outcrop. The Bachelor Shale is not exposed at this location, rather the Compton Limestone rest unconformably on the Chattanooga Shale. The Compton Limestone is light yellowish grey in color. The Northview is light grey to tan siltstone. The Northview could not be examined in detail as it is not easily accessible. The Pierson is a massive light grayish limestone with some vugs. The Pierson was also not accessible. The characteristic of individual unit within the Chattanooga Shale is described as follows.

4.3.11 Lower Unit

The lower unit was measured to be (2.7 meters thick) 9 feet based on the gamma ray signature. The unit is a massive black fissile shale with little evidence of iron oxidation. The shale is very brittle as it breaks easily along the bedding planes (Fig. 24). The unit is the hottest and most organically rich of the three units within the Chattanooga Shale in Eagles Bluff. The gamma values range from 364 to 632 API (table, 9). The uranium content of the shale indicates that the shale was deposited in an open marine environment. This is because the ratio of uranium is higher than that of thorium. The value of uranium ranges from 27.6 to 59.2 ppm with average value of 42.8 ppm. The concentration of thorium ranges from 9.8 to 16.8 ppm with average value of 12.9 ppm. The organic content of the shale indicates that it is organically rich shale. The total organic carbon content of the shale ranges from 4.2 to 7.0 wt% with an average value of 5.2 wt %. The highest gamma value of 632 API correspond to the second highest value of the total organic concentration, which is 6.9 wt%.

4.3.12 Middle Unit

The Middle unit is the thickest part of the unit with a thickness of 3.3 meters thick (11 feet) (Fig. 24). The TOC values indicate that the middle unit is less rich organically when compared to the upper and lower unit (Fig. 25) (table 10). The middle unit is cut by several vertical fractures. The middle unit is black in coloration and contains many platy to fissile shale beds. The shale is equally brittle as it breaks easily into paper like forms when pressure is applied. The unit is oxidized as some brown stains were observed within the unit, however it is not as oxidized at the upper and lower layer. The gamma value of the shale ranges from 248 to 362 API with an average mean value of 316 API. The uranium content of the shale is also higher than the value of the thorium. The value of the uranium ranges from 16.5 to 30.1 ppm with average value of 23.7 ppm; while that of thorium ranges from 9.9 to 15.2 ppm with average value of 12.9 ppm.

4.3.13 Upper Unit

The upper unit is overlain unconformably by Compton Formation. The thickness of the unit is 3.0 meters (10 feet) and is composed of black massive shale with intercalations of fissile beds and very thin lenses of blocky shale. The unit is characterized by vertical fractures that allow the separation of the shale into small numerous blocks. The weathered sample of the unit is platy and dark grey to black in color; while the unweathered rock is dark grey in color. The gamma ray values of the units range from 221 to 291 API with mean values of 262.4 API. The intensity of uranium ranges from 13.2 to 21.7 ppm with an average value of 19.2 ppm. Thorium ranges 7.4 to 12.8 ppm with average value of 10.3 ppm. The unit also contains some brown coloration indicating iron oxidation.

4.3.14 Relationship between total gamma value and TOC

The relationship between the total gamma value and total organic carbon content of the Chattanooga Shale in Eagles Bluff support the observation that an increase in gamma ray value correlates to a corresponding increase in the value of the total organic carbon (Fig. 27) (tables 9 &10). The total gamma content in this location increases with the total organic carbon content (fig. 25).

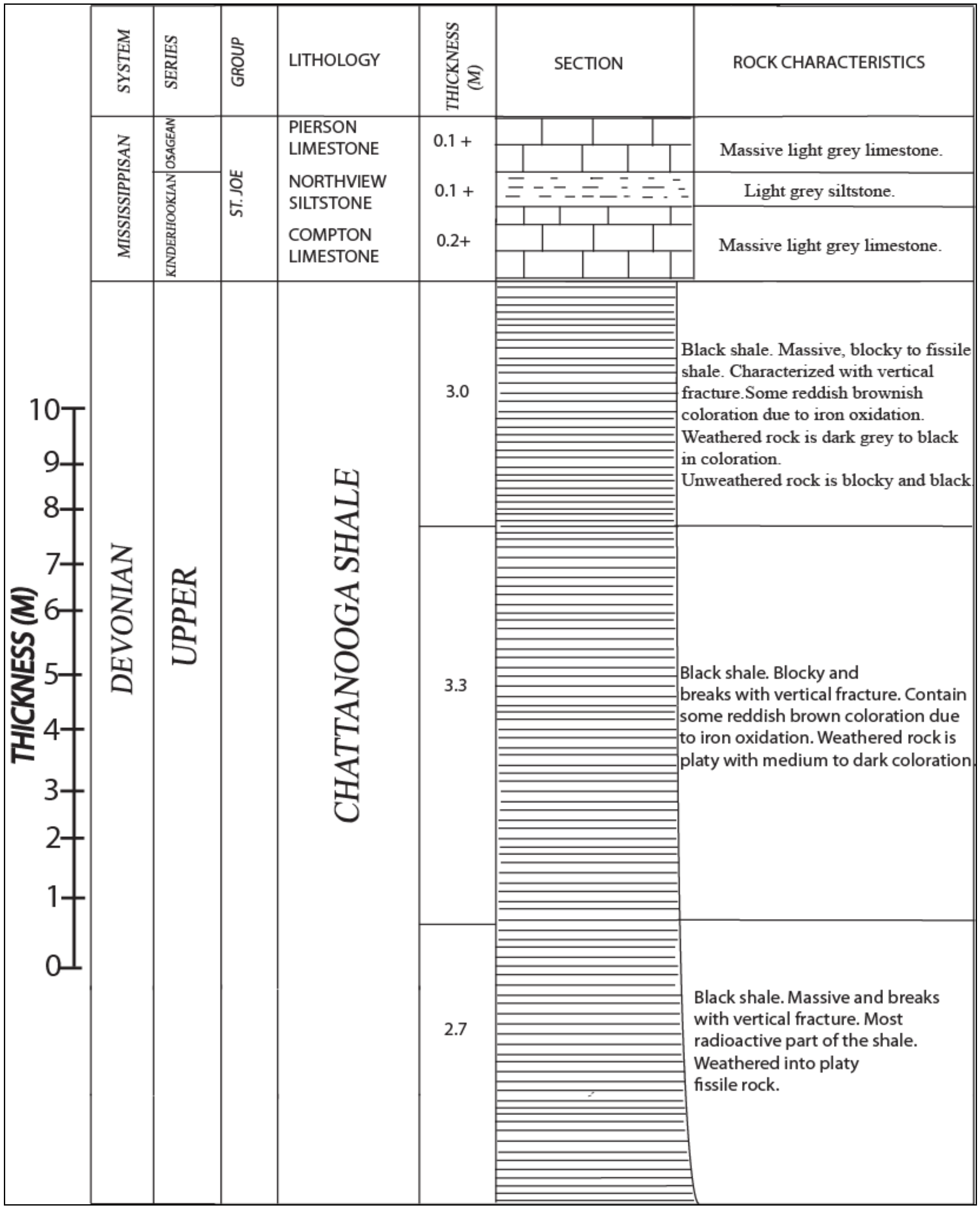

Figure 23: Stratigraphic section of the Chattanooga Shale at Eagles Bluff near Tahlequah Oklahoma.

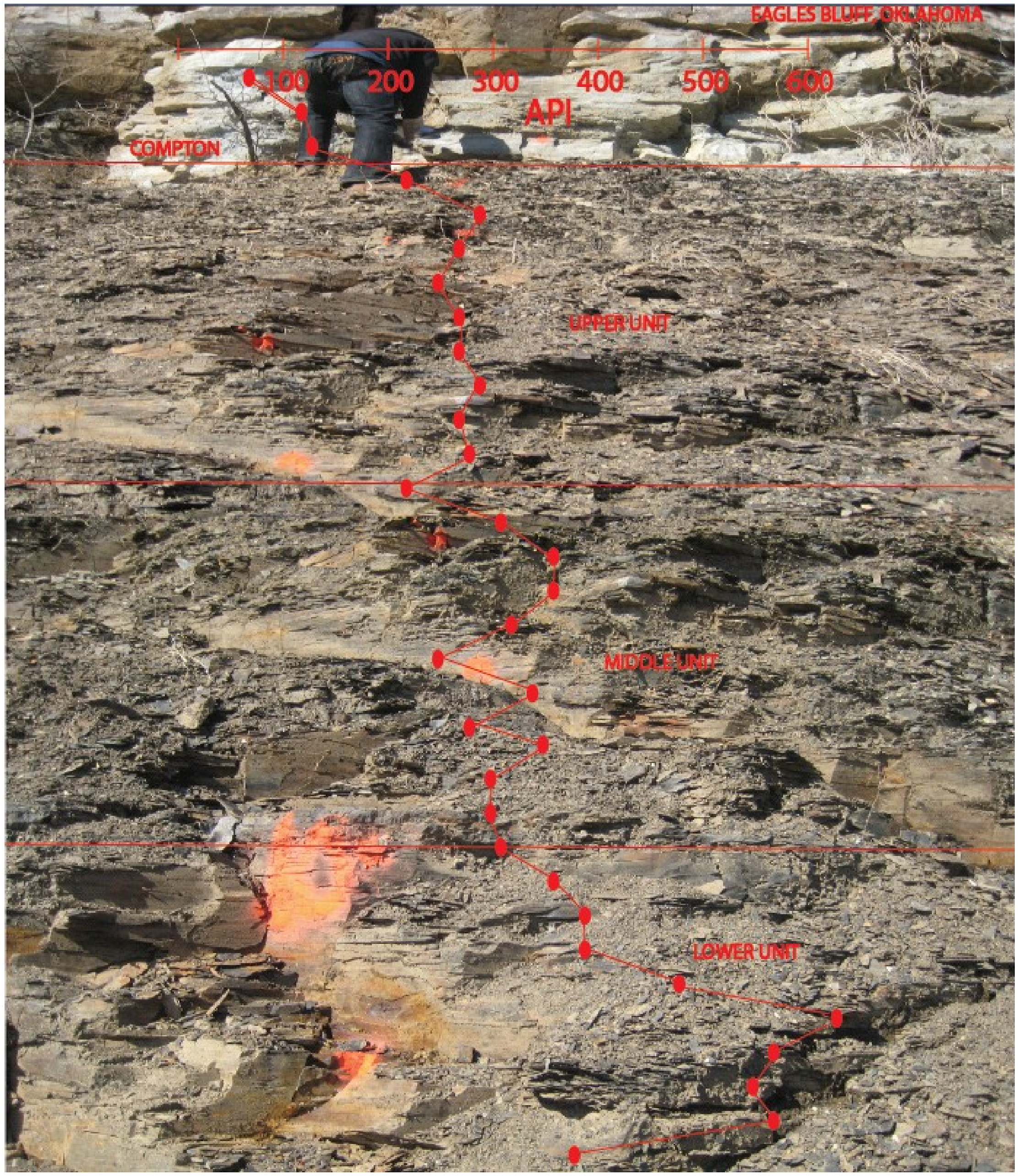

Figure 24: Photographic image of the Chattanooga Shale at Eagles Bluff Oklahoma. Note the intercalations of thin fissile beds and the blocky beds

SAMPLE #	Th (ppm)	U (ppm)	K (%)	Total GAMMA (API)
EB 1	11.2	13.2	4.5	222.4
EB 2	10.7	21.7	4.5	288.4
EB 3	11	18.8	4.6	268
EB 4	7.9	19.1	4	248.4
EB 5	12.8	18.8	4.4	272
EB 6	11.2	20.5	3.6	266.4
EB 7	11.8	21.5	4.5	291.2
EB 8	8.8	20.9	4.1	268
EB 9	10.4	20.4	4.6	278.4
EB 10	7.4	17.4	3.3	221.6
EB 11	9.9	25.7	4.2	312.4
EB 12	12.3	30.1	4.5	362
EB 13	13	28.4	4.9	357.6
EB 14	14.4	23.6	4.8	323.2
EB 15	12.6	16.5	4.1	248
EB 16	15.2	24.3	5.4	341.6
EB 17	12.8	20.2	4.1	278.4
EB 18	17.5	24.1	5.3	347.6
EB 19	10.8	23.5	4.6	304.8
EB 20	11.6	22.4	4.9	304
EB 21	11.8	23.1	4.9	310.4
EB 22	14.4	27.6	5.4	364.8
EB 23	12.1	30.5	5.9	386.8
EB 24	9.8	32.3	5.6	387.2
EB 25	11.7	43	5.6	480.4
EB 26	14.6	59.2	6.3	632.8
EB 27	11.3	56	4.6	566.8
EB 28	15.4	50.6	5.1	548
EB 29	16.8	52.5	5.4	573.6
EB 30	10.3	33.9	4.3	381.2

Table 9: Table showing the gamma ray intensities of the Chattanooga Shale in Eagles Bluff Oklahoma. Note the enrichment of uranium.

SAMPLE #	Total carbon (wt %)	Total inorganic (wt %)	Total organic carbon (wt %)
EB 1	4.1	0	4.1
EB 2	4.8	0	4.8
EB 3	3.9	0	3.9
EB 4	4.4	0	4.4
EB 5	4.5	0	4.5
EB 6	4.7	0	4.7
EB 7	4.0	0	4.0
EB 8	4.3	0	4.3
EB 9	4.4	0	4.4
EB 10	4.8	0	4.8
EB 11	4.9	0	4.9
EB 12	5.1	0	5.1
EB 13	4.5	0	4.5
EB 14	4.4	0	4.4
EB 15	4.2	0	4.2
EB 16	4.4	0	4.4
EB 17	4.4	0	4.4
EB 18	4.4	0	4.4
EB 19	4.2	0	4.2
EB 20	4.6	0	4.6
EB 21	4.6	0	4.6
EB 22	4.6	0	4.6
EB 23	4.5	0	4.5
EB 24	4.2	0	4.2
EB 25	4.5	0	4.5
EB 26	5.0	0	5.0
EB 27	6.8	0	6.8
EB 28	7.0	0	7.0
EB 29	5.0	0	5.0
EB 30	6.0	0	6.0

Table 10: Table showing the total organic carbon content of the Chattanooga Shale in Eagles Bluff Oklahoma.

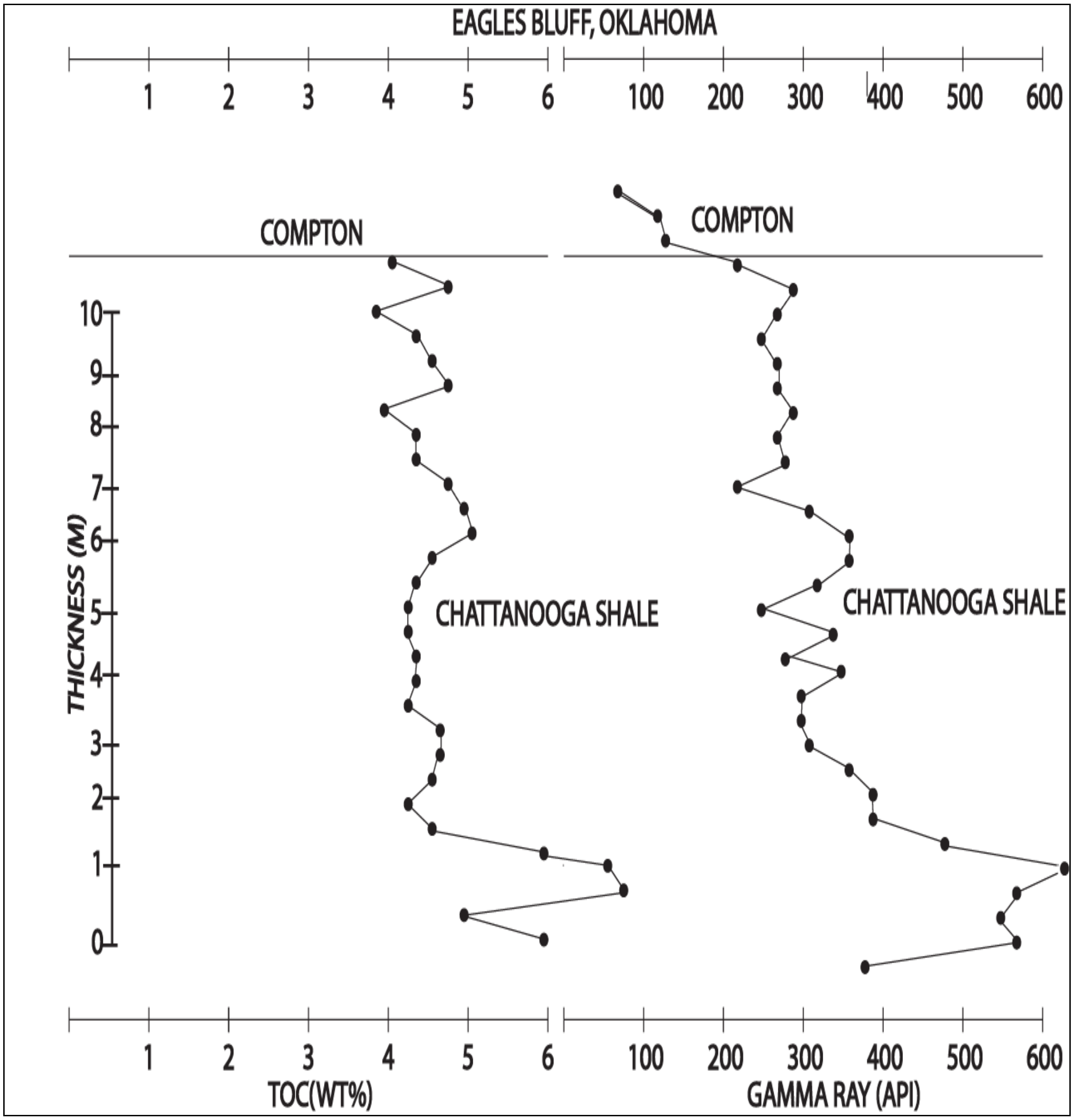

Figure 25: Graph showing the relationship between the gamma ray intensities and total organic carbon content of the Chattanooga Shale at Eagles Bluff Oklahoma.

4.4 Hanging Wall Rock, Oklahoma

The name Hanging Wall Rock was adopted for this outcrop because of the orientation of the outcrop (Fig. 26). The total thickness of the Chattanooga Formation at this location is 3.9 meters thick (13 feet) and contains lithologies of different ages (Fig. 27). The Chattanooga Shale is 3.9 meters (13 feet) and mostly blocky with little evidence of fissility. Unlike other Chattanooga Shale examined, the Hanging Wall Rock Chattanooga Shale is hard and shows very little effects from weathering. The shale was divided into three units based on gamma ray signature. The gamma ray value in the lower unit ranges from 323 to 566 API with an average value of 438 API (table, 11). The higher uranium content of the shale provides ample to opportunity to understand the position of the shale within the basin. The shale is thought to have been developed in an open marine environment under anoxic conditions. The shale is enriched in organic matter with total organic carbon concentration that ranges from 3.1 to 4.4 wt% (table, 12). The Bachelor Shale is 7 inches in thickness and overlies the Chattanooga Shale. Just like other Bachelor Shales examined, the Bachelor Shale at Hanging Wall Rock is characterized with green soft shale that is capable of been mold into any desired structure when wet. Above the Bachelor Shale lies the light to dark grey Compton. The lithology of the Compton is limestone, and consists of fractures. The Compton is overlained by the Northview, Pierson and Red Springs Formations. The division of the Chattanooga Shale based on gamma ray characteristics is described as follows.

4.4.1 Lower Unit

The lower unit was measured to be 1.5 meters thick (5 feet) (fig. 27). The lower unit is characterized with vertical fractures. The gamma ray values in the lower unit ranges from 322 to 533 API with a mean value of 432 API. The value of the uranium is higher than that of thorium indicating that the shale was deposited in a marine environment probably under anoxic condition. The value of the uranium ranges from 22.5 to 51.2 ppm while that of thorium ranges from 9.8 to 14.2 ppm with an average value of 11.9 ppm.

4.4.2 Middle Unit

The middle unit is the thinnest of the three units with thickness of 0.9 meters thick (3 feet). The middle unit is black in color with some brownish like stains as a result of iron oxidation. The unit is massive and could only be distinguished from the upper and lower unit by its gamma ray response. It contains hard blocky and some fissile shale interbeds. The total gamma value of the unit ranges from 488 to 566 API with mean value of 515 API. Also, the value of uranium is greater than that of the thorium indicating that the unit underwent the same type of depositional process as the lower unit. The uranium content ranges from 42.1 to 56 ppm with an average value of 43 ppm while that of thorium ranges from 11.3 to 15.6 ppm with an average value of 14.1 ppm.

4.4.3 Upper Unit

The thickness of the upper unit is the same as the lower unit where 5 feet was measured based on the gamma ray response. The TOC content and gamma ray value of this unit is very similar to the lower layer. It consists of black massive to fissile shale that breaks easily into thin plates of shale. The shale is brittle and contains numerous fractures. The unit consists of high gamma values that range from 323 to 443 API with a mean value of 397 API. The uranium content ranges from 23.6 to 37.2 ppm with an average value of 33 ppm while that of the thorium ranges from 14.1 to 14.7 ppm. The unit is also organically rich and consists of total organic carbon values ranging from 3.5 to 4.1 wt%.

4.4.4 Relationship between total gamma value and total organic carbon

The relationship between the total gamma value and the total organic carbon content of the Chattanooga Shale at Hanging Wall Rock indicates that an increase in gamma ray concentration results in an increase in total organic carbon concentration (fig. 28). The high uranium content in the Chattanooga Shale at this location indicates that it was deposited in a marine environment. The high total gamma content also signifies that the shale was deposited under anoxic conditions.

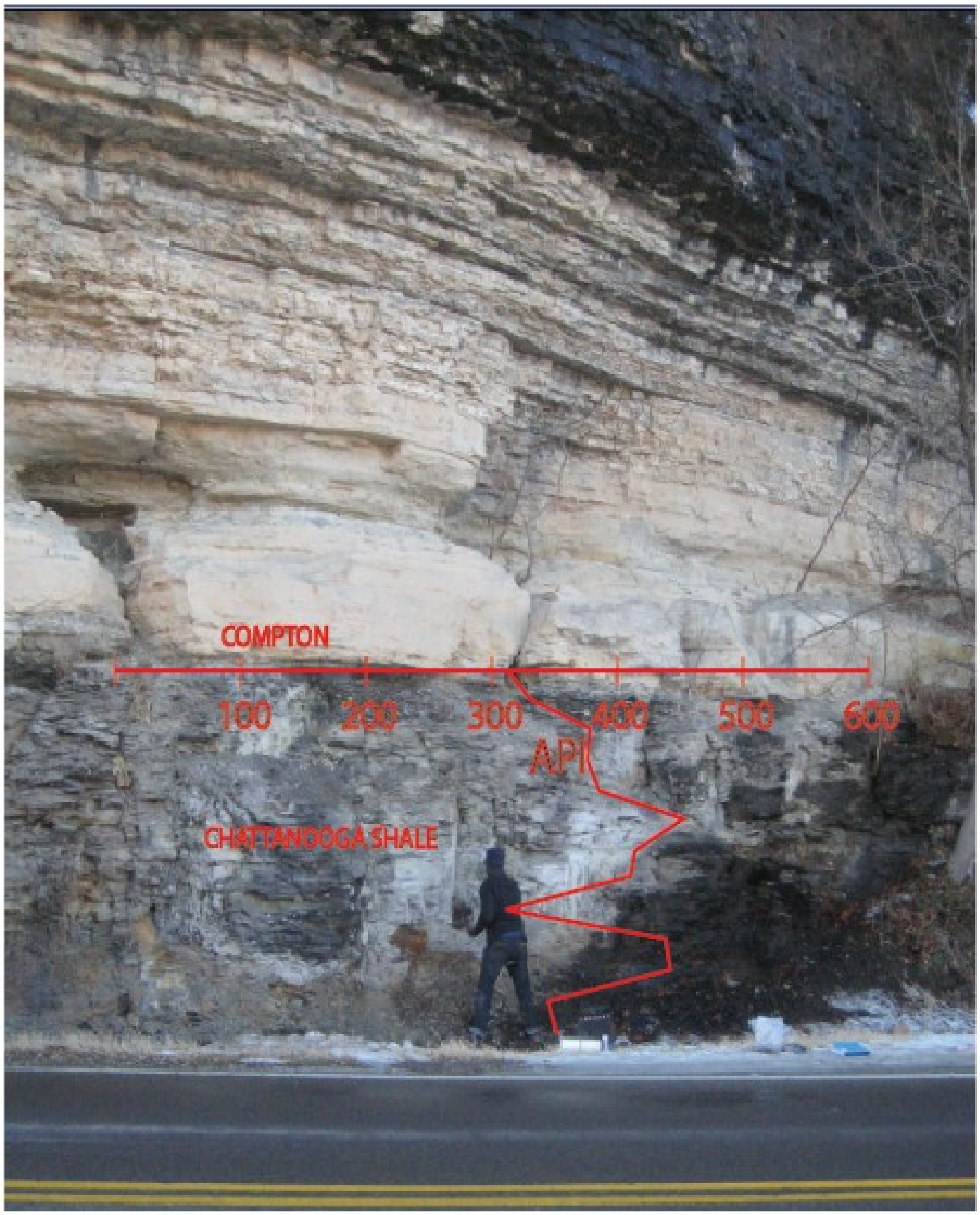

Figure 26: Photographic image of the Chattanooga Shale in Hanging Rock Oklahoma.

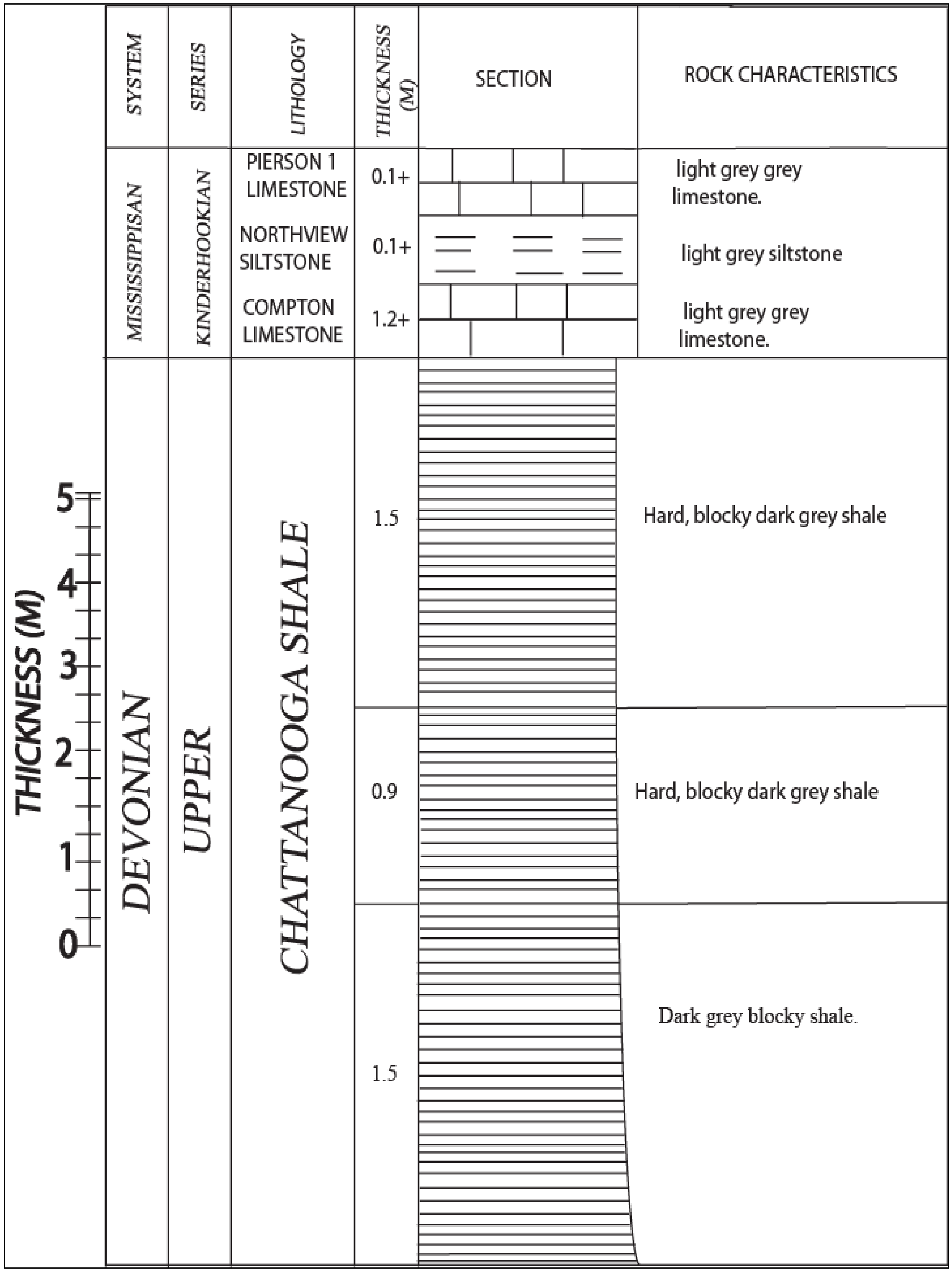

Figure 27: Stratigraphic section of the Chattanooga Shale at Hanging Rock, near Tahlequah Oklahoma.

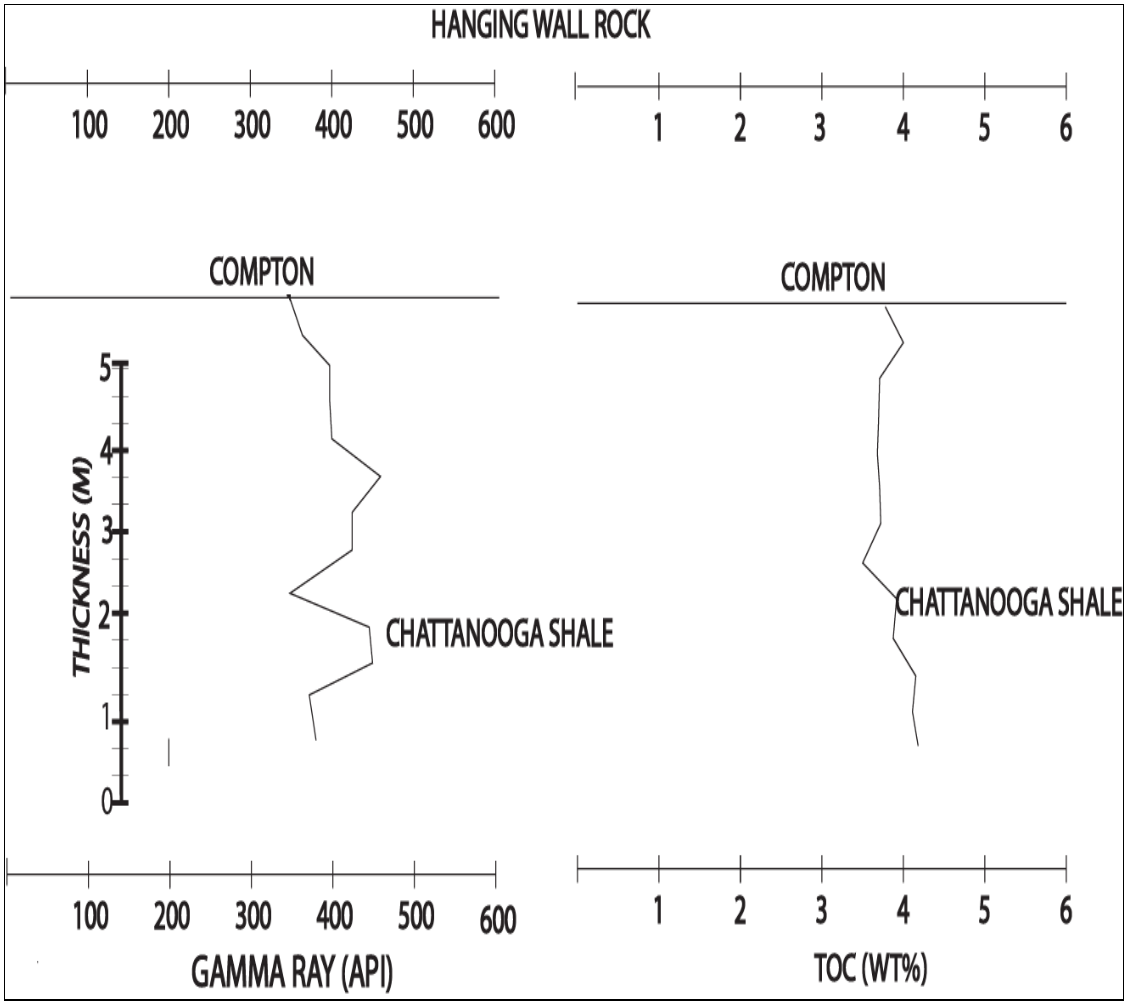

Figure 28: Graph showing the relationship between the gamma ray intensities and total organic carbon content of the Chattanooga Shale at Hanging Wall Rock, near Tahlequah Oklahoma.

SAMPLE #	Th (ppm)	U (ppm)	K (%)	Total GAMMA (API)
HRC 1	14.4	23.6	4.8	323.2
HRC 2	12.6	29.6	4.1	352.8
HRC 3	14.5	36.7	5.1	433.2
HRC 4	14.7	36.8	5.2	436.4
HRC 5	14.1	37.2	5.6	443.6
HRC 6	11.3	56.0	4.6	566.8
HRC 7	15.4	43.0	5.5	493.6
HRC 8	15.6	42.1	5.6	488.8
HRC 9	12.1	22.5	5.9	322.8
HRC 10	9.8	50.6	5.6	533.6
HRC 11	11.7	51.2	5.6	546.0
HRC 12	11.8	30.5	5.1	372.8
HRC 13	14.2	32.3	4.6	388.8

Table 11: Table showing the concentration of the total gamma intensities in the Chattanooga Shale at Hanging Wall Rock near Tahlequah Oklahoma.

SAMPLE #	Total carbon (WT %)	Total inorganic (wt %)	Total organic carbon (wt %)
HRC 1	3.7	0	3.7
HRC 2	4.1	0	4.1
HRC 3	3.6	0	3.6
HRC 4	3.5	0	3.5
HRC 5	3.5	0	3.5
HRC 6	3.6	0	3.6
HRC 7	3.6	0	3.6
HRC 8	3.1	0	3.1
HRC 9	3.9	0	3.9
HRC 10	3.9	0	3.9
HRC 11	4.4	0	4.4
HRC 12	4.4	0	4.4
HRC 13	4.4	0	4.4

Table 12: Table showing the concentration of the total organic carbon in the Chattanooga Shale at Hanging Wall Rock near Tahlequah Oklahoma.

4.5 Gamma ray and TOC correlation

The relationship between the total gamma ray intensities and the total organic carbon content of the examined outcrops have helped in supporting the hypothesis that close relationship exists between the gamma ray and TOC. Apart from this fact, results from this correlation gave insight about the position of each outcrop in the basin (Figs.29 & 30). The results showed that the Chattanooga Shales in Oklahoma are richer in uranium than their counterparts in Missouri and Arkansas that were noted for their enrichment in thorium. Also, the total organic carbon of the Chattanooga Shale outcrops in Oklahoma is higher than the outcrops in Missouri and Arkansas. These factors suggested that the Chattanooga Shales in Oklahoma are distal facies deposited in a moderately deep open marine environment under anoxic conditions. The outcrops in Missouri and Arkansas are thought to be shallow water facies deposited on the high shelf and are influenced by periodic oxic conditions. The correlation of the gamma ray values showed greater increase to the south where gamma ray values of over 600 API were recorded in the Eagles Bluff outcrop (fig. 29). The TOC values also increased to the south where an average value of 5% by weight was recorded (fig. 30).

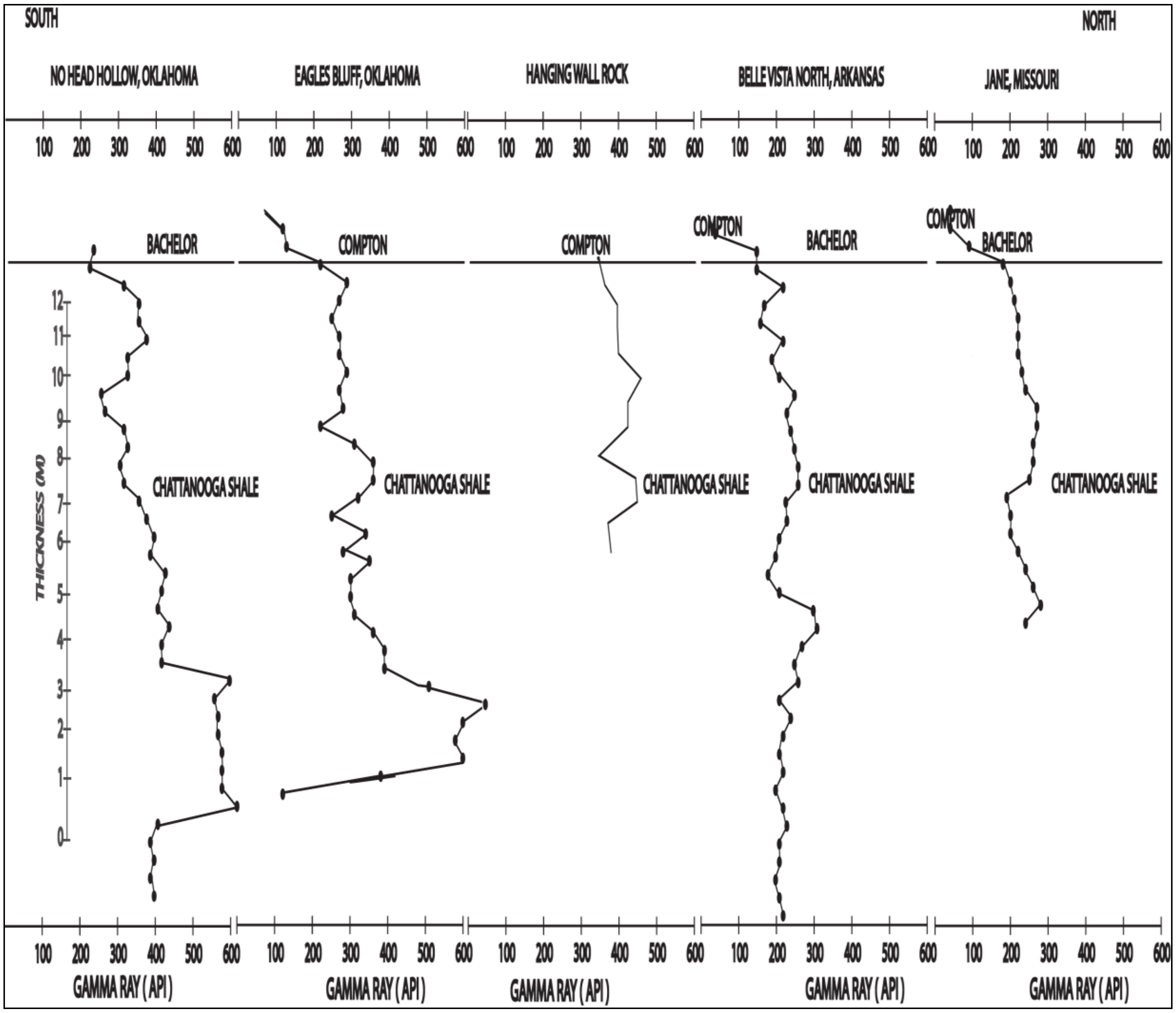

Figure 29: Cross section showing gamma ray intensity of the Chattanooga Shale in the study area.

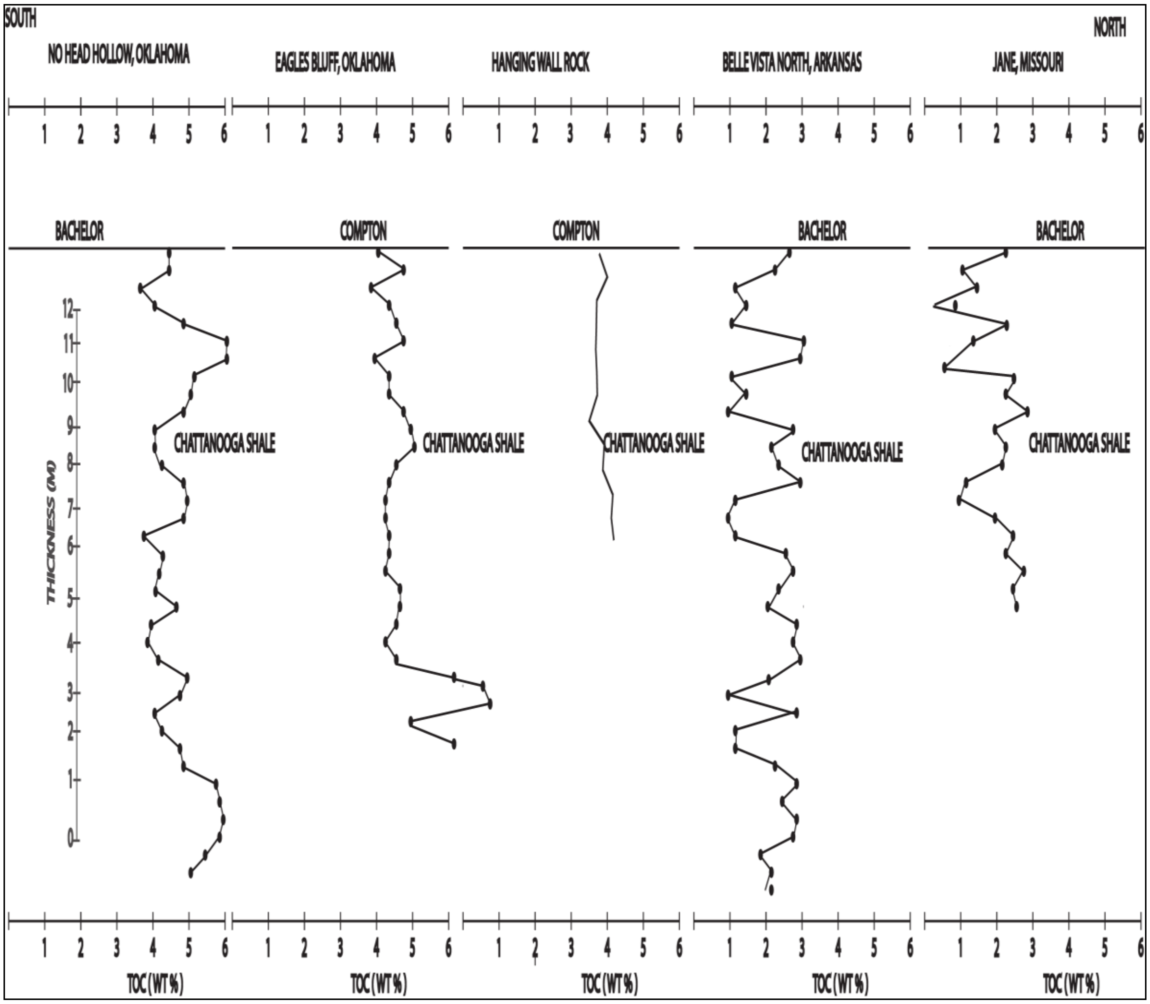

Figure 30: Cross section showing the total organic carbon concentration of the Chattanooga Shale in the study area.

4.6 Clay Mineralogy

The clay composition of the Chattanooga Shale is dominated mostly by illite and some traces of quartz and alumina (see appendix). From hydrocarbon point of view, the presence of illite in the Chattanooga Shale is a 'plus' since it doesn't swell like smectite. However, it is going to be a good idea for cores to be taken out of the shale to better understand the composition of the Chattanooga Shale in the subsurface.

CHAPTER V

CONCLUSION

5.0 Summary

There is a close relationship in the organic richness and gamma ray concentration of the Devonian-Mississippian Chattanooga Shale in the study area. In general, the Chattanooga Shale is radioactive ('hot') and organically rich except in a few cases in the Jane, Missouri and Bella Vista, Arkansas outcrops. The organic richness and radioactivity of the Chattanooga Shale varies from one locality to another. For instance, the Chattanooga Shale in Oklahoma is 'hotter', organically richer than the ones in Jane, Missouri and Bella Vista, Arkansas. The Oklahoma Chattanooga Shale is the deep water facies, while the Chattanooga Shale in Jane, Missouri and Bella Vista, Arkansas are the shallow water facies. The Chattanooga Shale was deposited in a shallow to deep water environment. The deposition of the Chattanooga Shale outcrops in Jane, Missouri and Bella Vista Arkansas have been influenced by greater influx of detrital sediments in proximity to a sediment source. The Chattanooga Shale in Hanging Wall Rock, Eagles Bluff and No Head Hollow of Oklahoma were deposited in a relatively deep water environment. Inferences from individual Chattanooga Shale outcrops are summarized below.

1. In Jane, the Chattanooga Shale was divided into three units based on physical appearance and gamma ray concentration. The middle unit is distinguished from

2. both the upper and lower units by reddish coloration due to pyrite oxidation. The Chattanooga Shale was influenced by greater influx of terrestrially derived clastic sediments. This is evident by the dominance of thorium relative to uranium in the results of the gamma ray survey. The relationship between the thorium and uranium content in Jane outcrop indicate that the shale was deposited in close proximity to the source area. The average total gamma ray value across the outcrop ranges from 178 to 273 API with a mean value of 226 API. The total organic carbon concentration of Jane outcrop is the lowest of all the five examined outcrops. The overall average values of the total organic carbon concentration across the outcrop ranges from 0.2 wt% on the minimum and 4.48 wt% on the maximum with a mean value of 1.94 wt%. The total organic carbon concentration of the upper unit ranges from 0.2 wt% to 2.3 wt%. The total organic carbon concentration of the middle unit ranges from 1.8 wt% to 2.7 wt%. The total organic carbon concentration value of the lower unit ranges from 0.8 wt% to 2.6 wt%.
3. The Chattanooga Shale in Bella Vista Arkansas is also characterized by high influx of terrestially derived clastic materials similar to the Jane, Missouri outcrop. This is evident by the high thorium content. The average thorium concentration in Bella Vista almost doubles that of uranium. The mean value of thorium is 18.1 ppm and that of uranium is 9.1 ppm. The shale is characterized by cycles of high and low total organic carbon concentration indicating influxes of non organic material during the deposition. The total organic content of the shale ranges from 0.9 to 3.1 wt%. The Chattanooga Shale in Bella Vista is equally hot

but contains strings of normal shale. In general, the Chattanooga Shale is a 'hot' shale as most of the intervals surveyed have gamma rays values greater than 200 API.

4. The Chattanooga Shale at No Hollow Head, Oklahoma was deposited under a relatively quite condition in a relatively deep marine environment unlike the Jane and Bella Vista outcrops. This is evident by the higher value of the uranium content when compared to that of thorium. The distribution of total organic carbon content varies across the outcrop. The basal part consists of the highest TOC within the shale body with a TOC mean value of 4.2 wt%. The gamma ray value in the basal part ranges from 322 to 533 API with a mean value of 432 API. The gamma ray intensity of the shale is highest at the middle part with gamma ray values ranging from 488 to 566 API with a mean value of 515 API.
5. The Chattanooga Shale at Eagles Bluff Oklahoma is characterized by a higher value of uranium just as the No Hollow Head outcrop. The uranium content of the shale is higher than that of thorium and increases from the top to the base. The shale was deposited in a relatively deep marine environment under anoxic conditions. The entire Chattanooga Shale at Eagles Bluff is radioactive and hence is referred to as a 'hot' shale. The gamma ray and TOC content of the shale increases from top to the bottom. The first 2.7 meters thick from the basal part is the hottest and most organically rich of the Chattanooga Shale. The gamma ray value ranges from 364 to 632 API with a mean value of 480 API. The value of uranium ranges from 27.6 to 59.2 ppm with a mean value of 42.8 ppm. The concentration of thorium ranges from 9.8 to 16.8 ppm with a mean value of 12.9

ppm. The organic content of the shale indicate that it is organically rich shale. The total organic carbon content of the shale ranges from 4.2 to 7.0 wt% with mean value of 5.2 wt %.

6. The Chattanooga Shale at Hanging Wall Rock is hard and shows very little effects from weathering. The uranium content of the shale exceeds the thorium content. The shale was deposited in an open marine environment under anoxic conditions. The shale is enriched in organic matter with TOC values ranging from 3.1 to 4.4 wt%. The gamma ray survey indicated that the shale is radioactive having values ranging from 323.2 to 566.8 API.

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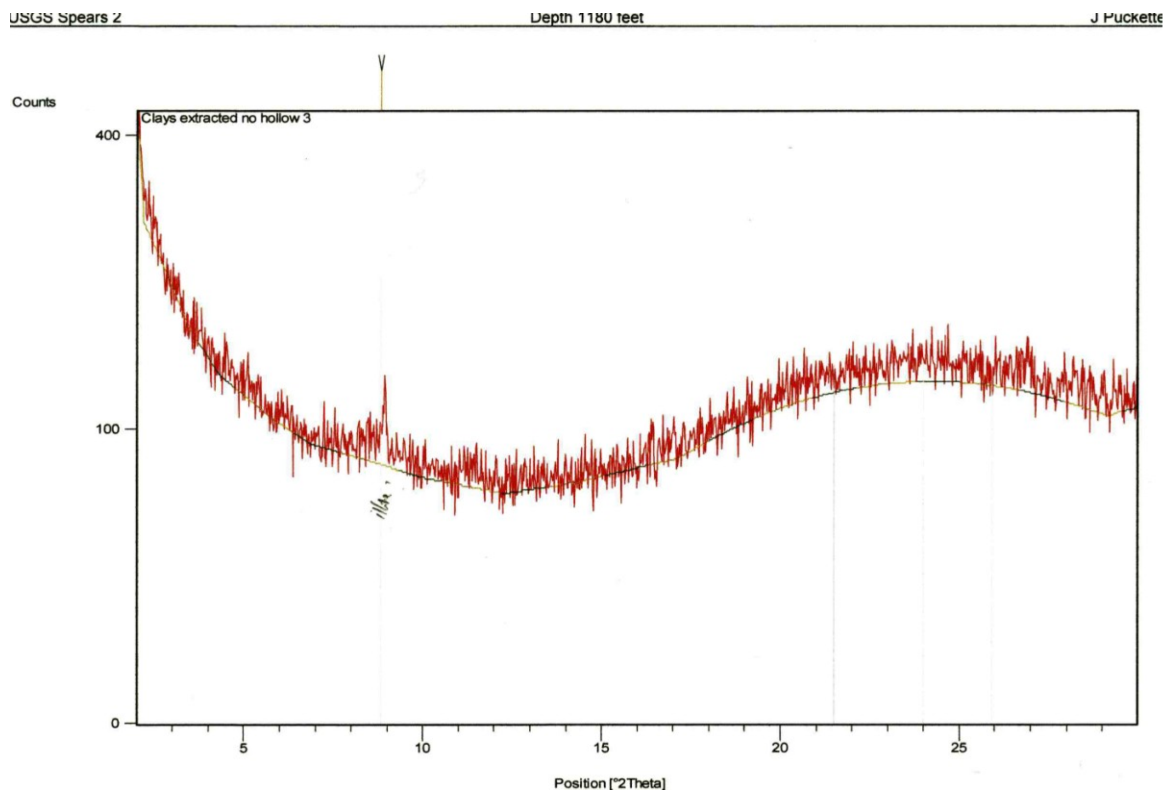
APPENDICES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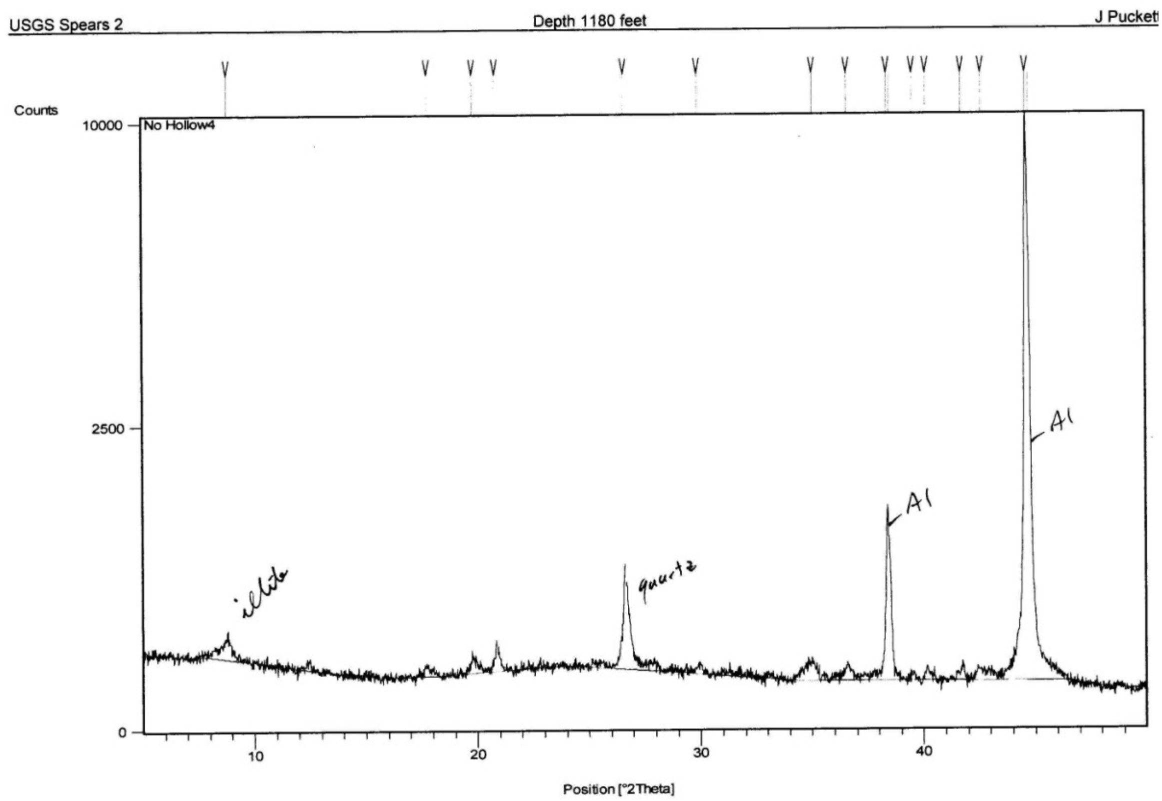
Position [°2Theta]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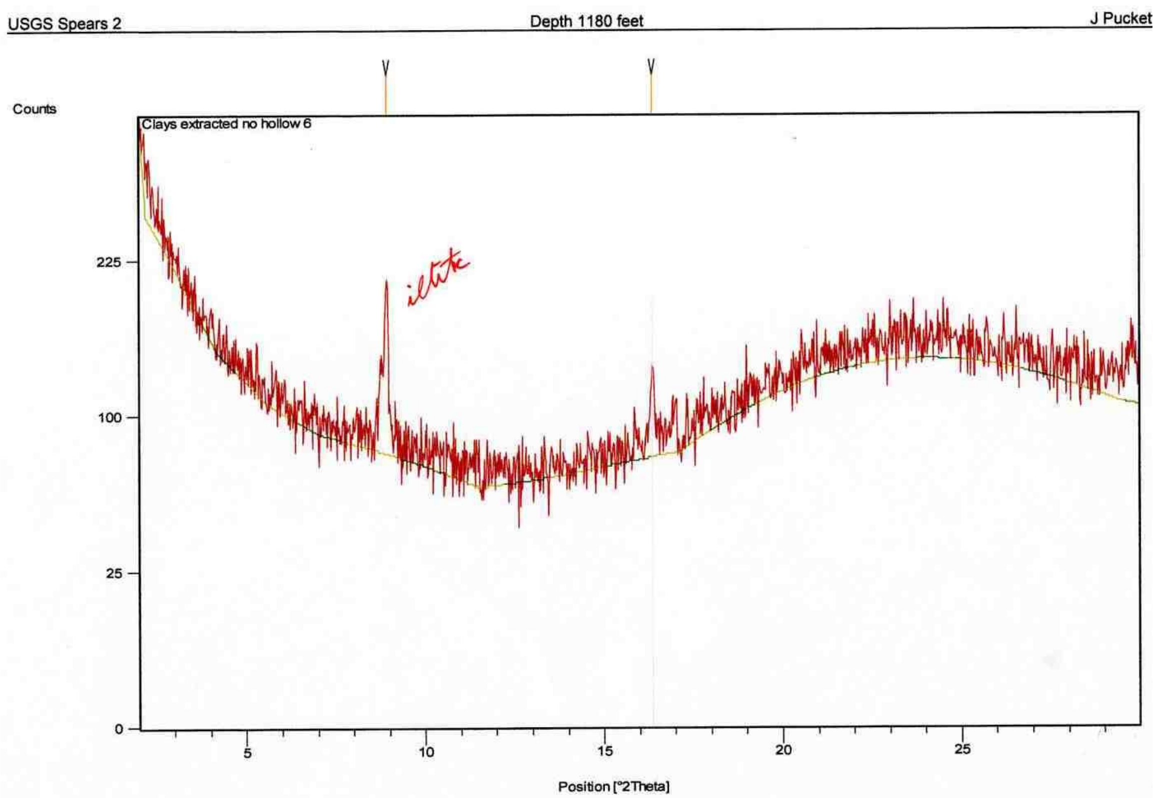

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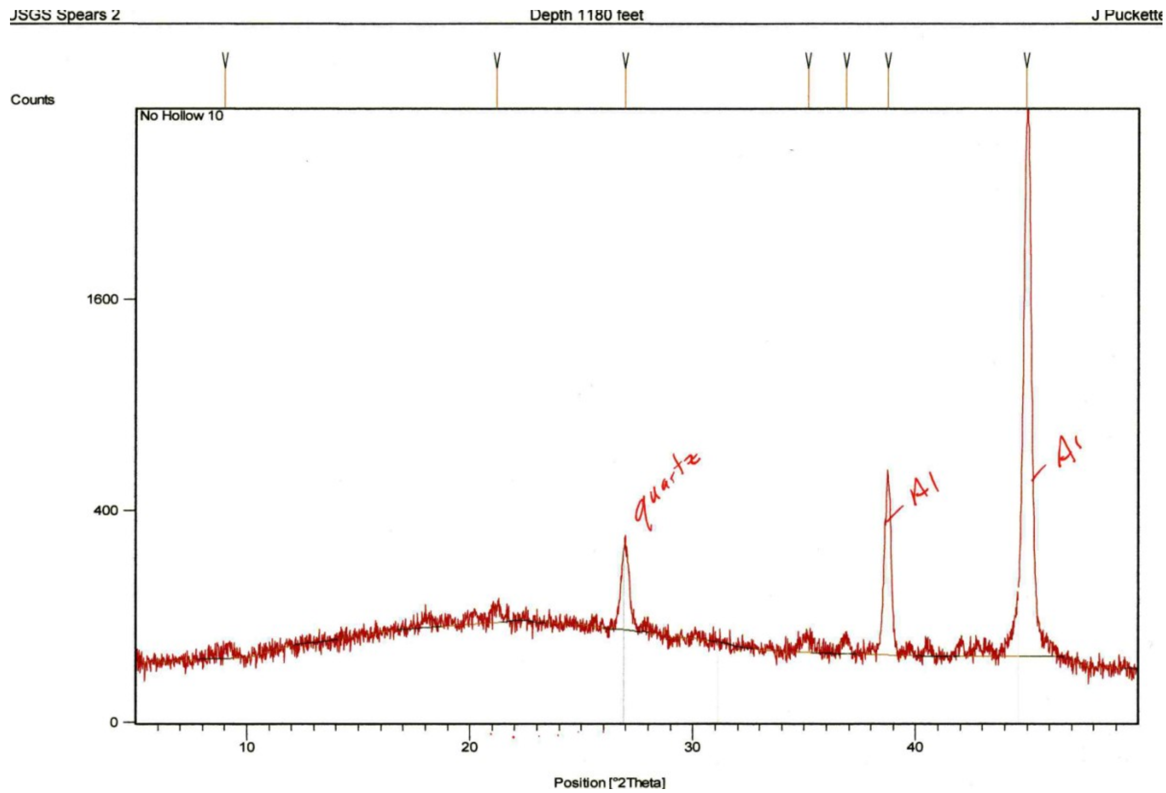
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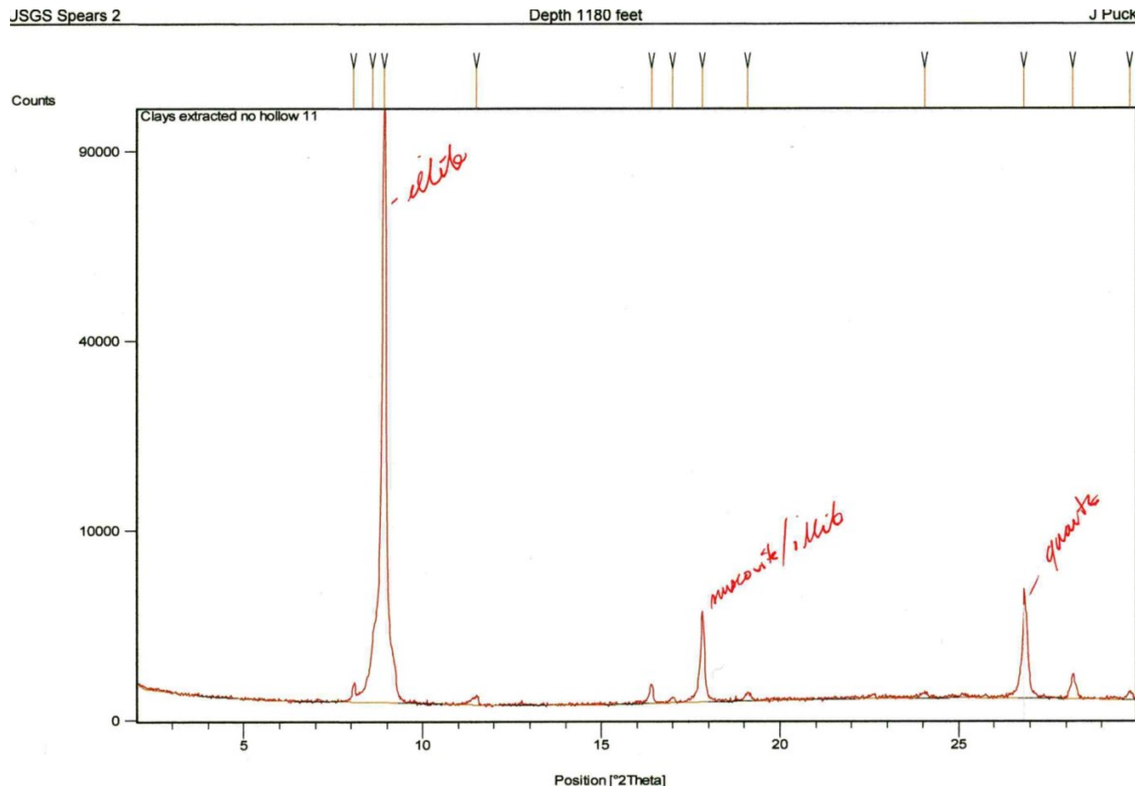
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Counts
Clays extracted no hollow 11
90000
40000
10000
0
5
10
15
20
25
Position [°2Theta]
- illite
muscovite/illite
- quartz

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Pages in Study: 112 Candidate for the Degree of Master of Science

Major Field: Geology

Scope and Method of Study: The aim of this project is to determine the values of gamma ray and total organic carbon content (TOC) of the Chattanooga Shale in the Ozark region. The result of this analysis will be used to test the hypothesis which states that an increase in gamma ray value often leads to an increase in the amount of total organic carbon. The methodologies adopted include detailed Spectral gamma ray measurements, total organic carbon (TOC) analysis and clay mineralogy.

Findings and Conclusions: The Devonian-Mississippian Chattanooga Shale of the Ozark region is organically rich black shale that provides an excellent opportunity to establish that a close relationship exists between the total spectral gamma ray signatures and total organic carbon (TOC) content of black shales. This thesis investigated and compared the gamma ray and total organic carbon (TOC) concentration of five Chattanooga Shale outcrops in the Ozark region. The area of study includes Jane Missouri, Bella-Vista Arkansas and Tahlequah Oklahoma. In the Ozark region, the concentration of total gamma intensity of the Chattanooga Shale increases with that of TOC southwards into the basin. Of importance, the high uranium and TOC content of the Chattanooga Shales in Oklahoma indicate that they are the distal water facies of the Chattanooga Shale deposited in an open marine environment. An average total gamma ray value of 500 API was recorded in the Chattanooga shales in Oklahoma while an average value of 200 API was recorded in Jane, Missouri and Bella Vista, Arkansas. The average value of total organic carbon content of the Chattanooga shales in Oklahoma was 5.0 wt%, while Jane, Missouri and Bella Vista, Arkansas has average TOC values of 1wt%.