GEOCHEMISTRY OF THE HAYNESVILLE FORMATION USING THE

CARTHAGE CORE IN PANOLA COUNTY, TEXAS

by

LAUREN A. WOOLSTON

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Abstract

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Lauren A. Woolston, M.S. Geology

The University of Texas at Arlington, 2014

Supervising Professor: Harry Rowe

The Haynesville Formation has been described as a fine grained, organic, homogeneous shale that was deposited during the warm upper Jurassic (Kimmeridgian) in the tectonically formed East Texas Basin (Mainali, 2011). The Late Jurassic is characterized by a world-wide transgression that flooded most of the Atlantic shelves, followed by a regression (Hammes and Frebourg, 2011). The Haynesville Formation was influenced by basement structures, local carbonate platforms (Sabine Island Complex), and salt movement that was associated with the opening of the Gulf of Mexico (Hammes, 2012). The focus of this proposed study is to provide more insight into the chemostratigraphy, lithology, depositional environments and eustatic cycles of the Haynesville Formation. This new insight is important for the true interpretation of the Haynesville Formation and its economic viability as an unconventional reservoir.

In this study the Carthage core, provided by Anadarko and housed at the Bureau of Economic Geology in Austin, will be studied. The core was scanned

with a Bruker Tracer III/IV electron dispersive X-ray fluorescence (ED-XRF).

The core was scanned at two inch intervals to aquire a high definition study of the

element percentages of the Carthage core. For the major elements (e.g. Si, Ti, Ca,

Al, Fe, Mg, and K), the instrument was run for thirty seconds per sample. While

for the trace elements (Ni, Cu, Zn, Th, Rb, U, Sr, Y, Zr, Nb, and Mo), the

instrument was run for ninety seconds per sample. Using previously drilled

powder samples by Pukar Manali, x-ray defraction (XRD) was performed. Also, a

core description for the entirety of the Carthage core was performed. For this core

description each box (34 in total) was broken down into three rows; each

containing three feet of core. A detailed description was created using

fabric/structure, inclusion, color and fossil accumulation as guidelines.

Currently the preliminary results have indicated that the clay fraction is

being diluted by the carbonate fraction. Additionally a majority of the bulk

elements mainly Si, Ti and K are associated with the clay fraction and show a

linear correlation with the clay indicator, Al. Furthermore geochemical proxies,

such as the association of Ca to Al, will help in the determination of eustatic

cycles. The eustatic cycles can be broken down into 4th and 5th order cycles such

as Milankovitch cycles.

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Chapter 1

Introduction

1.1 Project outline

During the Jurassic the world was warm and moist with a greenhouse climate. During this time the sea level oscillations were thought to have been high frequency and low amplitude (Smith et al., 1999). This environment presented excellent conditions for the formation of organically rich marine mudstone (Jabri, 2013). Dark shales, like the Haynesville, are organic rich, fine grained deposits which typically accumulate under anoxic-euxinic, deep water basinal locations (Demiason and Moore, 1980; Wignall and Maynard, 1993). The anoxic bottom waters of the Gulf Coast preserved the organic matter that would eventually become a source of hydrocarbons, later known as the Haynesville Formation (Jabri, 2013). According to a 2006 paper authored by Brumsack, the hydrocarbon reservoir potential of these types of organic rich shales from euxinic environments as prospective source rocks was recognized by Pompeck in his 1901 paper (as cited in Mainali 2011, pg. 1). In association with oil and gas exploration, an in depth model of these types of heterogenic mudstone's depositional environment is important since using only petrophysical analysis creates difficulty when making industry prognostications.

Since there have been advances in technology, the economic viability of unconventional reservoirs has increased. Additionally, due to the presence of toxic trace elements, the study of black mudstones has increased in importance in

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relation to the economic and environmental side of study (Piper and Calvert, 2009). Geologic factors driving richness of in total organic carbon (TOC) and mineralogical composition needs to be understood in geologic context to predict area of highest gas content (Steinhoff , 2011). Additionally, there is an academic interest when it comes to mudrock given that two-thirds of the sedimentary records consist of them (Manali, 2011).

   The study being proposed encompasses the chemostratigraphy and depositional environment of the Haynesville Formation located in the East Texas Basin. This research project will consist of data that has been recorded from the Carthage core which was extracted from west of the Sabine Uplift (figure 1.1). The drill core being studied in this research project contains the upper, middle and lower intervals of the Haynesville Formation as well as parts of the lower Bossier Formation.
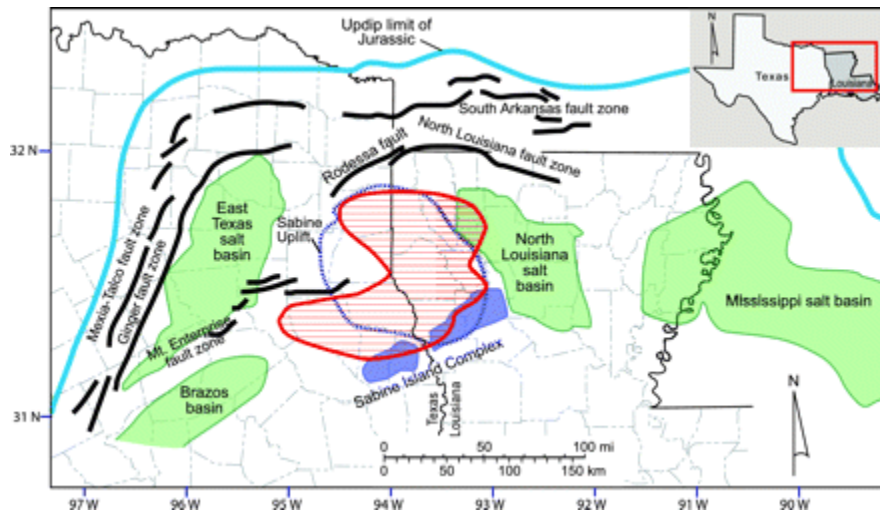
Figure 1.1 Map of the study area in the East Texas Basin. The Haynesville

Formation is outlined in red (Hammes at al., 2011).

By completing this study we will have a better look into to not only the
chemostratigraphy of the Haynesville Formation but also lithology, depositional
environment and stratigraphic zonation which provides insight to the eustatic
cycles. All of the data collected within this research project will help provide a
more concise characterization of the Haynesville Formation.

1.2 Geologic Setting

The Haynesville Formation is located near the East Texas Basin
and is composed of fine grain mudstone that is grey to black in color. The East
Texas basin was formed as a result of the European and African-South American
plates colliding with the North American plate to form the Ouachita Mountains
during the Mesozoic Era (Jabri, 2013). The Haynesville Formation was deposited
during the Kimmeridgian (upper Jurassic). The Haynesville reservoir spans along

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the boundary of East Texas encompassing 6 counties, and Western Louisiana

encompassing 5 parishes (Rowe et al, 2012).
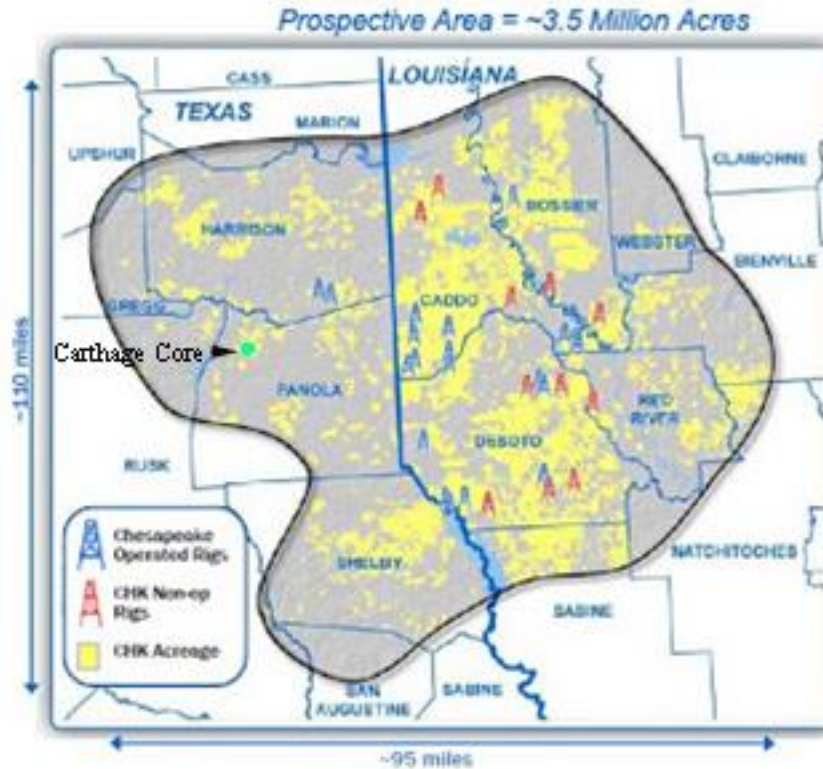
Figure 1.2 Geographical location of the Carthage core in Panola County, TX

within the Haynesville Formation. ("Chesapeake Update", 2009)

The Haynesville Formation was deposited above the Smackover lime and

below both the siliclastic Bossier Formation and the Cotton Valley Sand. The

organic-rich Haynesville shale is associated to the second-order transgression that

deposited organic-rich black shales worldwide (Hammes, 2011). This second

order transgressive systems tract (TST) encompasses back-stepping ramp

carbonates (proximal) and marine shales (distal) below a maximum flooding surface (MSF) (Hammes and Frebourg, 2011). Compositions of mudstones vary depending on stratigraphic position as well as their geographic location; with this respect the Haynesville is lithologically heterogeneous. The Haynesville occurs over both the shallower strata of the Sabine uplift and on the western side of the Louisiana salt basin (figure 1.1). This location constrained the Haynesville in the north by subsidence and rifting faults while, in the south, it was shortened by a structurally high island complex.

The Pennsylvanian epoch contained an orogenic event called the Ouachita thrust. This thrusting paved the way for later salt tectonics and the younger extensional event (Jabri, 2013). During the Triassic the Sabine uplift occurred; this uplift created fault blocks and thermal doming. This made way for the deposit of the Louann salt during the mid-Jurassic. The flow of this salt created turtles, diapires and pillows.
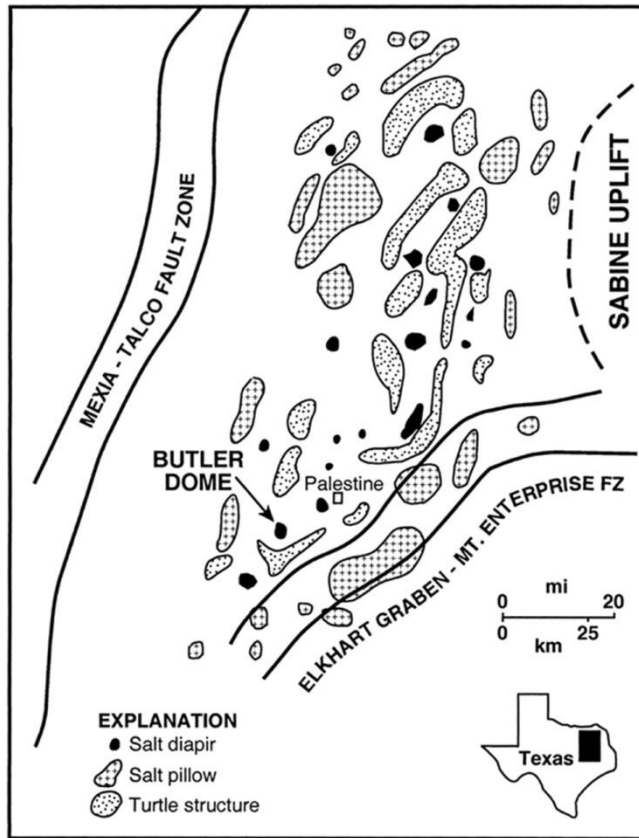
Figure 1.3 Diagram showing the various salt structures located within the East

Texas Basin (Enos and Kyle, 2002).

When this salt became mobile it left a void that was filled by the deposition of the

Haynesville Formation. Figure 1.3 is a stratigraphic column of the Carthage core

being studied as well as the overlying and underlying bounding formations.
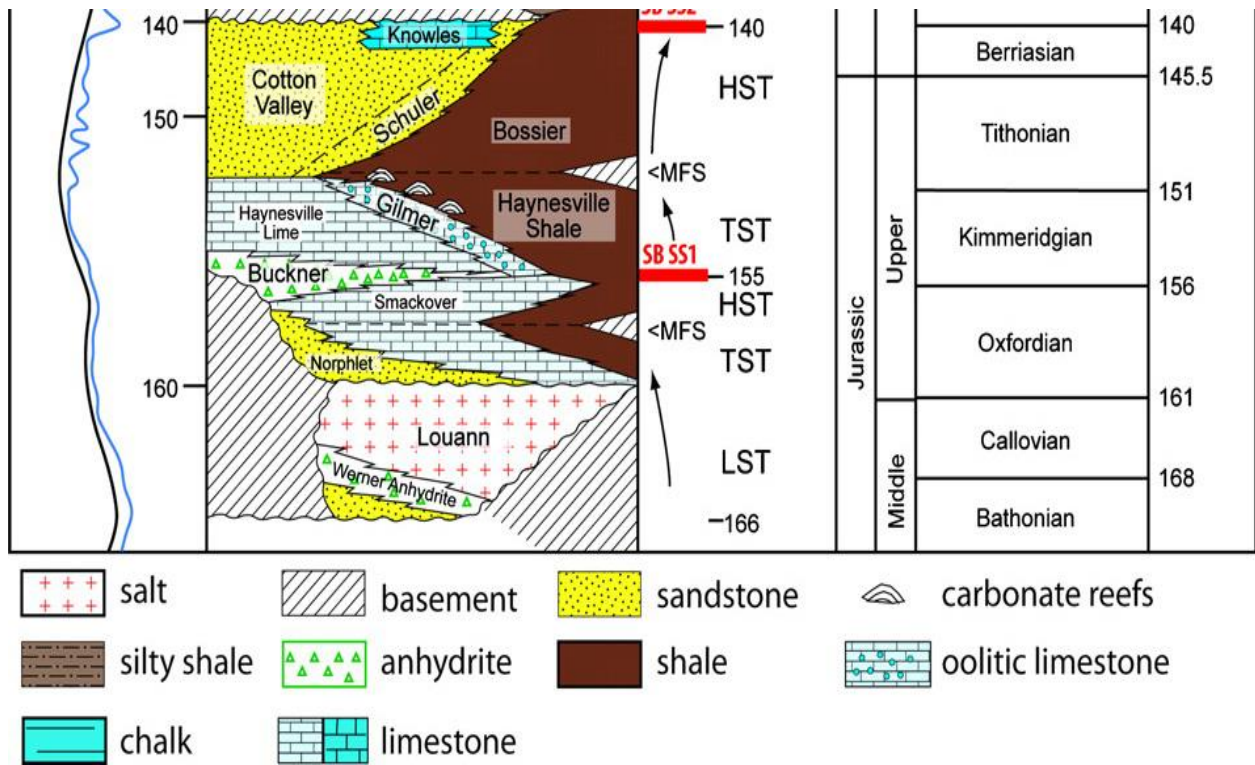
Figure 1.4 Stratigraphic Column of the Haynesville Formation along with

overlying and underlying strata (Hammes et. al, 2011).

The Kimmeridgian was a time of prolonged continental rifting, a rise in

sea-floor spreading, and a relative high eustatic sea level stand. These processes

jointly caused the fragmentation and flooding of the megacontinent Pangea as

well as the modification of the global paleoclimate (Moore et al., 1991). The

world was in a green house environment during the time of the Kimmeridgian.

The maximum warming occurred over the higher latitude oceans and over the

equatorial and subtropical regions, warming was the least (Manali, 2011). The

Haynesville and Bossier Formations were deposited during this green house

period, when sea-level oscillations are considered to have been of low amplitude

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and high frequency (Smith et al., 1999; Seranne, 1999; Frebourg et al., 2011). These formations were deposited during a second order transgressive/regressive depositional sequence (Goldhammer, 1998; Hammes et al., 2011) under dysoxic to euxcinic conditions (Rowe et al., 2008; Hammes, 2009; Mainali, 2011). This deposition occured below storm wave base (Hammes and Frebourg, 2011) far from any detrital sources.

Figure 1.5 Paleogeographic map of N. America during the Late Jurassic. ("Late Jurassic," 2011)

Chapter 2

Methods

2.1 Well and Core Information

In this study I am observing the chemostratigraphy of the Carthage core which was provided by Anadarko to the Bureau of Economic Geology in Austin, Texas. The Carthage core is located in Panola County, TX (Figure 2.1).
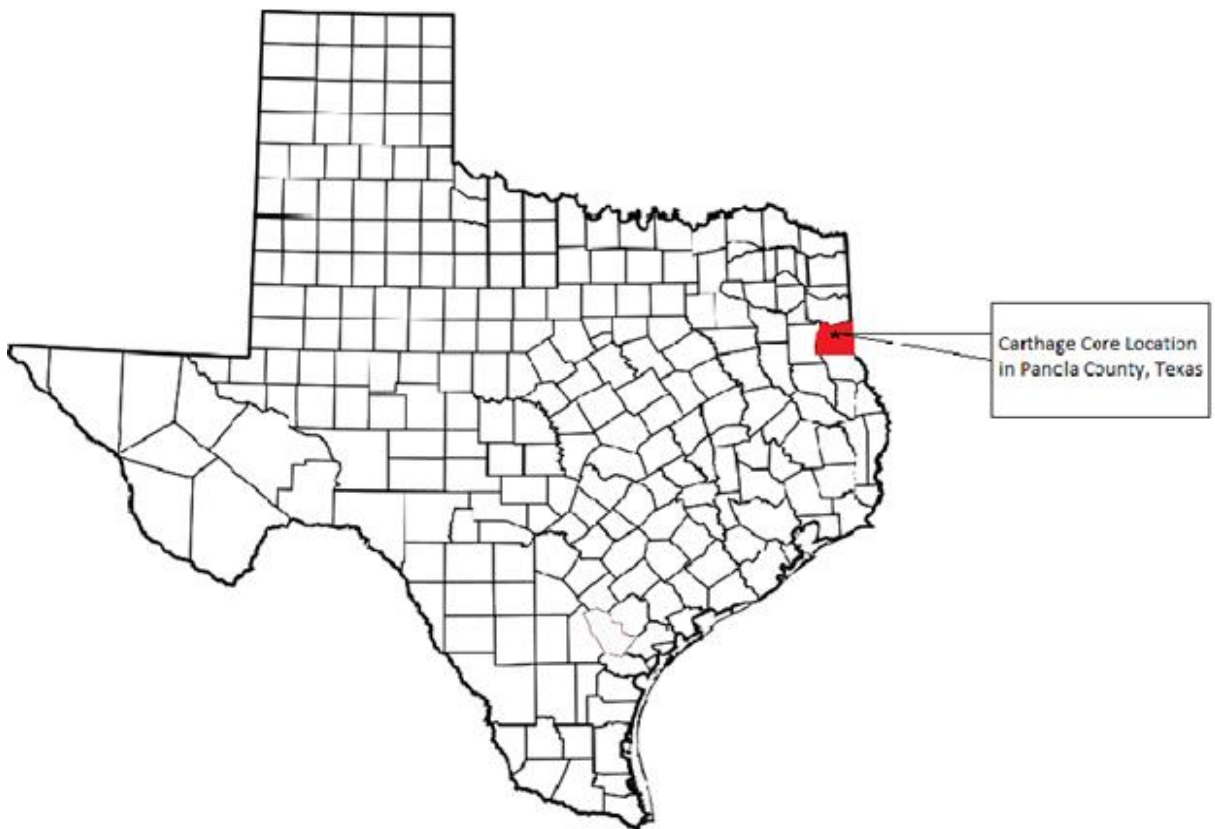
Figure 2.1 Location of Carthage core in Panola County, Texas.

The Carthage core was prepared for the attainment of chemical electron dispersive x-ray fluorescence data.

Table 1 Detail of core analyzed for this study

Core Name	Carthage
Location	Panola County (Figure 2.1)
Depth Interval	300.8 feet (10448-10748.8) 91.7 meters (3184.6-3276.2)
Box Numbers	1-34
Number of Samples	1,836

With each sample it is imperative to place a flat surface against the beam window. If there is not a solid connection between the sample and the instrument, you will get erroneous readings. This flat surface is also important to lower the risk of puncturing the thin film sticker that covers the nose of the instrument (Figure 2.2.D), insuring a tight vacuum seal. Placed on the nose of the instrument is the sample platform (Figure 2.2.B), this is used to stabilize the sample during scanning assuring uninterrupted contact between the sample and the instrument.

2.2 Electron Dispersive X-Ray Fluorescence

The Carthage core was analyzed for inorganic elemental chemistry using the Bruker III/IV electron dispersive x-ray fluorescence Boston instrument. The use of this instrument provides a reading of the percentage of an element present within the sample. Samples were taken every two inches throughout the core. This small sampling interval provides us with a high definition study of the Carthage

core. The instrument was kept stable using an instrument platform and the

samples were placed flushed with the 3mm by 4mm window located on the nose

of the instrument (Figure 2.2.D). Two independent studies were performed to

analyze the major and trace elements separately. Before running my samples I

washed to sample face with plain water and marked two inch sample intervals,

with chalk, throughout the core. Since my core was 306 feet in length I had a

sample size of 1,836 samples. The major elements (e.g. Si, Ti, Ca, Al, Fe, Mg,

and K) were run at thirty second intervals for each sample. While the trace

elements (e.g. Ni, Cu, Zn, Th, Rb, U, Sr, Y, Zr, Nb, and Mo) were run for ninety

second intervals for each sample. The major elements readings were taken with a

vacuum pump, reading no more than 2 Torr, to remove the air from between the

detector and sampling window (Figure 2.2.B). As for the trace elements, the

readings were recorded in a filtered instrument situation. This filter is used to

prevent low-energy s-rays from reaching the detector (Manali, 2011).
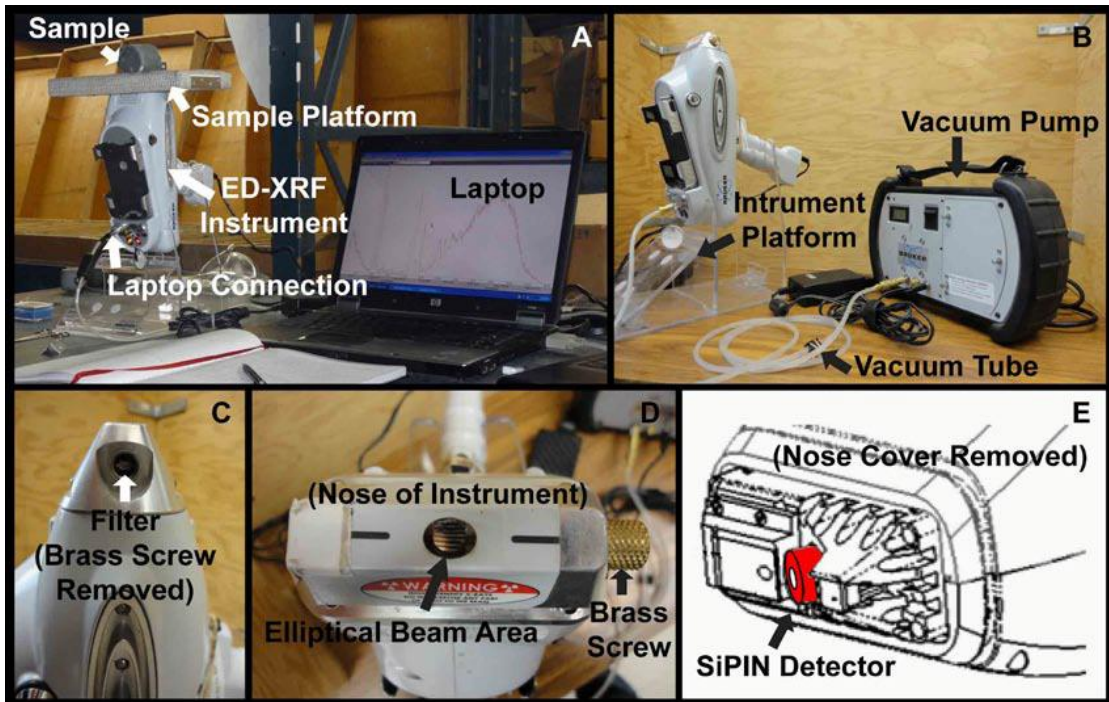
Figure 2.2 The Bruker III/IV ED-XRF Instrument. A) Shows the set up while

scanning, B) shows the instrument platform which is used to stabilize the

instrument during scanning; also, the vacuum pump is shown, which is used in

low energy acquisitions, C) this filter

2.2.1 Calibration of the ED-XRF

The calibration for the handheld ED-XRF instrument is matrix-specific, so

a calibration for major and trace elements of mudrocks was developed using a

suite of 90 reference materials. The calibration includes the following 90 mudrock

standards: 5 international, 7 Devonian-Mississippian Ohio Shale, 20

Pennsylvanian Smithwick Formation of Central Texas, 27 Devonian-

Mississippian Woodford Formation of West Texas, 15 Late Cretaceous Eagle

Ford Formation of South Texas, and 16 Mississippian Barnett Formation of

North-Central Texas. (Rowe and Hughes, 2010). These samples were crushed, mixed and then pressed into pellet form and analyzed using wavelength-dispersive x-ray fluorescence (WD-XRF) and inductively-coupled plasma mass spectrometry (ICP-MS) (Hughes, 2011). I performed routine calibration checks of the Bruker III/IV: Boston instrument every morning before sampling with a reference pellet 3 separate times; each time for a duration of 180 seconds. I also performed a routine calibration with the reference pellet once for 180 seconds in the evening after my sampling was finished. These routine calibration tests are run to make sure the instrument is working properly and is giving viable readings.

2.3 X-Ray Diffraction

Samples were taken every ten feet. This interval provided me with 30 samples. Samples selected for XRD were analyzed by the powder x-ray diffraction method at the Beureau of Economic Geology in Austin Texas. The pulverized samples analyzed were prepared by Pukar Minali. He samples were examined using an Olympus BTX X-Ray Diffraction Unit. Bulk powder spectra were analyzed from 2°-90° 2θ. Glycolated and unglycolated clay fractions were both prepared and analyzed using a suspension and powder-peel method across a 2θ angle range from 2°-22°.

2.4 Core Description

A core description for the entirety of the Carthage core was performed. For this core description each box (34 in total) was broken down into three rows; each containing three feet of core. A detailed description was created using

fabric/structure, inclusion, color and fossil accumulation as guidelines. As a result

of completing the core description, a detailed visual account of the Carthage core

is obtained (table 2).

Chapter 3

Results

Dispersive x-ray fluorescence, x-ray diffraction and core descriptions on

the Carthage core were used in the interpretation of this study. The Carthage core

had a depth interval of 300.8 feet. The high definition study of this core provided

a sample size of 1,836 to analyze. The major elements were measured in weight

percentage (wt %) of Si, Ti, Ca, Al, Fe, Mg, and K. whereas trace elements were

measured in parts per million (ppm). The core chemostratigraphy has been

separated into separate segments based on variations within the major elements

Ca, Al and Si. With the interpretation of these three key elements, a lithological

understanding of the rock is obtained.

3.1 Core Characterization

To provide a, visually acquired, physical description of the Haynesville

Formation a description of the Carthage core was completed. The fabric of the

Haynesville is a fine grained mudstone. In table 2, a detailed physical description

of the Carthage core is given. Due to the lack of physical identification markers in

the Carthage core, thin section samples are necessary to achieve a more accurate

in depth analysis of the Haynesville core studied. However, through visual

observation, calcite stringers and pyrite nodules are visible on the cut surface.

Along with the geochemistry data collected for this core, association between

changes in the depositional environment can be inferred. Overall the core is of a

medium to dark gray throughout the Haynesville sections of the Carthage core.

When observing the contact between the Haynesville and Bossier formation, one can visually observe a distinct color change between the more siliciclastic Bossier Formation and the underlying, carbonate rich Haynesville Formation.

Table 2 This table is a detailed look into the core description of physical visual characteristics of the Carthage core from Panola County, Tx

Depth (feet)	Sample Photo	Sample Description
10489 -10492		During the first 1/6 of the core there is a slight color change at 10487.5 which is our first indication of the boundary between the Bossier Formation and the Haynesville Formation. In the photo to the left we are looking at a long calcite vein that runs the entirety of row two in box five of the core analyzed.

Table 2- continued

10514		There are fossils at various depths within the Carthage core. Here we see an Ammonite mold/cast. There are also pectin and bivalves present in the core.
10489 -10492		During the first 1/6 of the core there is a slight color change at 10487.5 which is our first indication of the boundary between the Bossier Formation and the Haynesville Formation. In the photo to the left we are looking at a long calcite vein that runs the entirety of row two in box five of the core analyzed.

Table 2- continued
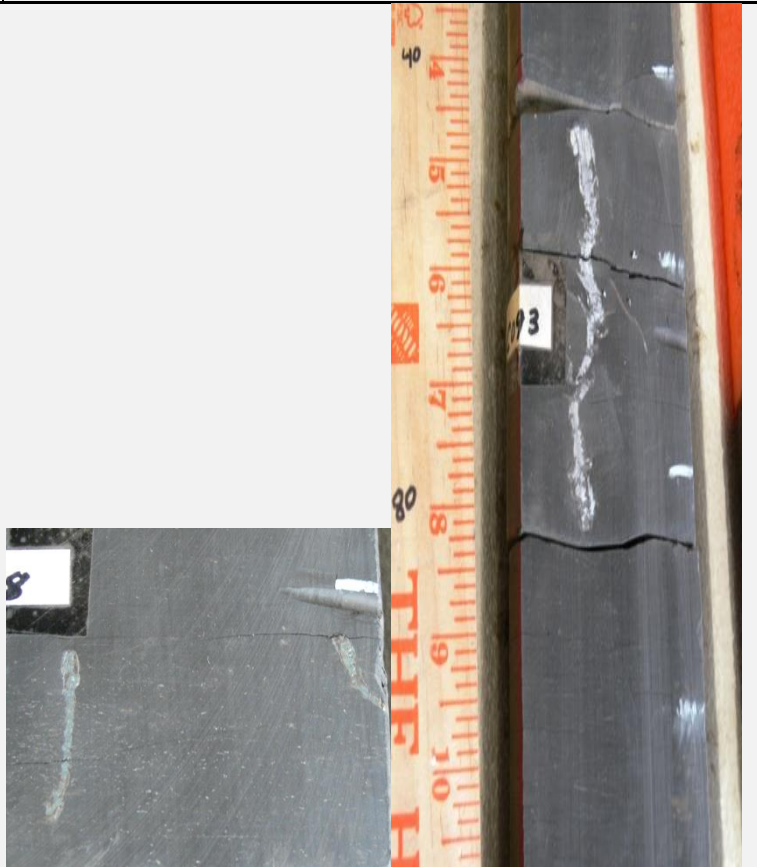
10514		There are fossils at various depths within the Carthage core. Here we see an Ammonite mold/cast. There are also pectin and bivalves present in the core.
10540 10545		In box 11 we have nicely defined pyrite at marker C088. In box 12 we have a 3.5 inch long calcite vein at marker C093.

Table 2- continued

10559		One inch above marker C104 we have a bivalve that has been replaced with calcite. We also see the bivalve replacement near marker C130 in box 15.
10577.2		
10582		Again we see quite visible pyrite inclusion in box 16.

Table 2- continued

10618.5		In box 20 we see a well defined pyrite nodule.
10628-10640		Here we can see the fissality that begins in box 21 and continues for 12 feet.

Table 2- continued

10641-10680		The core becomes quite solid with a dark black color at the beginning of box 23. This consists until the second row of box 27.
10684-10731		Beginning half way down row 2 of box 27, the core becomes increasingly fissile. This fissile nature lasts until box 33 at 10731 feet. From there the core is solid.

3.1.1 Chemostratigraphy

Using tertiary diagrams (figure 3.5) the comparison between 5 X Al_2O_3, SiO_2 and 2 X CaO can be seen. The SiO_2 represents the quartz mineralogy; the 5 X Al_2O_3 signifies illite, albite, chlorite or kaolintite; while the 2 X CaO denotes carbonate rich organics. The Carthage core was broken down into four separate sections; the Bossier, Upper Haynesville, Middle Haynesville and Lower Haynesville. The Bossier Formation is highly silisticlastic. It has higher concentrations of silica while possessing low concentrations of carbonates. When observing %Ca versus %Al, we are looking to compare the carbonate ($CaCO_3$) versus clay input. Since calcium has an inverse relationship with aluminum, the calcium within my Carthage core is associated with $CaCO_3$. When we look at %Si versus %Al we find a linear relationship which suggests that the silica in this core is associated with the clay. As we look into the relationship between %Mg and %Al we find that there is a linear relationship within the Haynesville Formation even though the relationship is not as strong as that of Ti, Si or K. The Bossier Formation samples located at the top of the Carthage core seem to drop off the line when it comes to its %Fe relationship with %Al; this could suggest that the iron within the Bossier formation is more closely associated with siderite or pyrite rather than clay. For the %Ti we have a strong linear relationship when compared to %Al. This could mean that Ti is associated with rutile within the lattice of Al. The potassium observed in the Carthage core is closely related to the clay as can be seen through its strong linear relationship with aluminum. As for magnesium,

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there is no relationship, linear or non. This suggests that the Mg is associated with Dolomite either as diagenetically altered limestone or dolomite that was created in situ during deposition.
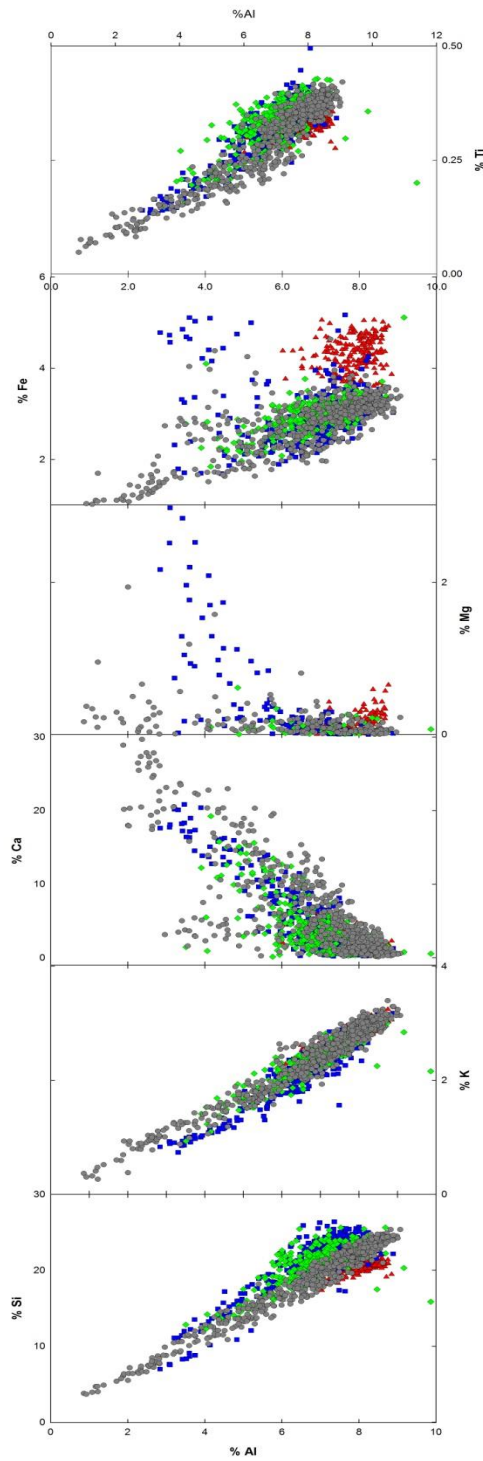
Figure 3.1 Relationships of %Ti, Fe, Mg, Ca, K, and Si with %Al.
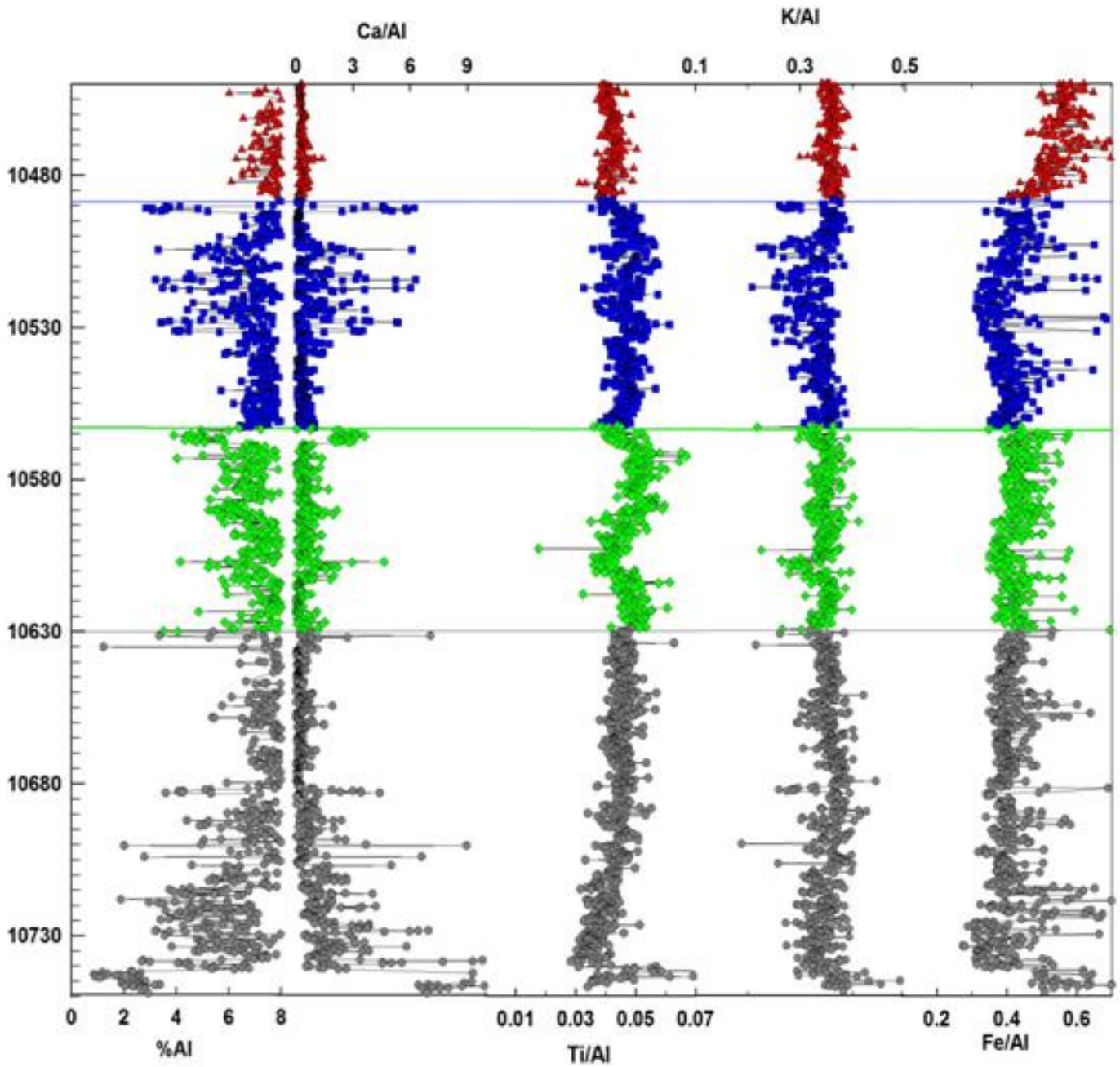
Figure 3.2 Illustration displaying the stratigraphic zonation of geochemical properties.
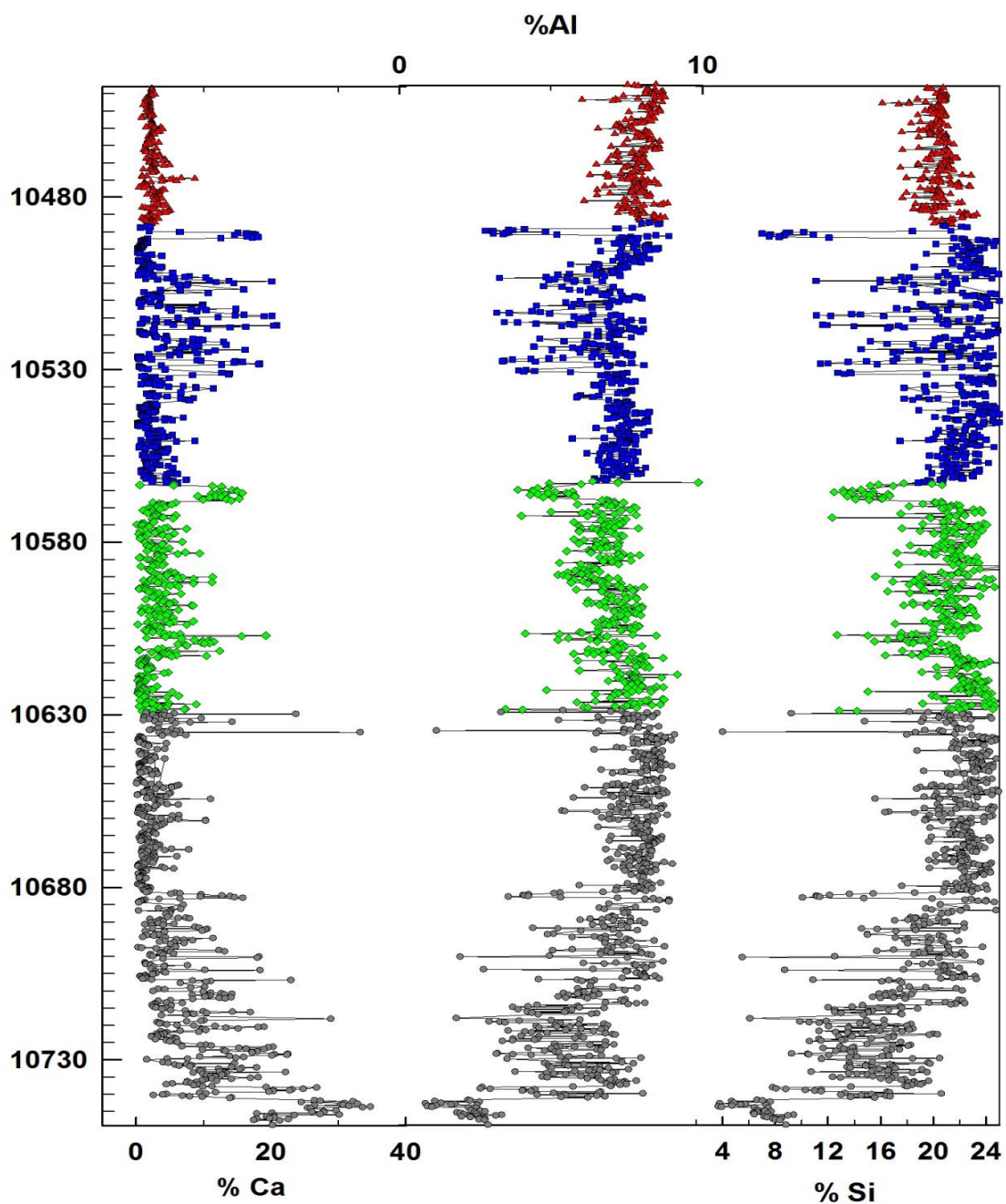
Figure 3.3 This graph represents the wt% of the major elements Calcium,

Aluminum, and Silica.
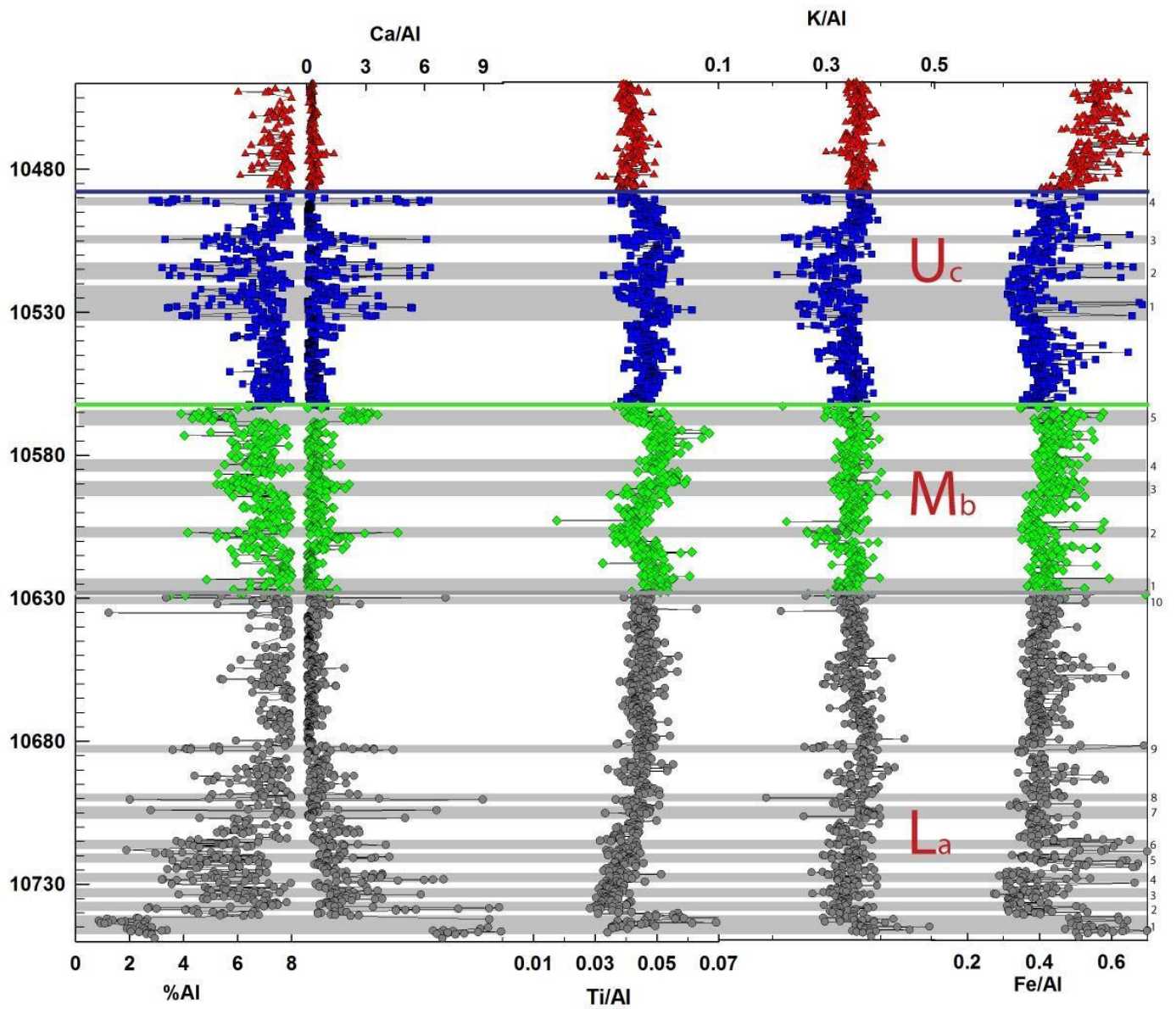
Figure 3.4 This graph is showing the chemostratigraphy of Major elements of the

Bossier and Haynesville Formations.

The Haynesville Formation is a lithologically heterogeneous, silty, organic

rich formation which was deposited in a restricted basin located on a sloping

continental shelf. While scanning, the biostratigraphy of the Carthage core was

taken into account. This core contained fauna including, but not limited to,

ammonites, coccoliths and bivalves. A correlation can also be seen when

observing the four tertiary diagrams (Figure 3.5). Each diagram represents a

different section of the Carthage core. Within the four diagrams we can see the

linear relationship between the Bossier Formation section and the Upper, Middle

and Lower Haynesville with the Ca dissolution line. Each section of the Carthage

core correlates with the average shale ternary readings.
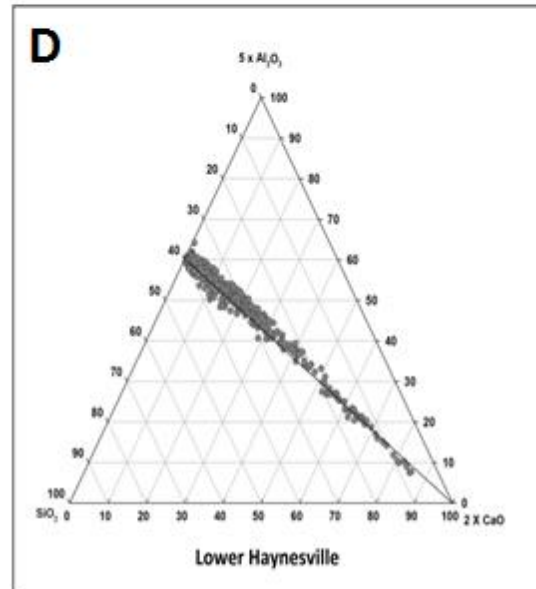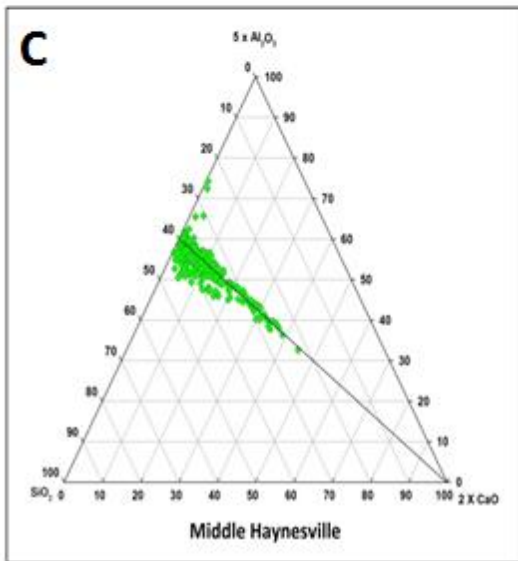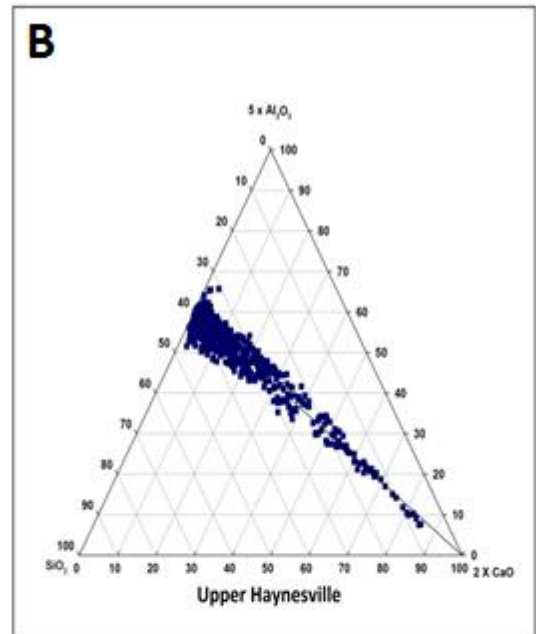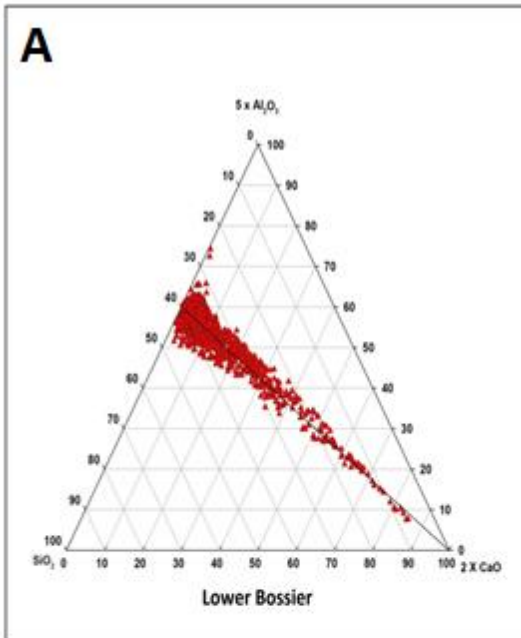
Figure 3.5 Ternary diagrams of the (A) Lower Bossier, (B) Upper Haynesville,

(C) Middle Haynesville and (D) Lower Haynesville Formation. The average shale

line is represented by the black line.
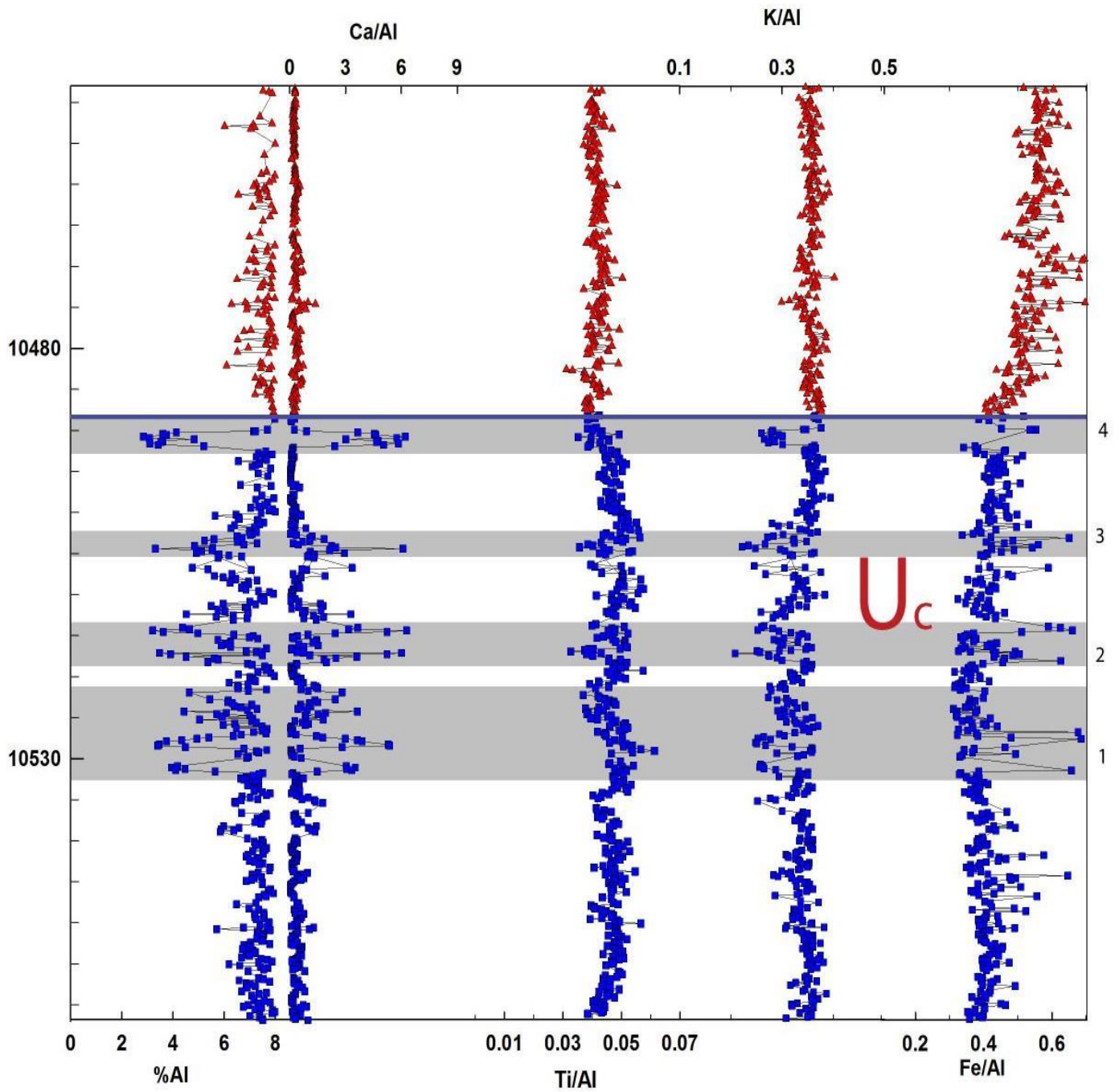
Figure 3.6 This figure is showing the chemostratigraphy of the upper Haynesville

Formation.
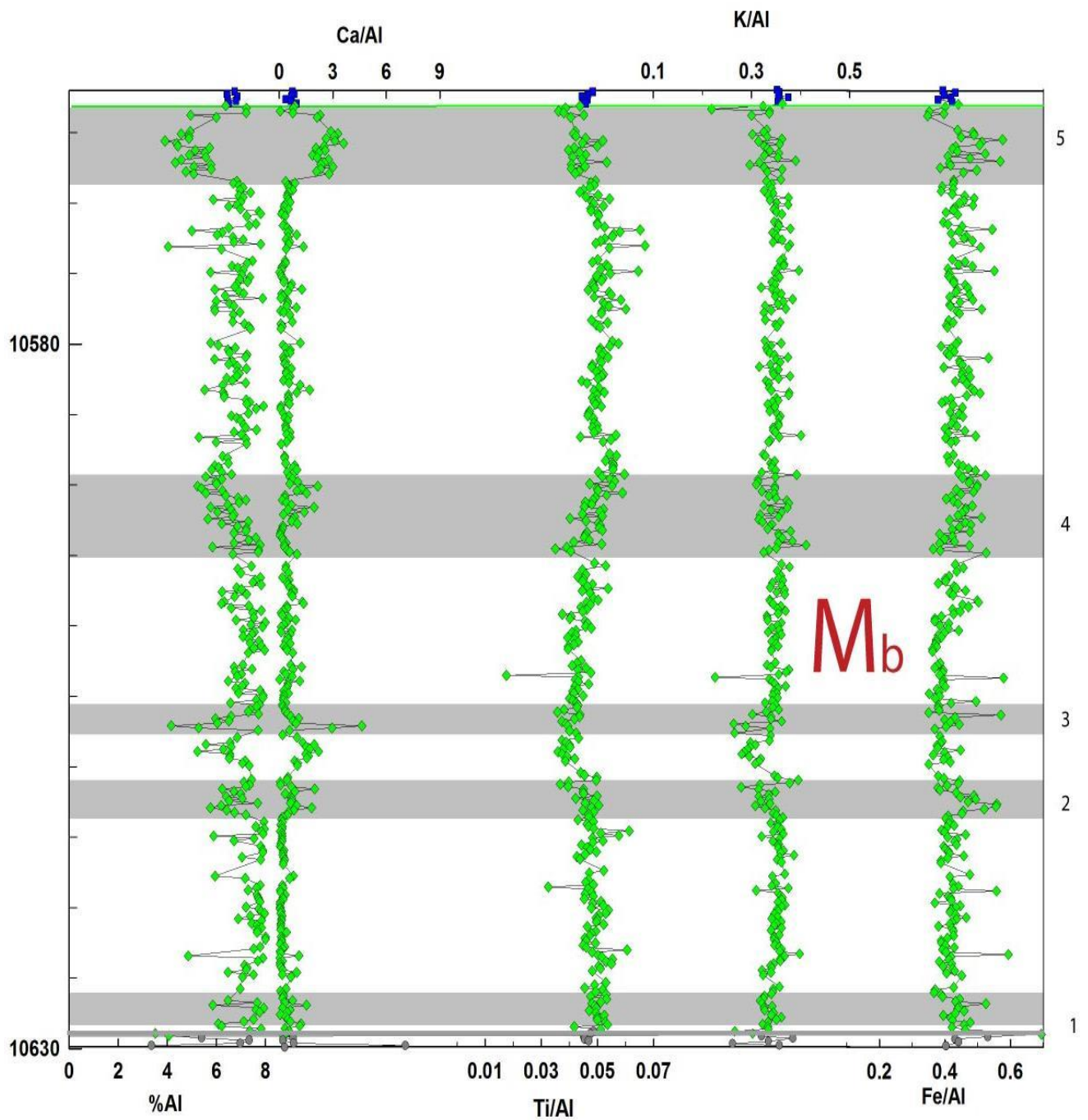
Figure 3.7 This figure is showing the chemostratigraphy of the middle

Haynesville Formation
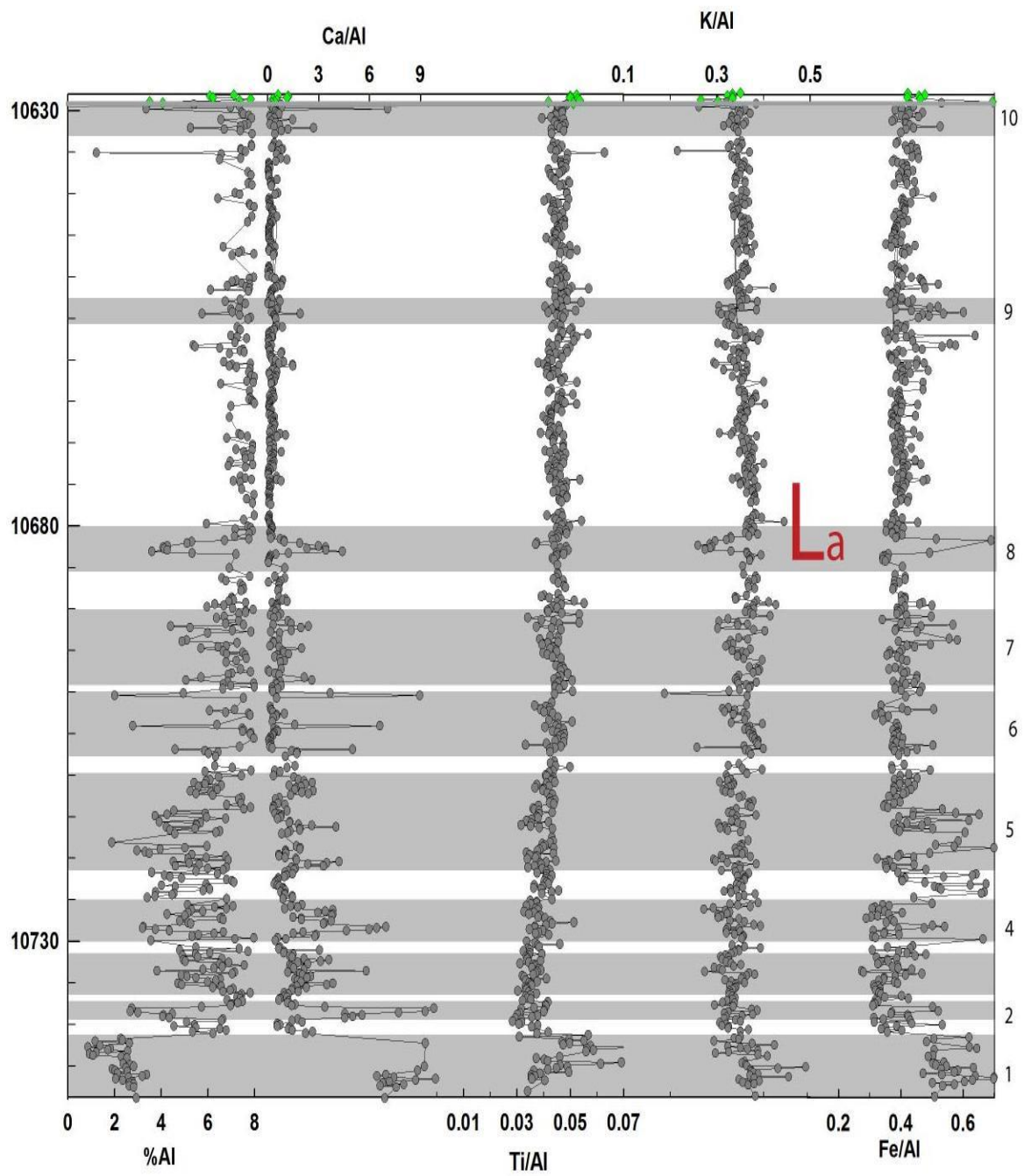
Figure 3.8 This figure is showing the chemostratigraphy of the lower Haynesville
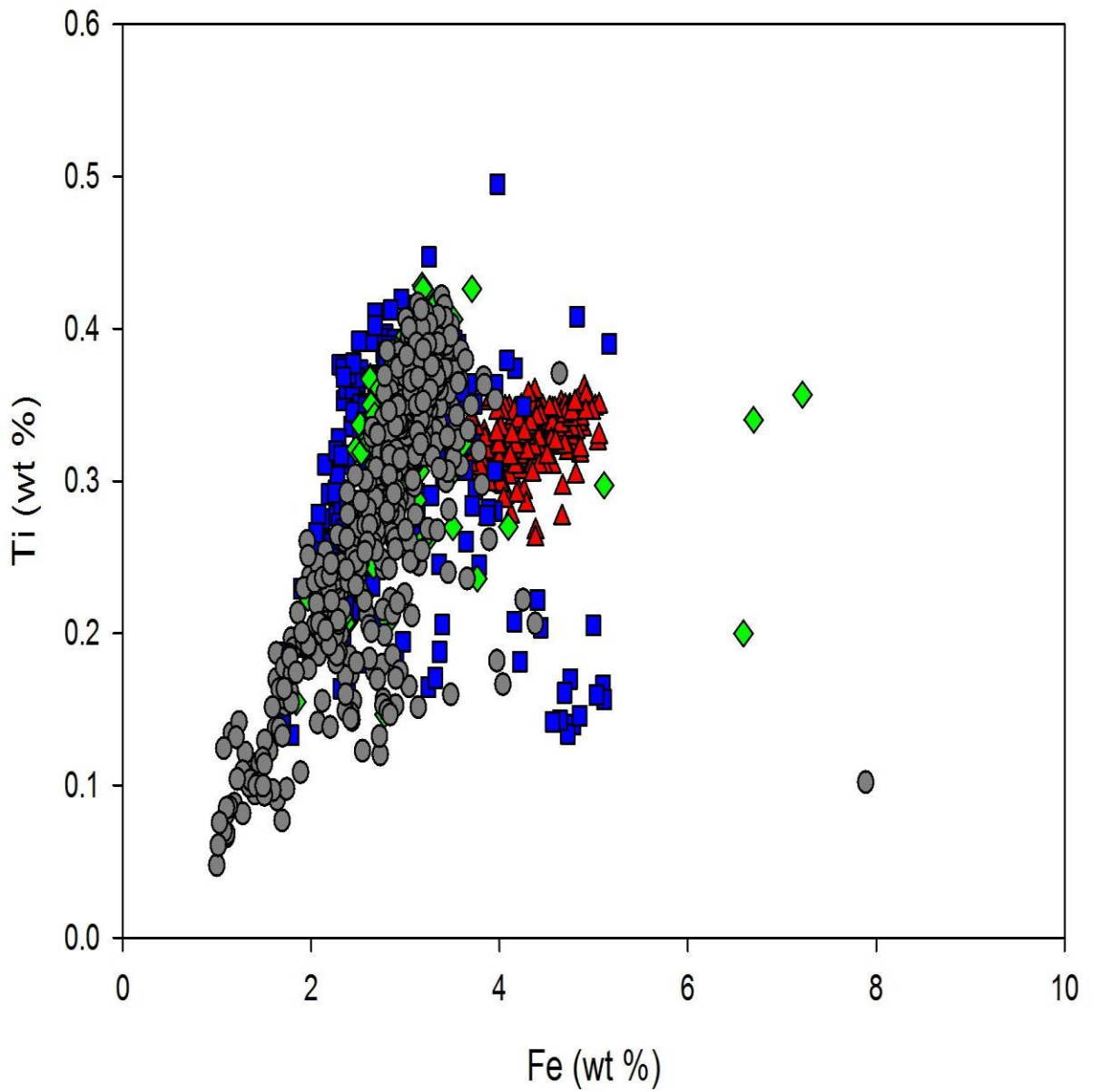
Formation

Figure 3.9 This figure is showing the chemostratigraphy of the lower Haynesville Formation

Table 3 Weight percentage mean, median and range (low and high) for the major

elements analyzed.

Element (wt%)	Mean	Median	Range	
			Low	High
Na %	0.54275	0.6192	0.1695	0.916
Mg %	-0.04374	-0.08435	-0.5573	2.9805
Al %	6.960892	7.28585	0.863	11.3885
Si %	20.13423	21.0746	3.6818	26.3898
P %	0.019752	0.007969	-0.0834	0.6838
S %	1.2695	1.13295	0.3573	10.6996
K %	2.413018	2.534	0.2639	3.3958
Ca %	4.875328	2.83775	0.102	34.7527
Ti %	0.312394	0.331	0.0476	0.495
Mn %	1.96^{E-02}	1.91^{E-02}	-6.60^{E-03}	0.0997
Fe %	3.097561	3.03835	0.9999	7.8886

3.1.2 Trace Elements

Trace elements are often used as proxies to understand information regarding paleoenvironments (Brumsack, 1989; Dean and Arthur, 1989; Rimmer, 2004; Cruse and Lyons, 2004; Tribovillard et al, 2006; Algeo et al, 2007; Algeo and Maynard, 2008; Algeo and Tribovillard, 2009; Piper and Calvert, 2009). These trace elements are reliable indicators of the water bottom environment. It assists in determining whether the environment is euxinic/anoxic or anaerobic. Figure 3.6 shows the chemostratigraphy of the lower Bossier and the Haynesville Formation in terms of trace elements. While in figure 3.1 we see a crossplot comparing %Al to various trace elements. In this figure we see a linear relationship between %Al and Lead (Pb), Rubidium (Rb), Thorium (Th), Zinc (Zn) and Zirconium (Zr) which indicates that the trace metals examined within the Carthage core are associated with the clay fraction within the core formations. There is an apparent inverse relationship with %Al and Molybdenum (Mo), this signifies a sub-oxic deposition (McManus et. al, 2006, Poulson et. al, 2006) which suggests that Mo can be utilized as a potential proxy for paleo-euxina environments.

3.1.3 Enrichment Factors

The enrichment factor (EF) is classified as any divergence from the average shale chemical composition (Mainali, 2011). The average shale values used to calculate the enrichment factor ratio were from Wedepohl, 1971. To calculate the enrichment factor ration the following equation was utilized:

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$$EF = \left[\frac{element(ppm)}{Al\ (ppm)} sample\right] / \left[\frac{elment\ (ppm)}{Al\ (ppm)} standard\right]$$

The samples that have an EF = 1, represent similar levels when compared to average crustal abundance which represents oxic depositional conditions. Additionally, for samples that are enriched compared to average shales would have an EF > 1, while samples with an EF < 1 are considered to be depleted relative to the average shale. Through this enrichment factor ratio, enrichment or depletion can be determined.
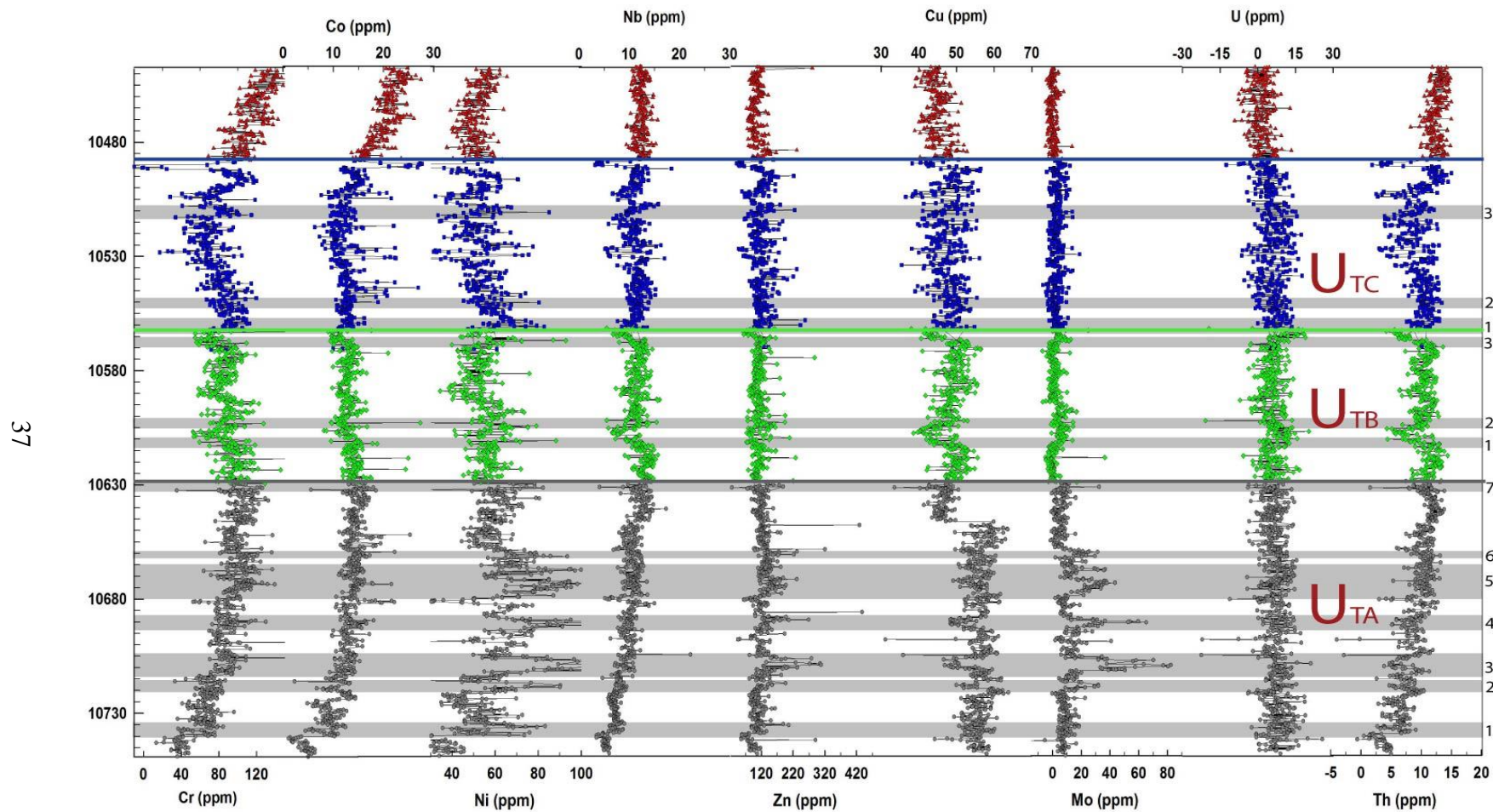
Figure 3.10 This graph is showing the chemostratigraphy of trace elements of the Bossier and Haynesville Formations.
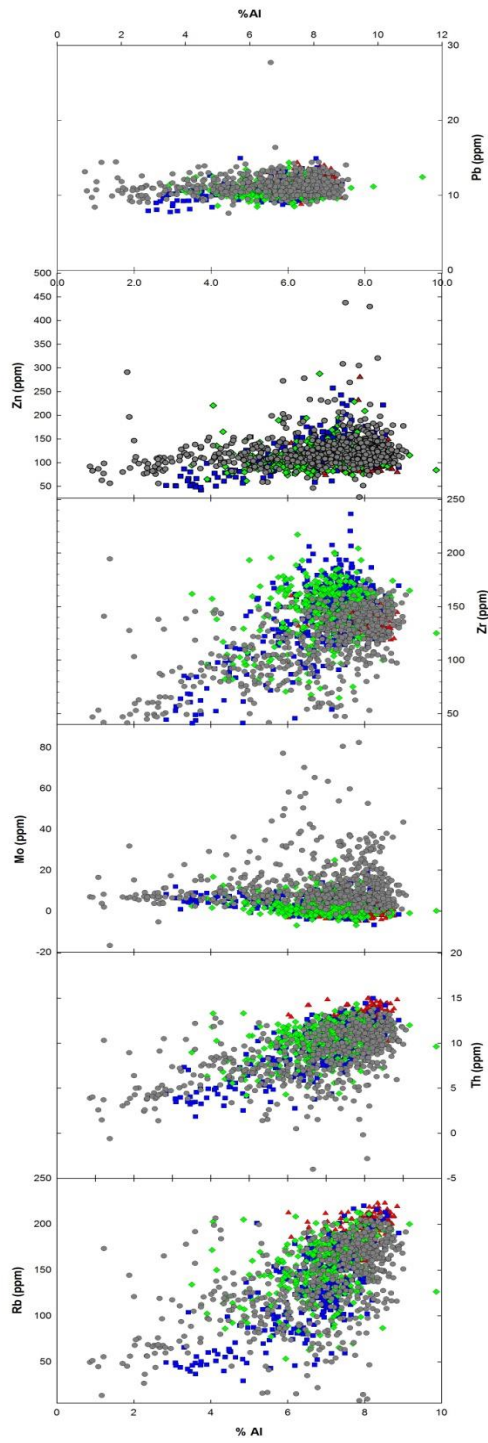
Figure 3.11 Relationships of Pb, Zn, Zr, Mo, Th, and Rb with %Al.
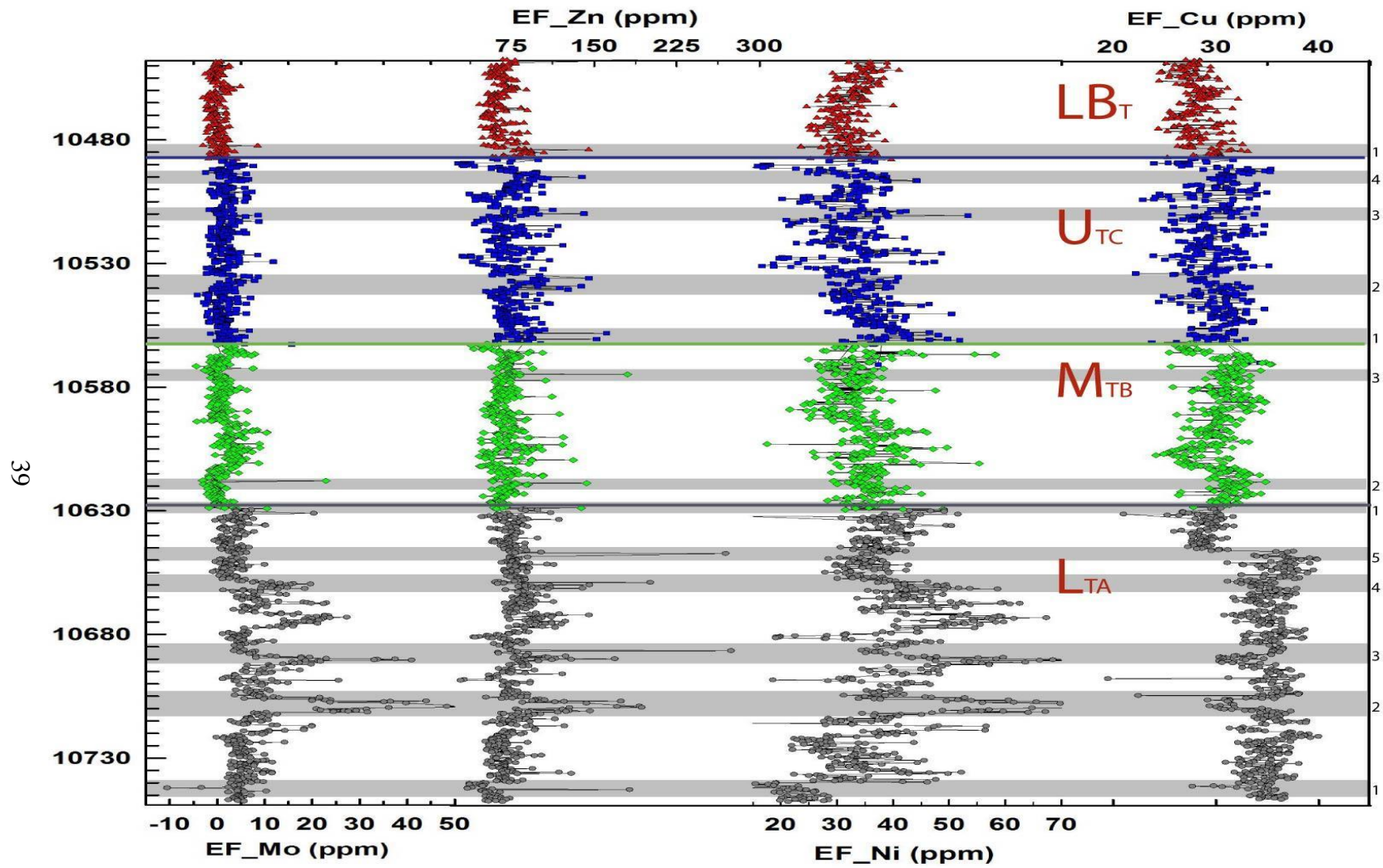
Figure 3.12 This is a chart showing the enrichment factor for the trace elements Mo, Zn, Ni, Cu.

Table 4 This table represents the mean, median and range (low and high) for the

trace elements analyzed.

Element (ppm)	Mean	Median	Range	
			Low	High
Cr	89	89	-35	580
Co	14	13	1	111
Ni	57	55	17	134
Nb	11	11	3	22
Zn	119	114	27	438
Cu	50	49	31	64
Mo	7	4	-17	82
U	6	6	-22	26
Th	10	10	-4	15

Chapter 4

Discussion

This discussion will be focused on the Upper, Middle and Lower

Haynesville Formation as well as the Lower Bossier Formation through the

analyzation of the Carthage core located in East Texas at Panola County. To

achieve a better understanding of the Haynesville Formation, detrital elements

(Al, Ti, Zr), organic associations (Mo, Zn, Ni, Cu, Cr, V) and carbonates (Ca, Mg,

Mn, Sr) (Brumsack, et. al, 2003, Vine and Toutelot, 1970, Manali, 2011)

generated through the use of X-ray fluorescence are evaluated. From this bulk

geochemistry, changes in mineralogy of the mudstone formation can be identified.

To determine the elements present in clay, crossplots of the major elements in

relation to aluminum are interpreted. To determine the paleo-redox conditions,

terinary diagrams of S, Fe and Mo are used while comparison between % Si, %Ti,

and %Zr against %Al is examined.

4.1 Major Elements

For this study the major elements Aluminum (Al), Silica (Si), Calcium (ca,

Potassium (K), Phosphorus (P), Sulfur (S), Titanium (Ti), Vanadium (V), Iron

(Fe), Manganese (Mn), Chromium (Cr) and Magnesium (Mg) were analyzed.

From these major element readings we are able to identify what the major source

of sedimentation was in the area during deposition, therefore providing a

lithological profile of the core. By observing the relationships between the clay

fraction (Al) and the clastic influx (Si, Fe, Ti, Ca), an understanding of the

mineralogical composition of the core is obtained. In figure 3.11, the linear

correlation between %Al and these clastic proxies shows that the main portion of

clay within the formation is directly related to the surrounding terrigenous inputs.

4.2 Trace Elements

Zinc (Zn), Copper (Cu), Molybdenum (Mo), Nickel (Ni), Thorium (Th),

Cobalt (Co), Uranium (U), Zirconium (Zr) and Strontium (Sr) were the trace

elements examined. These trace elements are often used by various researchers to

deduce information regarding the paleoenvironments (ex bottom water conditions

and malankovich cycles). Through the comparison of Mo with TOC, an insight

into the euxinic environment in which the Haynesville Formation was deposited

can be determined. This is due to the lack of oxygen, preserving the marine

organics, such as marine snow that have accumulated at the bottom. This is due to

the fact that without the circulation of oxygen throughout the water column, the

marine organics in question settle and are preserved as kerogen which is directly

related to TOC. Due to a rise in the level of the total organic carbon (TOC)

observed in the lower Haynesville, it may be the consequence of a major increase

in production of biogenic silica during its deposition (Manali, 2011, Sageman,

2002);

4.3 Detrital Influx

The Silica to Aluminum ratio has been utilized as a proxy for detrital influx. It is a representation of the quarts to clay ratio (Tribovillard et al, 1994; Caplan and Bustin, 1998; Murphy et al, 2000, Rimmer et al, 2004). In the Haynesville Formation, silica displays a linear relationship with Aluminum. This indicates that, within the Haynesville, the silica resides in the clay fraction. From the figure 3.11, it can be interpreted that there exist other silica minerals aside from the clay due to the data points that lie above the average shale line. It can be seen through the XRD data that there is a high amount of quartz and a lower amount of albite in the Haynesville Formation. As for whether the additional silica present in the Lower Haynesville Formation is biogenic or detrital, is not apparent (Manali, 2011). Due to the fact that biogenic silica in black shales could possibly originate from radiolarians, it could make silica or silica vs. aluminum ratios a challenging indicator of clastic influx (Schieber et.al, 2000; Rimmer et.al, 2004). Therefore, it is important to evaluate the other detrital proxies (Ti, Zr, Fe and Ca) before determining a definitive conclusion.

Since aluminum and titanium are stationary during diagenesis and are common detrital elements, the detrital provenance of any element can be confirmed by plotting it against these major elements (Tribovillard et al., 2006; Manali, 2011). Due to the fact that Aluminum is not affected by biological or diagenetic processes, it makes an important detrital element while additionally a

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good proxy for clay (Brumsack, 2009). However, aluminum is in short supply in seawater (Orians and Bruland, 1986; Mainali, 2011). When it comes to Ti and Zr, they have a high charge ratio and do not participate in biological cycling. Therefore, any peaks of these elements in the data set represent a detrital input (Piper and Calvert, 2009). Consequently, any elements that show a linear relationship with these detrital indicators, in turn, are of detrital origins. Titanium can be found in both clay and sand sized grains of both oxides (rutile or ilmenite) and pyroxenes (augite); hence a comparison with aluminum advocates the presence of minerals that contain Ti which are typically associated with coarser grained sediments (Mainali, 2011; Schmidts, 1987; Rimmer et al., 2004). Also, due to the heavy weight of titanium, it can be an indicator of the paleowind strength and sedimentation rate of the depositional period (Boyle, 1983; Rimmer et al., 2004). Since Ti is found in the heavier minerals such as rutile, it can be inferred that the Haynesville Formation was deposited in a deeper, highstand, inactive period (Mainali, 2011).

Silica (Si) can be indicated as detrital when it has correlating spikes with Ti and Al along with depth. This characteristic is inferred since Ti and Al are terrestrial elements. This relationship is shown in figure 3.11. In this crossplot a positive linear relationship between Si and Al can be seen. Due to the fact that both Ti and Si posses this linear relationship, both can be expected to have detrital

origins. Since this relationship exists, this can have implications relating to the abiogentic input of silica.

Iron (Fe) also possesses a linear relationship with Al which signifies the occurrence of Fe in illite or siderite and later in pyrite. The Fe particles were transported either with or as clay and could have later binded with the sulfur produced by sulfur reducing organisms creating pyrite and increasing porosity within the Haynesville Formation.

From the calcium (Ca) readings, the dissolution of the clay fraction by means of the carbonate fraction is observed. Through the inverse relationship between Al and Ca it is inferred that the Ca input has a closer association with $CaCO_3$. This $CaCO_3$ input could originate from near shore reefs that exsisted updip from the Haynesville Formation depositional area. Due to the degradation of these reefs and transportation by storm or gulf current, a large accumulation of $CaCO_3$ in the Haynesville Formation was possible.

Concentrations of Mg have no relation with the clay fraction and might have been created diagentically or through microbial nucleation in anoxic conditions resulting in the creation of dolomite. Marine sulfate-reducing bacterium in seawater, at low temperatures, precipitates mg-rich dolomite (Krause et al., 2012).

4.4 Depositional Environment

Through the utilization of geochemistry of both major (Al, Si, Ca, K, P, S, Ti, V, Fe, Mn, Cr and Mg) and minor (Zn, Cu, Mo, Ni, Th, Co, U, Zr and Sr) elements, a better understanding of both the lithology and depositional environment during the laying down of the Haynesville Formation. Molybdinum, chromium, uranium, zinc, nickel, copper and vanadium are redox sensitive trace elements are typically more soluble in oxic conditions and less so in reducing environments. This makes these trace elements more enriched in anoxic sediments (Tribovillard et al., 2006; Mainali, 2011). Due to this characteristic many researchers have used their concentrations to define the paleoenvironment during the deposition. These redox proxies have been said to be enriched anywhere up to two to three orders of magnitude in black shales when compared to those in grey shales (Algeo et.al. 2003). This is also accurate, or in some cases higher, for those with origins from anoxic/euxinic environments (Mainali, 2011).

Besides being indicators of redox environments, trace elements variations also provide information about other water mass properties in ancient marine depositional systems (Algeo and Maynard, 2008). Since sediment has the ability to record detailed outlines of aqueous trace elements, collecting chemostratigraphic data of ancient anoxic marine facies can potentially give insight into the degree of water mass restriction along with basin hydrography and aqueous chemistry (Alego and Maynard, 2008; Mainali, 2011; Rowe et al., 2012).

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The enrichment of the redox indicating trace elements located in organic rich facies are often interpreted through benthic controls which reflect the enhancement of absorption by the sediment where dissolved hydrogen sulfide triggers the aqueous trace element compounds (Zheng et al., 2000; Helz et al., 1996; Vorlicek and Helz, 2002). Additionally, this absorption of the trace elements by anoxic facies is also associated with the concentration of sedimentary organic matter and aqueous species (Alego and Maynard, 2004; Alego and lyons, 2006; Alego and Maynard, 2008). In restricted marine silled basins, such as the East Texas Basin, the concentrations of the trace elements could possibly become reduced due to the absorption by sediments without having any replenishment. This can lead to a reduction in the amount of trace elements per unit of organic carbon in the sediment (Algeo and Maynard, 2008).

The average organic rich mudrock is enriched in trace elements, but the quantity and comparative concentrations can fluctuate substantially in different formations (Piper, 1994; Cruse and Lyons, 2004; Piper and Perkins, 2004; Rimmer, 2004; Rowe et al, 2008; Piper and Calvert, 2009; Algeo and Maynard, 2010; Huges, 2011). Trace element concentrations have examined in various modern anoxic silled basins such as Cariaco Basin, the Black Sea, Saanich Inlet and Framvaren Fjord by previous researchers (Jacobs et al., 1987; Emerson and Huested, 1991; Crusius et al., 1996; Zheng et al., 2000, Algeo and Lyons, 2006; Algeo et al., 2007; Mainali, 2011), and the enrichment of the Mo has been found

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to be moderate which indicates sub-oxic deposition (Poulson, 2006; Mainali, 2011). As a result, sedimentary molybdenum has been utilized as a proxy for paleo-euxinia (Alego and Maynard, 2008). Also, trace metals have varying residence times which make the trace metals accountable for various time periods. Trace elements with comparatively short seawater residence times (Cu and Zn) are removed from the system more quickly than trace elements with longer residence times such as Mo and Ni (Alego and Maynard, 2008).

When evaluating the Haynesville Formation versus the overlying Bossier Formation, a higher enrichment of Mo can be seen in the former formation. Based on the data collected, the enrichment of Mo begins high (in the lower Haynesville) with an average of about 13 while both the middle and lower section of the formation have a lower concentration of an average of 3 (figure 3.12). However, even though the Mo concentrations lessen as you rise in the stratigraphy of the Haynesville, it is still higher than the Bossier which has an average of zero. Many of the readings collected in the Bossier Formation had a negative value for the concentration of Mo which indicates that the environment became more oxic as you grade from the upper Hayneville to the Bossier. The higher Mo concentrations in the lower Haynesville indicate that the depositional environment was anoxic to euxinic while the Bossier was deposited in a more oxygenated environment.

To have a more concise understanding of the redox characteristics of the Haynesville formation, the enrichment factor (EF) is calculated. The samples that have an EF = 1, represent similar levels when compared to average crustal abundance which represents oxic depositional conditions. Additionally, for samples that are enriched compared to average shales would have an EF > 1, while samples with an EF < 1 are considered to be depleted relative to the average shale. The trace metals that were evaluated for the enrichment factor were Mo, Ni, Zn and Cu. The average EF for the Carthage core for each trace metal, respectively, is 3.76, 1.86, 2.04 and 1.81. These ratios imply that the depositional environment during the time of deposition of the Haynesville Formation was anoxically dominated with a transition into dysoxic during the course of the mudstone accumulation. The other trace metals evaluated for EF (Ni, Zn and Cu) also possess an affinity for anoxic-euxinic environments (Alego et al, 2003; Alego and Maynard, 2008). Therefore, the similarity between the EF of said trace elements and EF_{Mo} supports the suggestion that the East Texas Basin had a transition from anoxic to dysoxic during the time of the Kimmeridgian.

Chapter 5

Conclusion

5.1 Remarks on the Haynesville Formation

During the Kimmeridgian age in the late Jurassic epoch (approximately
150 mya), the Haynesville formation was deposited in the deep, partly
anoxic/euxinic East Texas Basin. This basin was produced as a product of the
European and African/South American plates colliding with the North American
plate. This formed the Ouachita Mountains during the Mesozoic Era. The East
Texas Basin was buried beneath thick deposits of marine salt as the European and
southern continents continued to drift away from North America. The faults
within the East Texas Basin are normal and moved syndepositionaly. They were
formed by various processes associated with the gravitational induced creep of the
Louann salt gliding over a salt décollment zone, then followed by crustal
extension and collapse over salt pillows and turtle structures. Salt then dissipated
from beneath downthrown blocks (Jackson, 1982; Steinhoff, 2011).

The salt movements as well as the basement structures in this area
influenced carbonate and siliciclastic sediments associated with the Gulf of
Mexico. The Haynesville deposition is related to the 2nd order transgression that
deposited organic rich black shales worldwide (Hammes et al, 2011; Hammes and
Frebourg, 2011; Jabri, 2013). It was deposited on a gently dipping ramp,
intraplatform basin to the north and distally steepened ramp to the south. The

Haynesville lies as the upper member of the Louark group between the Cotton Valley Group and the Smackover Formation. The Haynesville is considerably more calcareous than the overlying Bossier Formation and less calcareous than the underlying Smackover Formation of the mid-Jurassic age. The Haynesville is unique in that it acts as both the source rock and reservoir rock which is characteristics of unconventional reservoirs.

The geochemical data collected for this research is utilized to reconstruct the chemostratigraphy of the Haynesville Formation. Various geochemical proxies were examined to reconstruct the paleoenvironment of the Kimmeridgian aged Haynesville Formation of the East Texas Basin. The comparison between 5 X Al_2O_3, SiO_2 and 2 X CaO can be seen. The SiO_2 represents the quartz mineralogy; the 5 X Al_2O_3 signifies illite, albite, chlorite or kaolintite; while the 2 X CaO denotes carbonate rich organics. Due to the higher concentrations of Si in the Lower Bossier Formation while having lower Ca readings indicates that the Bossier is silisticlastic when compared to the carbonate rich Haynesville Formation. The inverse relationship between Al and Ca within the Carthage core, illustrates how the Ca within the Haynesville is associated with the carbonate fraction since the carbonate fraction dilutes the clay fraction. The Fe examined in the Bossier Formation suggests that the Fe has a closer association with siderite or pyrite rather than the clay fraction due to the data that falls off the average shale line. The relationship between Ti and Al represents that the Ti is

associated with the clay fraction through rutile in lattice with the clay. When observing the Mg versus Al data, there is neither a linear nor non linear relationship. This indicates that the Mg is associated with dolomite. Either as diagenetically altered limestone or dolomite that was created in situ during deposition.

Due to the redox sensitivity of the trace elements measured, they are more enriched in anoxic sediments; because of this characteristic, they are utilized to define the paleoenvironment during deposition. Resonance times vary among these trace elements creating accountability for various time periods. Based on the data collected, the enrichment of Mo begins high (in the lower Haynesville) with an average of about 13 while both the middle and lower section of the formation have a lower concentration of an average of 3. The other trace metals evaluated for EF (Ni, Zn and Cu) also possess an affinity for anoxic-euxinic environments (Alego et al, 2003; Alego and Maynard, 2008). Therefore, the similarity between the EF of said trace elements and EF_{Mo} supports the suggestion that the East Texas Basin had a transition from anoxic to dysoxic during the time of the Kimmeridgian.

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Biographical Information

Lauren Ashley Woolston Graduated from the University of Texas at Arlington with his B.Sc. in Geology. She is currently working towards his Masters in Petroleum Geology, proudly as a UTA Maverick. She is auspiciously employed in the hydrocarbon industry. Lauren's main focus is the exploration and development of the hydrocarbons by any technique available/possible. Many different aspects go into successfully producing economical energy. Geochemistry, Sedimentology and Biostratigraphy were her most valued subjects. She was mostly influenced by Dr. Harry Rowe, Dr. John Holbrook and Dr. Wickham. Additionally, she maintains a intense appreciation for all things related to science. Her desire for knowledge was well challenged by the highly competent faculty at University of Texas at Arlington.