Rare Earth Elements (REEs) in Crude Oils in the Lansing-Kansas City Formations in Central Kansas: Potential Indication about Sources of the Oils, Locally Derived or Long-Distance Derived*

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Abstract

There are some who hold the view that liquid hydrocarbons in the upper Paleozoic formations in Kansas are being locally derived. It has been the long held belief that the liquid hydrocarbons found in Kansas have come from distant sources in Oklahoma. To shed further light on this issue about the origin of hydrocarbons in the upper Paleozoic formations in Kansas, a study was conducted to analyze the geochemical characteristics of REE in Lansing-Kansas City Group oils that were collected from several locations in a small area within Rooks County, Kansas. The total REE contents in these oils ranges from about 3.1 ng to about 131 ng per liter of oil. The pattern of relative distribution of the REEs for each oil sample was normalized to the PAAS. The PAAS-normalized patterns of relative distribution of the REEs in the Lansing-Kansas City oils from Rooks County, Kansas are significantly diverse. Although nearly all oil samples investigated in this study have varied degrees of light REE-enrichment across the REE series from La to Sm, they differed in their relative Ce abundances. Some samples have positive Ce anomalies; some have negative Ce anomalies, and some others with the absence of any Ce anomaly. The oils also differed in their PAAS-normalized relative distribution of the middle rare earth elements (MREEs). All oil samples were apparently enriched in the MREEs, but ranging from a prominent one to almost a barely noticeable one.

The oils differed in their relative distributions of Eu, as some were with a positive Eu anomaly, some with a negative Eu anomaly, and some with the absence of any Eu anomaly. The trends of the heavy rare earth elements (HREEs) from Tb to Lu among the oils ranged from nearly

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flat for most oils to a progressive depletion across the series for few samples. Furthermore, the oils were varied in having anomalous relative distributions for some specific individual heavy rare earth elements, positive distributions for Tb, Ho, and Tm.

Different zones in the Lansing-Kansas City formations also show distinct REE distribution patterns. There are four broadly classified distribution patterns. The oils not only differed significantly in their REE-geochemical characteristics, they also had a wide range of K/Rb weight ratios from about 877 to about 2000. The variations in REE characteristics and in the K/Rb ratios are reflections of different source materials. The diversity in the REE distribution patterns and K/Rb ratios in oils collected from central Kansas makes a strong argument against long distance transportation from a distant source in Oklahoma.

Introduction

The Lansing-Kansas City Group is the second largest producing unit in Kansas, with over one billion barrels recovered to date. This prolific rock unit accounts for 19% of Kansas' total oil produced each year. The majority of Lansing-Kansas City production has come from conventional production due to the nature of the rock unit (thin interbedded limestone and shale), but there could be the possibility for unconventional production in the future. The unique property of the Lansing-Kansas City Group is that it has the ability to produce from multiple zones in one well. In Rooks County, Kansas the Lansing-Kansas City consists of 14 zones of alternating limestone units (zones A-L) separated by shales. Of these 14 zones, the Lansing-Kansas City produces from 7-8 different limestone zones.

This study focuses on determining geochemical characteristics of Rare Earth Elements (REE) of oil from the Lansing-Kansas City formations in Central Kansas. REE have proven to be useful tracers in many geological and geochemical investigations and demonstrate important applications in igneous, metamorphic, and sedimentary petrology (Rollinson, 1993). To date, studies on REEs in organic rich shales have been very limited (Abanda and Hannigan, 2006; Dao-Hui et al., 2013; Ramirez, 2013). Investigations of REEs in crude oils have been very few. Ramirez (2013) was the first to use the REE geochemical potential for crude oil correlations. In Ramirez (2013), REE geochemical investigations were targeted on oils generated in the Woodford Shale and overlying Mississippian Formation located in the Anadarko Basin, in north-central Oklahoma. This study on the Lansing-Kansas City crude oils from Rooks County, Kansas takes the same approach as that by Ramirez (2013).

This study had two-fold purposes. One of these was to find correlations among the oils produced from different zones within the Lansing-Kansas City formations within a limited area in Rooks County, Kansas. A second goal was to examine if REE data can be used to provide any clue as to the source of the oil. It is believed by most geologists that crude oil in many parts of the mid-continent is sourced primarily from the Woodford Shale in central Oklahoma. By placing the source of the Midcontinent petroleum system in central Oklahoma, oil in northwestern Kansas and northern Kansas, as the oil in Lansing-Kansas formations, would have to be transported approximately two hundred miles. The REEs geochemical characteristics, specifically the REE distribution patterns, may shed important light on the history of transportation of the crude oil. The REE geochemical investigations may prove to be useful to test the validity of long-distance transportation (migration) of the Lansing-Kansas City oil. Long-distance transportation of crude oils, generating from different source beds, will likely entail nearly uniform REE distributions at the reservoir sites far distant from the sources. On the contrary, crude oils originating from locally situated diverse source beds may show widely different REE distribution characteristics. This study hypothesizes that oil in the Lansing-Kansas City Group in central

Kansas is being locally sourced, rather than originating from the Woodford Shale source in central Oklahoma (<u>Figure 1</u>). To provide evidence for this hypothesis, this thesis has analyzed 9 different samples from different zones in the Lansing-Kansas City formations. Many of these samples are producing from multiple zones within the Lansing-Kansas City.

Investigations of metals in crude oils have been carried out in many past studies including Corbett (1967), Filby (1975), Shirey (1931), Witherspoon (1957), Yen (1975), Lewan and Maynard (1982), and Schumacher (1986). A review of these different studies is included in Lewan and Maynard (1982). Vanadium and nickel in crude oils appear to be useful for the history of liquid hydrocarbons. Lewan and Maynard (1982) concluded that the vanadium/nickel ratios remain unchanged during migration of the liquid hydrocarbons from source bed to the reservoir rocks, implying that the ratios of the liquids would be a good indicator of the sources from which the liquids are derived. The REEs investigations may also hold promise for crude oil correlations and the migration history of crude oils.

Geologic Setting

The study area is located in northwestern Kansas in Rooks County. The major structural features that affect the study area are the Cambridge Arch and the Central Kansas Uplift. Together these two structures are referred to as the Central Kansas Uplift. These anticlinal structures are ridges of Precambrian granite trending northwest-southeast that formed during major periods of tectonic movement during pre-Mississippian and Middle Pennsylvanian times. Movement of the Cambridge Arch also occurred during Mesozoic time (Newell et al., 1987). Above the basement granite lays the Cambro-Ordovician Arbuckle Dolomite, which is the primary oil producing rock unit in Kansas. As the Central Kansas Uplift is approached, the formations below the Pennsylvanian and above the Arbuckle tend to pinch out until the Lansing-Kansas City rests upon the Arbuckle. At points on the Central Kansas Uplift the Arbuckle is completely eroded away. The Central Kansas Uplift and Cambridge Arch are bound on each side by similar basin areas: the Salina Basin to the northeast, the Hugoton Embayment to the west, and the Anadarko Basin to the south. The study area, Rooks County, is located on the eastern flank of the Central Kansas Uplift. The majority of Lansing-Kansas City oil production in Kansas occurs on the Central Kansas Uplift.

Deposition of the Lansing-Kansas City

The Lansing-Kansas City formations are part of the Missourian Stage of the Upper Pennsylvanian series. Most Pennsylvanian rocks in Central Kansas were deposited in shallow seas that alternately covered, then retreated from the land. The reoccurrence of the rising and falling sea levels caused the Pennsylvanian rocks in Kansas to occur as interbedded limestone and shales with occasional coal deposits and sandstones. In northwestern Kansas, carbonate facies in the Lansing-Kansas City are highly variable (Watney, 1980). The Lansing-Kansas City ranges from 200-400 ft in thickness over the Central Kansas Uplift. Moving south from the Cambridge Arch towards the Anadarko Basin, the Lansing-Kansas City Group become more massive. This indicates the Anadarko Basin was subsiding and expanding northward from Morrowan through Missourian time, after which subsidence decreased, resulting in shoreline regression and basin filling during Virgilian and later time. The act of subsidence and expansion created the alternating cyclic terrigenous clastic and carbonate strata. Individual cycles less than 30 meters in thickness were deposited in northwestern Kansas as a response to fluctuations of sea level and progradation of sediments. Each cycle in this area is characterized by four basic components: a thin but distinctive basal transgressive unit, overlain by marine shale, followed by the regressive carbonate and regressive shale (Merriam 1963) (Figure 2).

Materials and Methods

The crude oils collected in this study were taken from different stratigraphic zones in the Lansing-Kansas City formations at different locations in Rooks County, Kansas. 1000 ml of crude oil was taken from each well. The samples were centrifuged at high speeds for four hours to remove the presence of any water. The centrifuged oil samples were processed for ashing to determine their metal contents. The aliquots of the oil samples were processed for gas chromatographic analysis.

Initially, 100 ml of oil was treated with 30 ml of vacuum sealed doubly distilled purified nitric acid. This 4N volume of oil provided no detectable amount of REEs by ICP-MS analysis. Next we used 200 ml of oil that was ashed and then treated with the same volume 4N diluted concentrated nitric acid. Again, no REE could be detected by ICP-MS analysis. Next we used 500 ml of oil, and this time only La, Ce, and Nd were detectable. Sm to Lu was not detectable at all. Finally, 1000 ml of oil was used with the same amount of reagent added to it as before. All REEs were detectable by ICP-MS analysis.

REE Sample Preparation

The sample processing began by extracting crude oil from sample bottles. The sample bottles contained a mixture of crude oil and brine that is associated with oil. The oil was extracted by carefully pipetting out of the sample bottle, avoiding contact with the brine. The pipetted oil sample was placed into 22 cleaned 50 ml centrifuge tubes. Each sample was then centrifuged for 4 hours to ensure separation of oil and brine. It was observed that centrifuging removed 2-3 milliliters of brine from each centrifuge tube full of oil. Each oil sample was then weighted by the milliliter, in an electronic scale to know the sample's mass in grams. After this separation process was completed, the evaporation process began for the oil samples.

A process (Figure 3) implemented by Ramirez (2013) was used for crude oil evaporation and ashing. The initial evaporation started at 200 degrees Celsius on a covered hot plate. At this temperature the samples will emit smoke, but not boil. Each oil sample took an average of 100 hours for slow evaporation. The temperature was increased incrementally during the 100 hours. After 100 hours of heating the temperature was gradually raised to 550° C for another 100 hours. At this point the oil has evaporated off the light fraction materials, leaving nearly a solid substance in the bottom of the evaporation beaker. To continue the evaporation processes, 30 ml 4N Vycor vacuum double distilled HNO₃ solution was added to the crude oil. This process caused the sample to turn into a hard ash substance. The samples were left on the hot plates overnight and evaporated to dryness. After each sample was cooled, the substance was broken into small fragments. 60 ml of 4N HNO₃ was used to rinse the dried ash and the solution was collected in a 100 ml crucible. A known fraction of this was drained out and evaporated to dryness. The dried sample was then redissovled in 15 ml of 1N HNO₃, which made the final solution for the REE and other metal analysis.

Analytical Precision

REEs, Rb, U, Th, and Pb were determined by the ICP-MS and the K and other major elements were analyzed by the ICP-AES. These analyses were done at the University of Strasbourg, France. A blank sample of the nitric acid used in this study was run on the ICP-MS and the total REE concentrations were approximately 2.5 ng. The amounts of reagents used in this study were the same for all oil samples, each of which

started one liter volume. Smaller volumes of oil (100 ml to 500 ml) were used in preliminary laboratory preparations, taking same volume of reagents as that was used for the one liter volume of oil, but these smaller volumes failed in giving any measurable REE data. Only the one liter volume of oil provided detectable amounts of all the REEs.

The routine REE analysis done at the University of Strasbourg laboratory has found the analytical errors are limited to 10% or less. The errors of the analytical precisions for other metals (K, Rb, etc.) are between 5-10%. Repeat analyses for the same oil samples were not done in this study. A previous study by Ramirez (2013), which followed the same analytical procedure as this one, duplicated the analyses and found the data in agreement within 10%. An unpublished study by Alvarez in our laboratory was also able to duplicate the results within 10%. Thus, the precision of the data in the present study should be limited to 10% error.

Discussion

Gas Chromatographic Data

Biomarkers are a group of compounds found in hydrocarbons that are considered "molecular fossils." Biomarkers are structurally similar to living organisms, but have been diagenically altered. Biomarkers allow exploration geologists to evaluate the type of source rock, maturity of the oils, and alterations incurred upon the oils following accumulation (Evans, 2011). The two groups of biomarkers looked at in this study are the n-alkanes and the isoprenoids.

The original chromatograms show three different trends with normal alkanes or n-alkanes. The first trend shows a high peak around nC6 and nC7 with a rapid decrease until nC11/nC12, then a small hump between nC13-nC15 and a gradual decline until the end of the chromatograph. There are six samples showing trend one: MM-JS-02, MM-JS-03, MM-JS-04, MM-MC-01, MM-WM-11A, and MM-JK-01. The second trend is similar to the first, but without a prominent peak and decline around nC6/nC7. This trend shows one high peak at nC7 with nC8 significantly lower. Between nC8 and nC12 there is a gradual increase in size of the peaks, with the top of the hump occurring at nC13/nC14 and a gradual decrease until the end of the chromatogram. There are four samples showing trend two: MM-MC-1A, MM-MC-3A, MM-MC-4A, MM-DJ-02. The third trend only occurred in one sample, MM-PJ-01. This pattern shows the possibility of biodegradation of the oil. The values of the biomarkers between nC6 and nC12 are significantly lower than the ten other samples. There is a large hump that forms between nC13 and nC17 and a rapid decrease until the end of the chromatogram. Values for the n-alkanes between nC11 and nC30 were converted into a normalized percent and plotted on a graph for correlation of all 11 samples (Figure 10). The largest differences are observed between nC11 and nC17, as well as towards the end of the sequence.

After n-alkanes were determined, isoprenoids were studied and values were converted to normalized percent. Isoprenoid signatures show little differences between the eleven samples. In general, IP14 and IP15 share about the same value. IP16 has the highest peak with depletion in IP17 and a high peak at pristine. The normalized percent of the isoprenoids were plotted on a graph for correlation of the eleven samples (Figure 11).

The pristine and phytane values were calculated and converted into a normalized percent, the same as the rest of the isoprenoids. A pristane/phytane ratio was calculated for each sample (<u>Table 3</u>). Pristane and phytane are commonly looked at together as a ratio (Pr/Ph). The

Pr/Ph ratio of a crude oil is a reflection of the source of the original organic matter and the paleoenvironmental conditions during decomposition and early burial. Higher Pr/Ph values (3 to 15) indicate a source from mostly land derived organic matter that has passed through a highly oxygenated state in its decomposition. Low Pr/Ph values (1.1 to 2) indicate oil that has been generated from marine organic source materials. The Pr/Ph values for each of the eleven samples range from 1.15 to 1.48 (<u>Table 3</u>). These values indicate that the source of oils in the Lansing-Kansas City formations is a collection of marine organic source materials.

Finally, the carbon preference index (CPI) was calculated for each oil sample (<u>Table 3</u>). The CPI is a measure of the odd and even n-alkane chain length preference in crude oil. Values for the Lansing-Kansas City oils ranged from 0.98 to 1.01, indicating the source contains marine biologic materials which may be associated with carbonate and/or organic rich argillaceous rocks (Evans, 2011). The CPI thus corresponds to Pr/Ph ratios in reference to the source.

REE Relative Distribution Patterns

Although samples for this study were taken from a relatively small area in central Kansas, the REE distribution patterns vary greatly. Nearly all oil samples investigated in this study have varied degrees of light REE-enrichment across the REE series from La to Sm, they differed in their relative Ce abundances. Some samples have positive Ce anomalies; some have negative Ce anomalies, and some others with the absence of any Ce anomaly. The oils also differed in their PAAS-normalized relative distribution of the middle rare earth elements (MREEs), ranging from Sm to Tb. All samples collectively had varied enrichments in MREE ranging from a prominent degree in one or two samples, to a slight enrichment in one, to no enrichment (Figure 4). One sample with a highly anomalous REE distribution pattern (MM-MC-01, Figure 6) may suggest depletion in MREE. The oils differed in their relative distributions of Eu, as some were with a positive Eu anomaly, some with a negative Eu anomaly, and some without a Eu anomaly (Table 2). The trends of the heavy rare earth elements (HREEs) from Tb to Lu among the oils ranged from nearly flat for most oils, to a progressive depletion across the series for few samples. Furthermore, the oils were varied in having prominently anomalous relative distributions, in some cases with a positive anomaly and in others with negative anomaly, for such elements as Tb, Ho, Tm, and Lu, which potentially implies biogenic enzyme influence (Figure 5, Figure 6, Figure 7, and Figure 8).

Cerium and Europium anomalies are measured by finding the value of cerium or europium that the distribution pattern should follow if there was no depletion or enrichment, by interpolating between the normalized values of Lanthanum and Praseodymium for cerium anomaly, and Samarium and Terbium for the europium anomaly. The calculated value is designated as Ce^* or Eu^* . The analytical value of Ce and Eu is divided by the Ce^* and Eu^* calculated values. Due to analytical error margin of 10% from the laboratories used, when calculating the anomalies, a standard is set where my value is considered an anomaly when having a value of $\pm 10\%$ for enrichment or depletion ($\underline{Table 1}$ and $\underline{Table 2}$).

MREE Enrichment

Seven out of the nine samples have been found to have MREE enrichments (MREE with convex upward trends). MREE enrichments can generally be attributed to increases in phosphates. It can be reasonably argued that organic matter associated with the source of the Lansing-Kansas City was a prime source of this phosphorous, which became available during organic matter transformation.

Europium Anomalies

A commonality found in the most of the MREE portion of the distribution patterns is a Eu positive anomaly. Five of the nine samples exhibit a strong Eu positive anomaly. Two samples (MM-JS-04 and MM-MC-3A) recorded no Eu values because the element was below detection limit (Table 2). The Eu anomaly could not be calculated for sample MM-MC-01 because Gd was below detection limit.

Most geochemists working on crustal inorganic materials have attributed positive Eu anomalies in such materials to crystallographic effects, especially feldspar minerals which favor accommodation of Eu²⁺ over a trivalent species. But those who have worked on modern plants, like Chaudhuri and Clauer, have found Eu positive anomalies in plants relative to their growth substrates. The evidence from such studies does not support the idea of a crystallographic effect. Often finding differences in Eu anomalies among different organs of the same plant, Chaudhuri and Clauer (2007) believe that plant enzyme effect plays a significant role in Eu anomalies in the organic materials.

HREE Enrichment

There are several samples that show a Tb, Ho, or Tm positive anomaly (Figure 5 and Figure 6). These anomalies were determined by looking at the overall trend of the REE distribution patterns. The anomalies have been common with Eu and Ce in natural materials because of the difference in the oxidation states from the natural (III) oxidation state for all the REEs. Thus, Ho, Tb, and Lu anomalies, varied in different degrees among the samples, and these are reflections of the growth history of the organic source material, arising potentially from enzymatic influence during the growth of the organic materials.

LKC Zone Correlation

There are four broadly distinct REE distribution patterns. These patterns correlate well to specific zones of production in the Lansing-Kansas City formations. The first pattern (Figure 7) includes wells MM-WM-11A, MM-MC-1A, and MM-MC-4A. The REE distribution patterns in general were slight LREE enriched to nearly flat. All samples show a slight MREE enrichment. La enrichment is due to La-Ca replacement. Ca is an important component needed for plant growth. La has a similar size to Ca, often times replacing Ca in plant enzymes.

The second pattern (Figure 8) includes wells MM-JS-02, MM-JS-03, and MM-JK-01. All samples in this pattern show a slight MREE enrichment due to a phosphate influence. Each sample has mixed zone production. The mixed zones deferred sometimes to a positive Gd anomaly, in other situations Ho and Tm negative anomalies.

The third pattern (<u>Figure 5</u>) includes wells MM-JS-04 and MM-MC-3A. These distribution patterns are described as having nearly flat REE distribution patterns with a slight LREE enrichment. MM-JS-04 has very prominent Tb and Ho positive anomalies, unlike MM-MC-3A with a flat distribution pattern.

The fourth pattern (Figure 6) contains MM-MC-01. This pattern is showing production from solely the LKC "A" zone. It was characterized by a very rough concave upward distribution pattern, which may suggest an influence of phosphate depletion. Nevertheless, the most significant

features of this distribution pattern are marked with positive anomalies of a number of REEs. The oil coming from this single zone must be derived from varied organic sources. MREE enrichment (<u>Figure 7</u> and <u>Figure 8</u>) can be observed in samples with production from the middle Lansing-Kansas City zones (G-I). In samples with comingling LKC zones (<u>Figure 5</u> and <u>Figure 8</u>), amplification of anomalies from differing source materials can be observed.

K/RB Ratios in Crude Oil Samples

Potassium (K) is essential for all forms of life and is taken up by plants in its cationic form (K+). Rubidium (Rb), a trace element with similar properties as K, in contrast, has no biological function. The uptake of Rb is also much more sensitive to changes in soil properties such as K availability, acidity, and absorption properties of the soil. This results in typically higher K/Rb ratios in biological materials than in soils (Peltola et al., 2008). Based upon assumptions regarding average chemistry of smectites and illites, the average shale requires 13.4% potassium feldspar to provide the necessary K+ (Totten and Blatt, 1996). As the average shale only contains 5% feldspar (Blatt, 1992), an additional source for potassium is required. A study by Chaudhuri et al. (2007) also showed that when K is studied in conjunction with Rb, the K/Rb ratio can be a strong geochemical tracer for the source of potassium into a system. Their study concluded that K/Rb ratios are much higher in organic materials than in common K bearing silicate minerals, like feldspar and mica.

K/Rb ratios taken from eight Lansing-Kansas City crude oil samples range from 877 to 2000, which indicates a large influence from organic matter in the crude oils. According to Chaudhuri et al., 2007, silicate minerals have a K/Rb ratio range from 50-650, significantly lower than the crude oil samples in this study (Figure 9). According to the currently accepted petroleum system model for the midcontinent (Figure 1), oils in the Lansing-Kansas City group would have migrated from two potential sources in northern Oklahoma: Ordovician and Devonian aged rocks (Gerhard, 2004). The hypothesis presented by Gerhard argues that the intersection of fractures of the Nemaha and Central Kansas Uplift form a structural barrier to migration, so that oil moving from the south is shunted along the major fractures to fill reservoirs on and along the uplifts. If the oils in the Lansing-Kansas City reservoirs migrated along fracture pathways from the Anadarko Basin, K/Rb ratios will be expected to have a narrow range of values. If the oils migrated such a long distance, the oils exchanged K/Rb values with the silicate values. This study is supportive of the idea based on significantly high K/Rb ratios in Lansing-Kansas City oil samples the local oil generation in the northwest Kansas is a strong possibility. The ratio range of 877-2000 is indicative of local source rock variations. The local source rocks may not appear to have attended the appropriate vitrinite reflectance in conformity with the accepted oil-window temperature. Hence the assertion of local source derivation for the oil will require an explanation. If either a metal aided catalytic effect on the organic matter transformation or natural radioactive source radiation promoted a reaction, or both might have played an important role in this local source transformation to generate oil.

Conclusions

Walters (1958) and Price (1980) both advanced the theory of long-distance migrations of oil from the Anadarko Basin to central Kansas through Arbuckle rocks, during the Mid-Permian. Their model calls for decreasing amounts of oil and gas to be emplaced northward as traps fill and correspondingly decrease the supply of petroleum for more northerly traps. The barriers to this migration model suggested herein simply adds one more complication to the migration story and does not assume a restricted supply of petroleum from the Anadarko Basin

(Gerhard, 2004). It can be argued from this study that the belief that liquid hydrocarbons in northwest Kansas did not all migrate from the Anadarko Basin, but instead have some component of local source generation.

When comparing results from tools such as REE distribution patterns and K/Rb ratios there are a significant amount of differences between each sample. Total REE concentrations range from 0.0032 to 0.131 ng/L of oil. REEs also vary in their distribution patterns, specifically in the HREE values. Depending on which elements are enriched or depleted could mean a different type of source material or difference in source rock. K/Rb values show the largest amount of differences, with values ranging from 877 to 2000. These values indicate a K/Rb source originating from organic materials. The difference in these results suggests a local oil source. We believe that if the oils in the Lansing-Kansas City originated from the Anadarko Basin, the REE and K/Rb data for all the oil samples would be expected to be similar due to potential hydrocarbon mixing over long distances. Looking at gas chromatograph data for each oil sample, there are three distinct oil classifications shown. Differences in biomarker patterns also supports the idea of varying sources. The collective information from this study strongly suggests local source variation is a strong case for oil generation and accumulation in the Lansing-Kansas City formations in Rooks County, Kansas.

Much work still needs to be done to determine an exact source of the oils in the Lansing-Kansas City Group. Shale units in the Lower Kansas City and other formations around Kansas that show strong gamma ray signatures should be investigated for REE concentrations, TOC, and vitrinite reflectance.

Chaudhuri et al. (2011) have shown that oil field brine can be a useful tool for understanding organic processes during sediment deposition and hydrocarbon generation. Lansing-Kansas City brines collected during this study should be analyzed and compared to the hydrocarbon data.

The idea of hydrocarbon generation, while probable in deep basin environments, only focused on the temperature increase on organic matter but does not take into account all five regimes present in petroleum source beds. Those regimes are the atmospheric gases, lithosphere or mineral matrices, hydrosphere or H20, biosphere or organic materials, and the ergosphere or energy produced from temperature increase and radioactive decay of isotopes present in source beds (Kelly, 2014).

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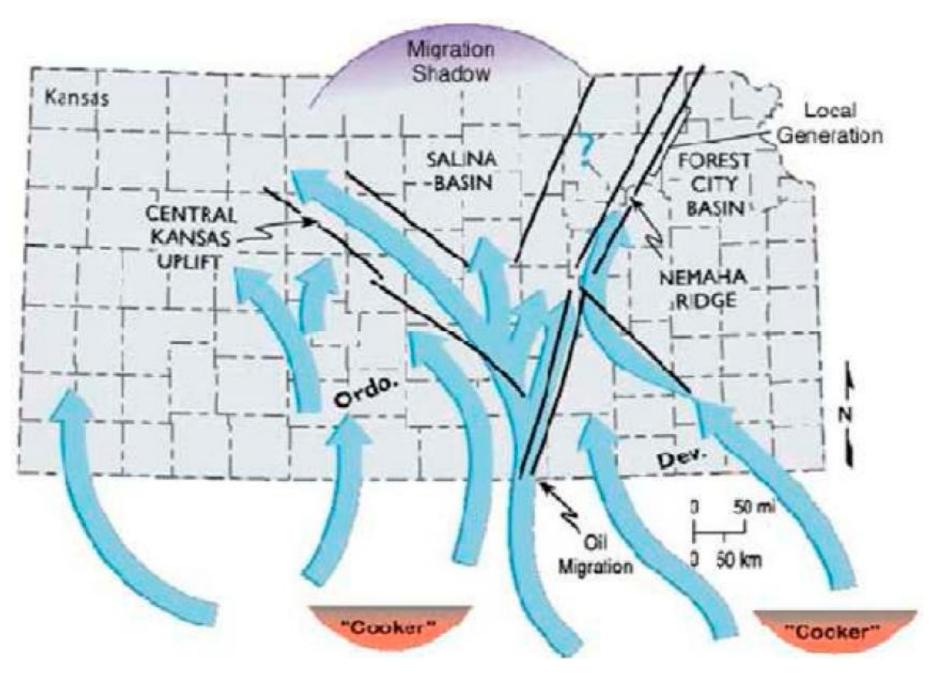


Figure 1. Map of hypothesized northward migration routes of oil originating from the Woodford Shale sources in Oklahoma.

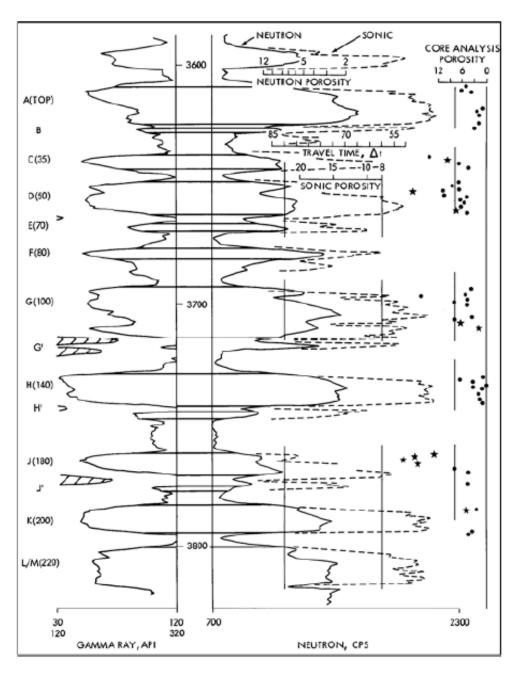


Figure 2. Example electric log showing cyclic nature of Lansing-Kansas City Group strata.

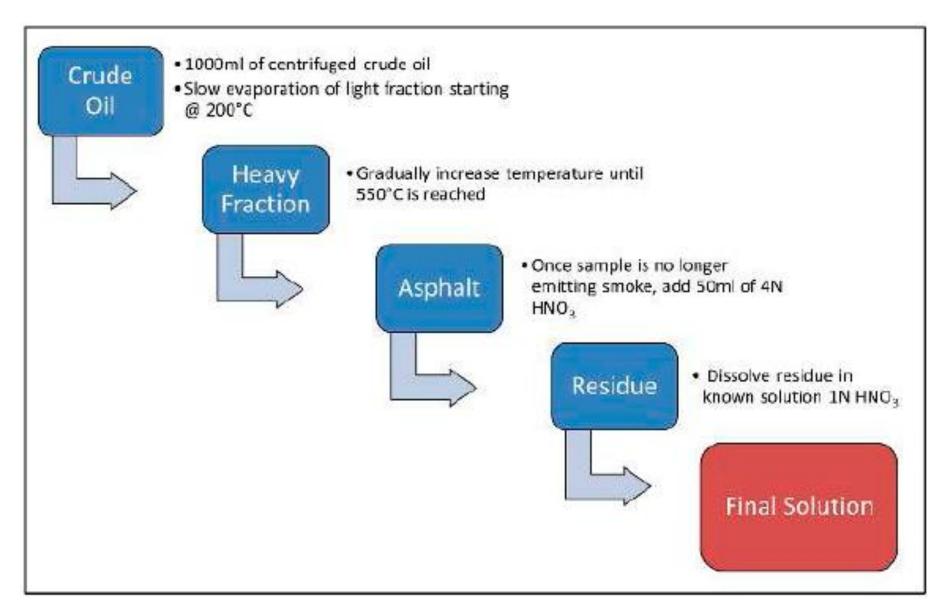


Figure 3. Schematic showing the process implemented by Ramirez (2013) and used for crude oil evaporation and ashing.

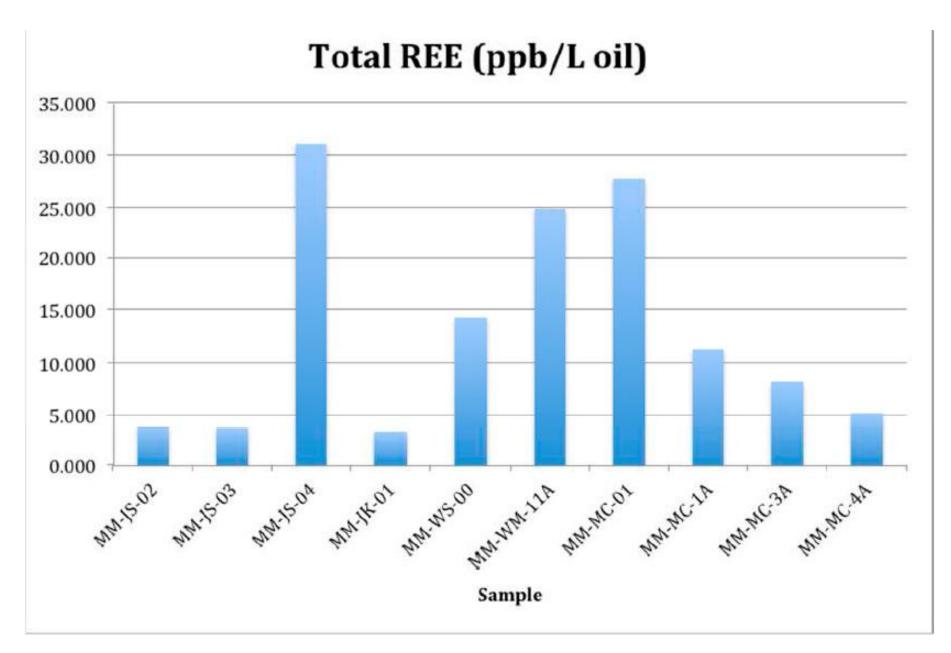


Figure 4. Total Rare Earth Elements (REE) chart of 10 study samples.

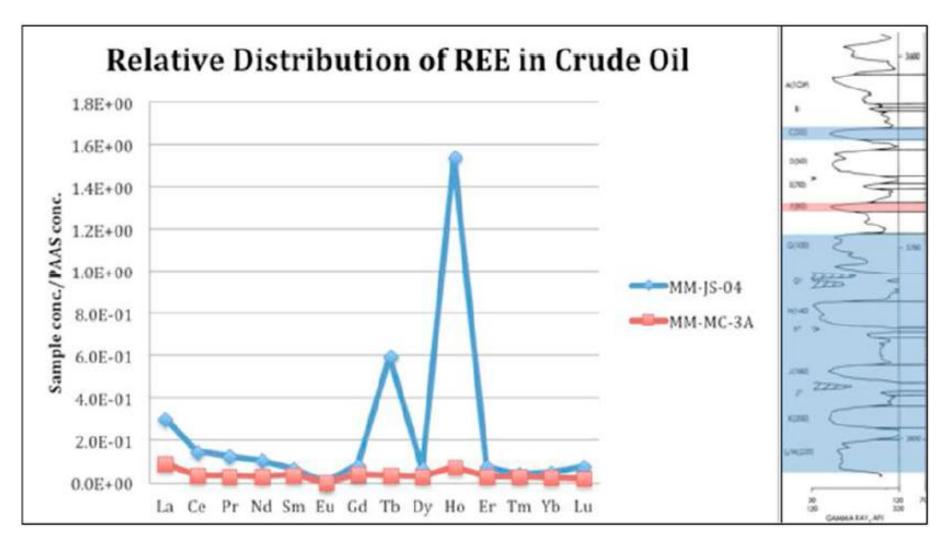


Figure 5. Relative distribution of REE in crude oil from two study samples of the Lansing-Kansas City.

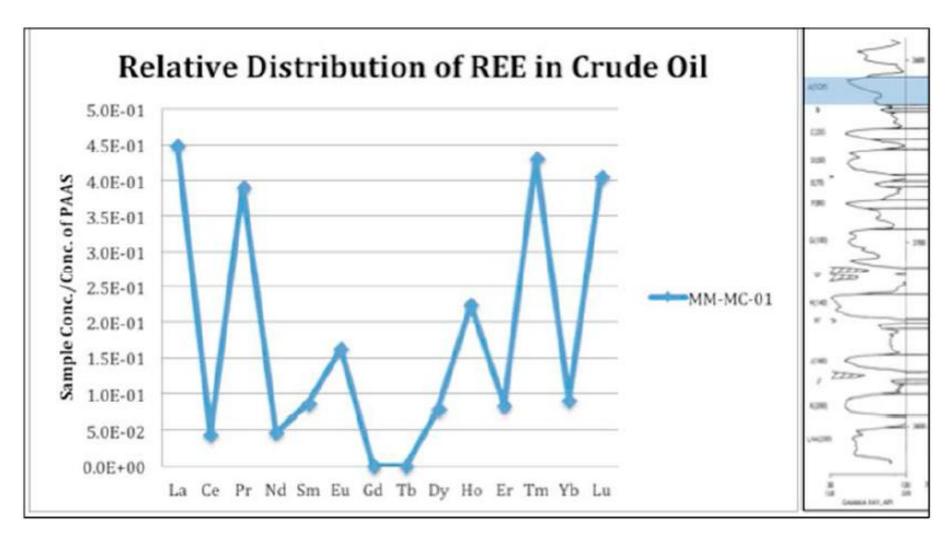


Figure 6. Relative distribution of REE in crude oil from one study sample of the Lansing-Kansas City.

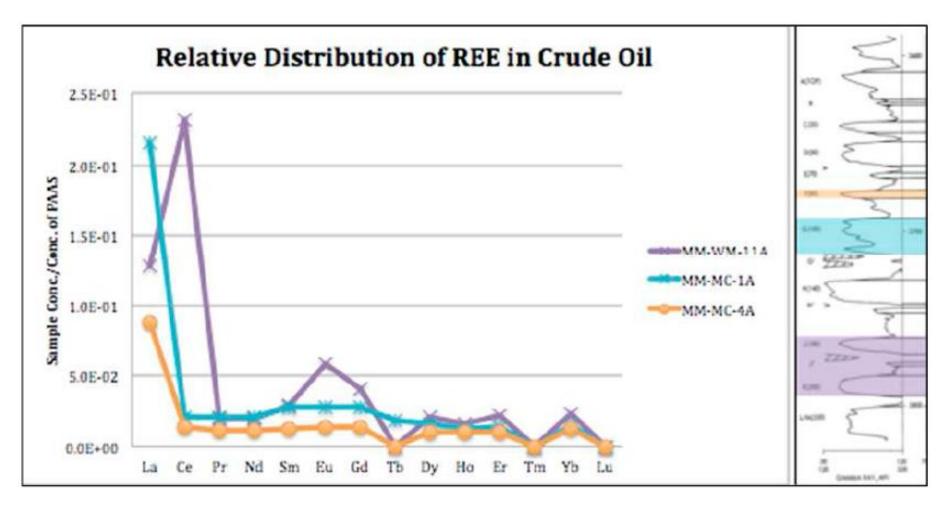


Figure 7. Relative distribution of REE in crude oil from three study samples of the Lansing-Kansas City.

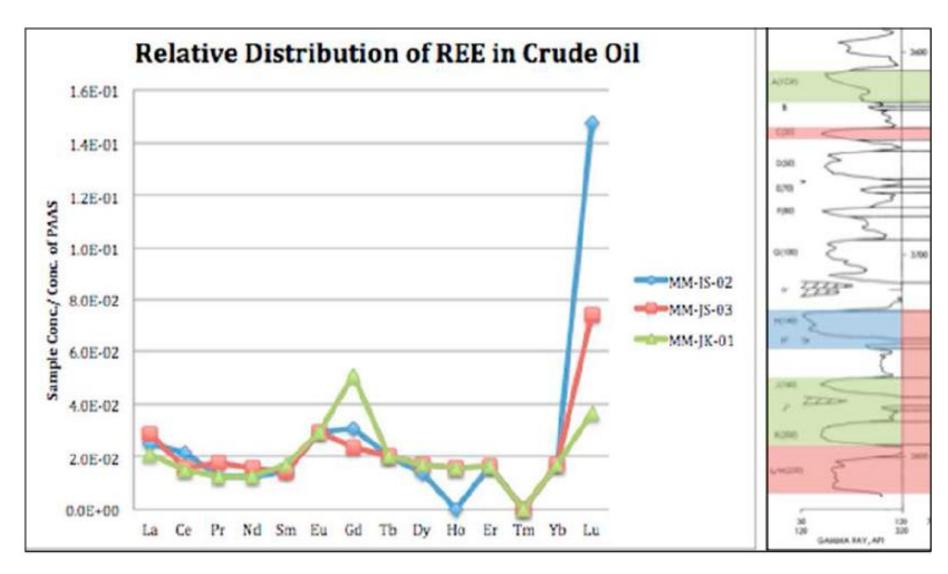


Figure 8. Relative distribution of REE in crude oil from three study samples of the Lansing-Kansas City.

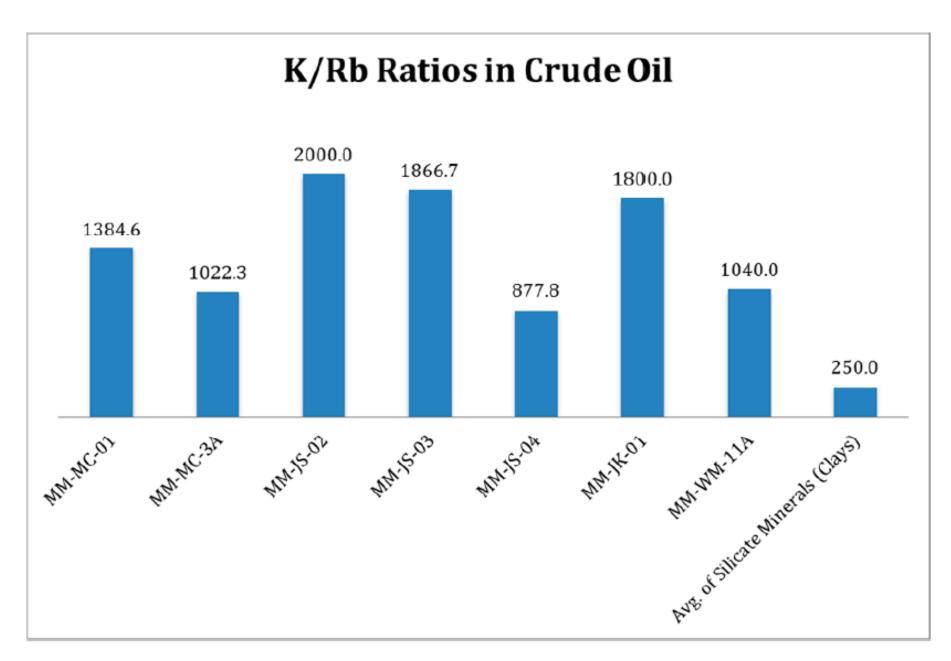


Figure 9. K/Rb ratios graph of seven study samples.

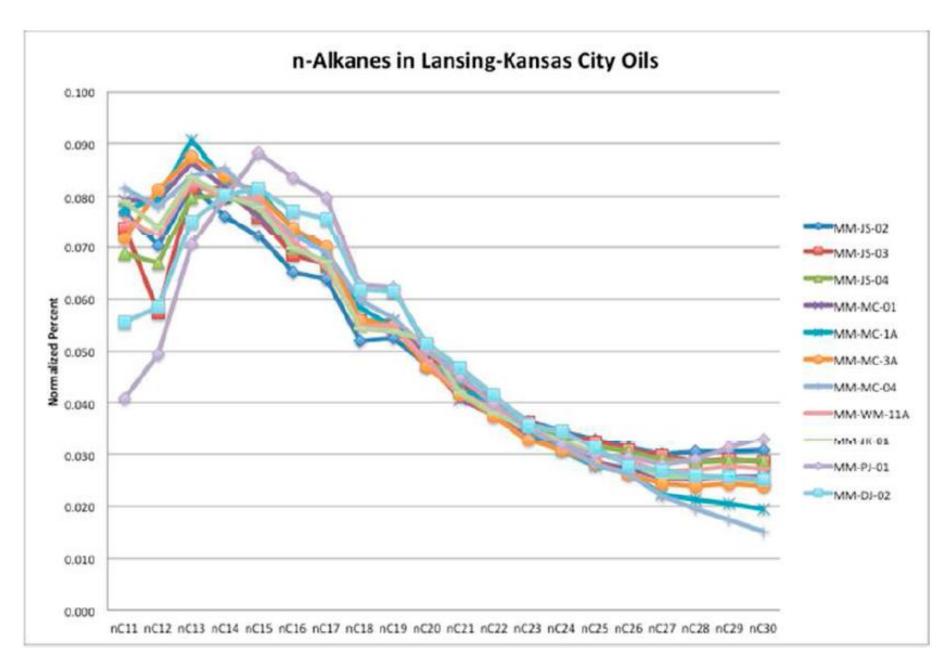


Figure 10. Graph of n-Alkanes of the studied Lansing-Kansas City oil samples.

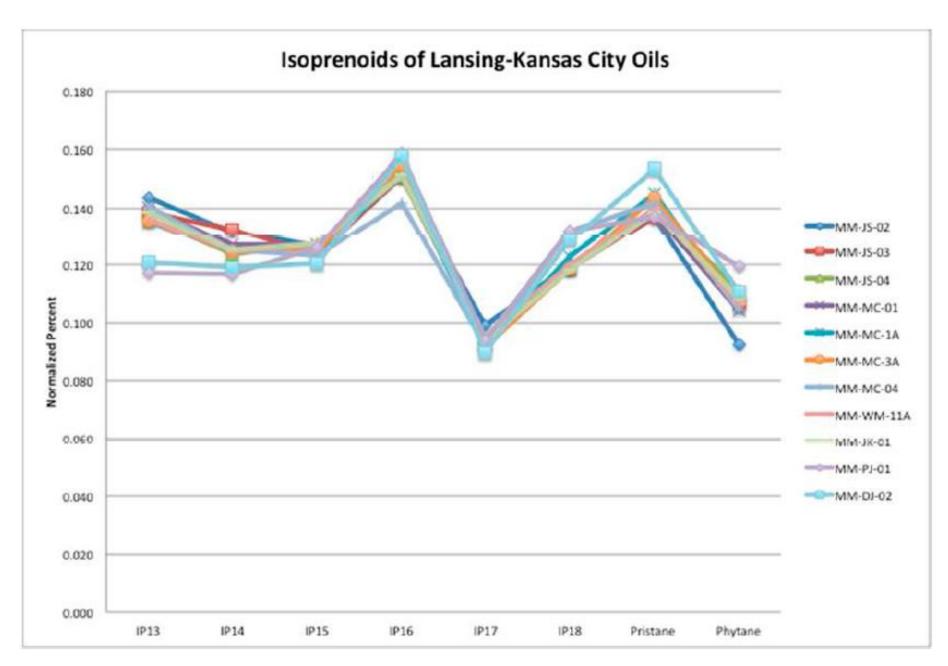


Figure 11. Graph of Isoprenoids of the studied Lansing-Kansas City oil samples.

Sample	Ce/Ce*
MM-JS-02	1.14
MM-JS-03	0.68
MM-JS-04	0.68
MM-JK-01	0.91
MM-WM-11A	3.13
MM-MC-01	0.10
MM-MC-1A	0.18
MM-MC-3A	0.57
MM-MC-4A	0.27

Table 1. Normalized Cerium values of nine samples.

Sample	Eu/Eu*
MM-JS-02	1.31
MM-JS-03	1.54
MM-JS-04	-
MM-JK-01	0.86
MM-WM-11A	1.69
MM-MC-01	-
MM-MC-1A	1.01
MM-MC-3A	_
MM-MC-4A	1.03

Table 2. Normalized Europium values of nine samples.

Sample	Pr/Ph Ratio
MM-JS-02	1.48
MM-JS-03	1.29
MM-JS-04	1.26
MM-MC-01	1.33
MM-MC-1A	1.38
MM-MC-3A	1.34
MM-MC-04	1.35
MM-WM-11A	1.32
MM-JK-01	1.28
MM-PJ-01	1.15
MM-DJ-02	1.39

Table 3. The Pristane/Phytane ratio was calculated for each of the eleven samples.

Sample	CPI
MM-JS-02	0.989
MM-JS-03	1.008
MM-JS-04	0.987
MM-MC-01	0.981
MM-MC-1A	0.974
MM-MC-3A	1.001
MM-MC-04	0.988
MM-WM-11A	0.988
MM-JK-01	0.990
MM-PJ-01	0.980
MM-DJ-02	1.011

Table 4. The Carbon Preference Index (CPI) was calculated for each oil sample.