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Maturation and Alteration of Crude Oils
In the Cherokee Group (Middle Pennsylvanian)
of Southeastern Kansas

by

George F. Gould

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MATURATION AND ALTERATION OF CRUDE OILS IN THE CHEROKEE GROUP (MIDDLE PENNSYLVANIAN) OF SOUTHEASTERN KANSAS

by

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A B S T R A C T

Three gradational ranges of crude oils are found in the clastic reservoirs of the Cherokee Basin of southeastern Kansas:

1) light oils (36 to 42° API gravity, less than 0.2% sulfur) which are produced from depths of 1400 to 2600 feet in the western part of the Basin.

2) medium oils (25 to 35° API gravity, 0.2 to 0.6% sulfur) which are produced from depths of less than 1400 feet in the central and eastern parts of the Basin.

3) heavy oils (less than 25° API gravity, 0.6 to 1.0 % sulfur) which are produced from depths of less than 1400 feet in the central and eastern parts of the Basin.

Hydrocarbon group analyses carried out on samples of each of these types of oils indicate that the differences in these oils are the result of alterations of the oil that occurred in the reservoir after generation and migration processes were essentially complete. The light oils show the higher API gravity, increased hydrocarbon content, lower sulfur content, and decreased asphaltene and non-hydrocarbon content typical of thermally altered oils. The medium oils show similar effects of thermal alteration, but to a much smaller degree. The heavy oils show the effects of extensive water washing and bacterial alteration. Both of these alteration processes result in lower API gravity, increased sulfur content, and greatly increased asphaltene and non-hydrocarbon contents, and both occur when meteoric waters invade a petroleum reservoir.

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I wish to express my gratitude to Dr. Gerard W. James for suggesting this research project and for his patient direction, encouragement and support in bringing it to completion. I also wish to thank Dr. E.E. Angino for his generous guidance and encouragement, not only on this project, but also in developing my program of graduate studies in geology. I am indebted to Drs. M.J. Brady and W.J. Ebanks for reading the manuscript and making helpful suggestions.

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G.F.G.

I N T R O D U C T I O N

The Cherokee Basin is the dominant geological structural feature of southeastern Kansas. On the surface, the basin extends about 150 miles west of the Kansas - Missouri border and about 75 to 100 miles north of the Kansas - Oklahoma border. In this region, petroleum of highly varying quality is produced from clastic reservoirs in the Middle Pennsylvanian Cherokee Group. Although the quality of these oils is gradational, they may be grouped into three classes, high, medium, and low quality oils on the basis of API gravity and sulfur content.

The high quality oils have API gravities greater than 35^{o} (but less than 42^{o}) and sulfur contents of less than 0.2%. Oils of this quality are produced in the western part of the region from depths greater than 1400 feet (ranging down to 2600 feet).

The medium quality oils have API gravities between 25 and 35^{o} and sulfur contents between 0.2 and 0.6%. These oils are produced from depths of less than 1400 feet in the central and eastern part of the region.

The low quality oils have API gravities of less than 25^{o} and sulfur contents greater than 0.6%, but less than 1.0%. The low quality of oils are found at the same range of depths and in the same geographical regions as the medium quality oils.

The purpose of this investigation is to account for the variation in quality of the Cherokee oils in terms of modern concepts of petroleum evolution. The formation of petroleum involves three major phases: generation of the oil in the source rock, migration of the oil to the reservoir, and alteration of the oil in the reservoir. The role played by each of these processes in the formation of the Cherokee oils will be evaluated through the interpretation of the results of hydrocarbon group analyses of samples of the high, medium, and low quality oils.

G E O L O G I C F R A M E W O R K

The crude oils examined in this study were produced from sediments of the Cherokee Group in southeastern Kansas. The petroleum reservoirs are elongated sand bodies generally surrounded by shales and silts. This section will review the stratigraphic position, lithology, and shape of these sand bodies. Then, after a discussion of likely depositional environments for these sand bodies, an account will be given of the geologic history of these sediments, emphasizing those aspects that are particularly important to the generation of petroleum.

The rocks of the Cherokee Group (Desmoinesian) form the earliest of the cyclic deposits which characterize sediments formed in this area from middle Pennsylvanian to early Permain times. They are mainly terrigenous detrital sandstones and shales, interbedded with thin coal deposits and a few thin limestone beds. The oil-bearing sands generally occur as unusually long, narrow, sinuous lenses, ranging in thickness from zero to 100 feet or more, with less than 50 feet being a typical average thickness. Ebanks and James (1974) characterize one producing sand as 2.5 miles long and $\frac{1}{4}$ mile wide, with an average thickness of about 40 feet. This particular sand body has a base convex downward and a range of sedimentary structures and lithologies typical of channel-fill and overbank de-

posits of a perennial, low-gradient meandering stream. Most other oil-bearing Cherokee sands share this long, narrow, relatively thin shape, though some have other characteristics which have led to different origins being proposed for them. The name "shoestring sand" is commonly used to describe these sands; and whatever the conditions of deposition, they seem to have prevented the formation of widespread sheet-sand bodies during Cherokee time.

Weirich (1953) views the Cherokee Basin at the beginning of Cherokee time as a relatively shallow platform or shelf extending northward from the Arkoma Basin, bounded on the east by the Ozark Uplift and on the west by the Nemaha Uplift. To the north, a subtle relief on the pre-Pennsylvanian surface only partially separated the Basin from the deeper Forest City Basin. During Cherokee time, sediment was apparently supplied from the east and west, while the basin subsided gently toward the south. The result was a northward-transgressing sea with sediments onlapping the eroded Mississippian surface as the major axis of deposition moved generally northward. The portion of the basin which extends into what is now southeastern Kansas could be pictured as a shallow embayment, surrounded by low hills from which small streams and rivers carried sediment to the basin. Fluctuations in basin subsidence and in sediment supply resulted in the variation in the sediments and their rate of formation.

> "In this setting, the Cheokee Basin has been depicted as the site of shifting and prograding alluvial and deltaic plains, estuaries, tidal delta complexes, beaches, and shallow marine shelf environments (Bass, 1936; Baker, 1962; Hayes, 1963; Visher et al., 1971). Individual sand bodies in the Cherokee section have been described variously as ancient nearshore bars (Dillard, et al., 1941), barrier islands (Bass, 1936), tidal flat - tidal channel deposits (Hayes, 1963), and alluvial valley-fill sediments (Rich, 1923; Charles, 1941; McQuillan, 1968). Probably each of these interpretations is correct in some area." (Ebanks and James, 1974)

The sand bodies and their enclosing mud deposits which formed during Cherokee time were buried by later Pennsylvanian and early Permian sediments as the Cherokee Basin continued to subside. As much as 2000 feet of Pennsylvanian and Permian sediments overlie the Cherokee deposits in portions of the western part of the basin today. McKee et al (1967) estimate that 800 to 1000 feet of Permian deposits may once have covered the Cherokee Basin. Thus the Cherokee sediments may have been buried to a depth of 3000 feet by middle Permian times. At that time, the region ceased to subside and became emergent during middle and late Permian times. During Cretaceous times, subsidence of the basin resumed long enough for an estimated 500 feet of sediments to cover the basin (Ebanks and James, 1974). This would be the time of maximum depth of burial for the Cherokee sediments, since the area has been emergent since Cretaceous time. The maximum depth of burial is thus estimated to be 3500

feet. This figure will be important in our disscussion of petroleum generation in these sediments.

Today in eastern Kansas, most of the overlying deposits have been removed from the Cherokee sediments and the outcrop belt trends northeastward from Oklahoma across eastern Kansas into western Missouri. Lee and Merriam (1954) estimate that west of the outcrop area, the Cherokee section varies in thickness from 350 to 900 feet and dips slightly north of west at a rate of 20 to 30 feet per mile from western Missouri to the east flank of the Nemaha Uplift. It should be noted that the Cherokee sediments have not only undergone prolonged gentle uplift for most of the time since middle Permian time, but they have also been tilted to alter their initial southward dip to their present westward dip.

O I L Q U A L I T Y

The quality of the crude oils, as defined by API gravity and sulfur contents, found in the Cherokee Basin ranges widely, from less than 15° API gravity to over 40°API, with sulfur ranging from less than 0.2% to about 1%. The distribution of these oils also varies with geographic regions and depths of burial. The distribution of API gravities and sulfur contents of some typical Cherokee crude oils is shown in Table 1. The location of these reservoirs is illustrated in Figure 1.

Crude oils with API gravities ranging from 36 to 42° are defined as high quality, light oils; typical sulfur values for these crudes are on the order of 0.2%.

Crude oils with API gravities ranging from 25 to 35° are classed as medium quality oils, with average sulfur values nearer to 0.5%.

Heavy crude oils, with API gravities of less than 25° and sulfur contents averaging about 0.7%, are called low quality oils. It should be noted that even though the low quality oils contain about three times as much sulfur as the high quality oils, they are still relatively low sulfur oils.

The lighter oils are produced from reservoirs in the western part of the Cherokee Basin from depths of 1400 to 2600 feet; and the medium and heavy oils are produced from depths of less than 1400 feet in the central and eastern

T A B L E 1 .

Oil Quality of Some Typical Cherokee Crudes.

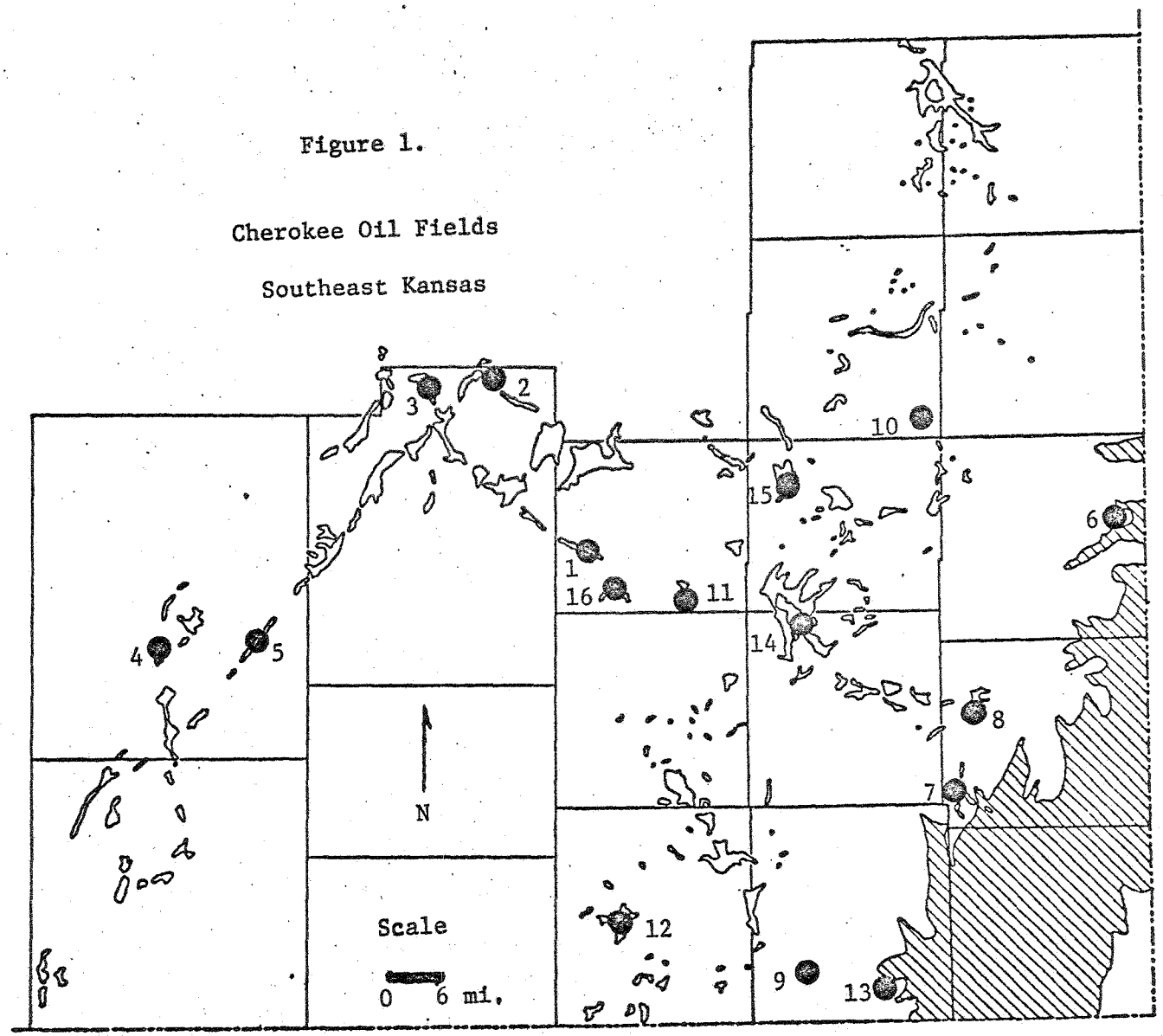
Field	County	Map Index	Depth	API°	S-%
High Quality					
Quincy	Woodson	1	1450'	40	.19
Fankhouser	Greenwood	2	1850'	41	.19
DeMalorie-Souder	Greenwood	3	2240'	42	.18
Haverhill	Butler	4	2250'	39	.21
Keighley	Butler	5	2632'	39	.21
Medium Quality					
Ft. Scott	Bourbon	6	140'	30	.51
McCune	Crawford	7	278'	31	.29
Walnut	Crawford	8	400'	28	.42
Edna	Labette	9	520'	26	.56
Kincaid	Anderson	10	720'	28	.50
Rose East	Woodson	11	1010'	25	.35
Jefferson-Sycamore	Montgomery	12	1208'	35	.23
Low Quality					
Bartlett	Labette	13	300'	15	.71
Humboldt-Chanute	Allen	14	800'	23	.60
Iola	Allen	15	900'	20	.74
Big Sandy	Woodson	16	1230'	22	.64

Data Source: U.S. Bureau of Mines, Reports of Crude Petroleum Analysis, Bartlesville, Okl.

Figure 1.

Cherokee Oil Fields

Southeast Kansas



portions of the basin.

An inspection of the data in Table 1 also shows that oils differing by 15° API gravity may be found in different reservoirs at approximately the same depths; e.g., the McCune oil (31°) and the Bartlett oil (15°) are found at very shallow depths of about 300 feet, and the Quincy oil (40°) and the Big Sandy oil (22°) are found scarcely 10 miles apart at depths of 1200 - 1400 feet.

It should also be noted that the classification of crude oils into low, medium, and high quality crude oils is somewhat arbitrary, as the characteristics within each group as well as between each group are gradational.

M E T H O D S

Sample Collection:

"Typical" samples (based on API gravity and sulfur content) of the low, medium, and high quality crude oils of the Cherokee sands were collected by personnel of the Kansas Geological Survey, as were a highly weathered outcrop sample and three drill core samples of the Cherokee oil sands. A high-grade sample of the Athabasca tar sand was also obtained (from the U.S. Bureau of Mines) for purposes of comparison. Additional details regarding these samples are found in Appendix I. The locations of the wells from which the Cherokee samples were taken are shown in Figure 2.

Analytical Techniques:

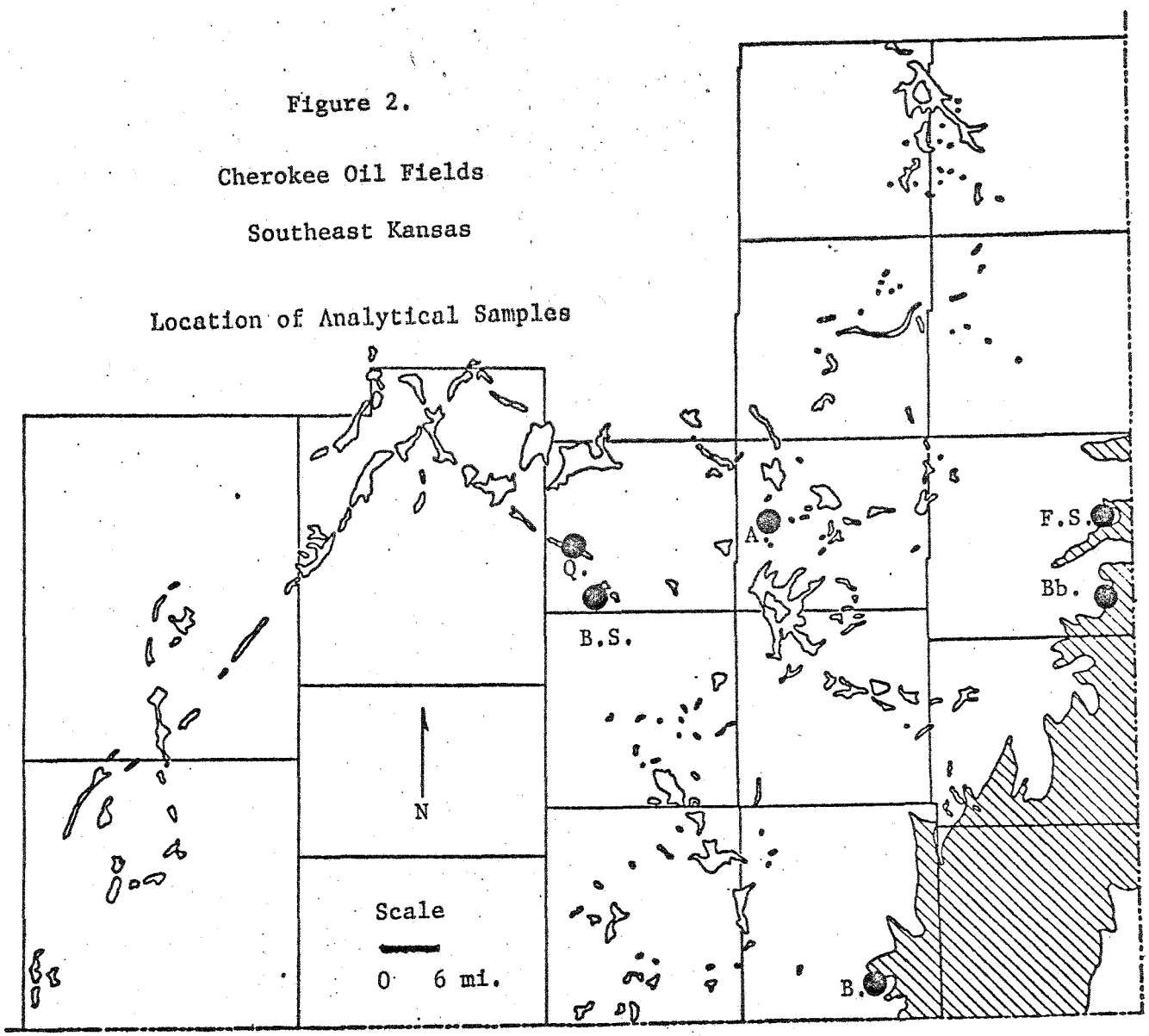
The Cherokee crude oils were characterized by API gravity, sulfur content, and hydrocarbon-type group analysis of the heavy "C 15+" fraction (boiling point above 270° C). The C 15+ oil fractions of the crude oils and oil sands were obtained by topping the oils in an oven for 19 hours at 45°C, or by extracting the oil sands with benzene in a Soxhlet extraction apparatus for 24 hours. The asphaltenes were precipitated from the C 15+ oil fraction with n-pentane, and the deashpalted oil (n-pentane soluble) fraction was separated into saturated hydrocarbon, aromatic hydrocarbon, and NSO heterocyclic fractions

Figure 2.

Cherokee Oil Fields

Southeast Kansas

Location of Analytical Samples



by elution chromatography on silica gel (Davison 950) and alumina (Alcoa F-20) columns by successive elutions with n-pentane, benzene, and 1:1 benzene-methanol. The C 15+ saturated hydrocarbon fraction was further characterized by gas-chromatography utilizing a eutectic salt column packing.

A more detailed treatment of the analytical procedures utilized in this study may be found in Appendix II.

R E S U L T S

The three oil samples selected for analysis (Quincy, Ft. Scott, and Bartlett) are representative of the three groups of quality of Cherokee crude oils (see Table 1), that is, high, medium, and low quality. Table 2 summarizes the results of the hydrocarbon-type group analyses and includes production depth, API gravity and sulfur contents as reported in the U.S. Bureau of Mines Crude Petroleum Analysis Reports. The results given in Table 2 represent duplicate, and in some cases, triplicate analyses. Accuracy of the results cannot be assessed, as no suitable standards exist, but the results of the group separations by elution chromatography can be consistently reproduced within one percent.

Section I, Table 2, characterizes the oils, using properties taken from Table 1. Note the range of API gravities, sulfur contents, and depths represented by these three samples. The Quincy sample is a light, high quality oil; the Ft. Scott sample is a medium gravity, medium quality oil; and the Bartlett sample is a low gravity (heavy), low quality oil.

Section II, Table 2, shows the composition of the oils in terms of low- and high-molecular weight materials. The "light hydrocarbon fraction" is taken as the sum of the light ends lost during the topping process plus the solution gases lost during deasphalting and column chroma-

T A B L E 2 .

Quality and Composition of Three Cherokee Oils.

	Quincy	Ft. Scott	Bartlett
I. Oil Characteristics			
Depth (feet)	1450	140	300
API gravity	40	30	15
% Sulfur	0.19	0.51	0.71
Quality	High	Medium	Low
II. Oil Composition*			
% Light HC's	35.7	24.9	10.8
% C 15+	64.3	75.1	89.2
III. C 15+ Oil Fraction			
% Sat. HC's	62.1	58.7	42.2
% Aro. HC's	30.9	30.1	33.3
% NSO's	4.6	7.4	10.0
% Asphaltenes	2.4	3.8	14.6
Sat/Aro	2.0	1.9	1.3
IV. Normalized C 15+**			
% Aro. HC's	81.4	72.9	57.5
% NSO's	12.2	17.9	17.4
% Asphaltenes	6.4	9.2	25.1
V. Oil Composition***			
% HC's	95.5	91.7	78.3
% non-HC's	4.5	8.3	21.7

* By molecular weight range.
** Normalized without saturated hydrocarbons.
*** By groups of compounds

tography. It is roughly equivalent to Fractions 1-7 of the U.S.B.M. Routine Distillation Analysis, but is usually somewhat higher due to the inclusion of the solution gases. The light hydrocarbon fraction is almost directly proportional to the change in API gravity for these three oils. The C 15+ fraction, recovered after topping, is roughly equivalent to the sum of the Gas-Oil, Lube-Oil, and Residium (Fractions 8-15, plus residium) groups of the U.S.B.M. Routine Distillation Analysis.

Section III, Table 2, presents the major hydrocarbon group components of the C 15+ oil fractions. The saturated hydrocarbon fraction shows a direct relationship with API gravity, the aromatic fraction appears to remain almost constant, and the NSO's and asphaltenes show an inverse relationship with the API gravity.

Since the amount of saturated hydrocarbons in the C 15+ fraction of these oils changes by almost a third, the changes in the other components may be only apparent changes resulting from the concentration of the oil components. To determine whether there was any change in the amount of aromatic, NSO, or asphaltene material present, the percentages were recalculated omitting the saturate fraction. The results in Section IV, Table 2, show that the aromatics, instead of remaining practically constant, actually show a marked decrease, especially between the medium and heavy oils. The asphaltenes show

a similar pattern, except that they are present in increased amounts from light to heavy oil. The NSO content increases slightly between light and medium oils, but remains unchanged between the two medium and heavy oils.

The hydrocarbon and non-hydrocarbon composition of the oils is given in Section V, Table 2. The hydrocarbon fraction includes the light hydrocarbons, and the saturated and aromatic hydrocarbons of the C 15+ fractions. The asphaltenes and NSO heterocyclic compounds make up the non-hydrocarbon fraction. The markedly higher non-hydrocarbon content of the low gravity oil is particularly noteworthy.

The extracted oil from four Cherokee oil sand samples were also examined in the same manner, and the results are presented in Table 3. Three of the oil sand samples (Big Sandy, Allen, and Bourbon) represent heavy oil sands found in drill cores; the Cherokee outcrop sample (Vernon Co., Missouri) represents a highly weathered surface oil sand exposure present in a stream cut. A high-grade sample of the Canadian Athabasca Tar Sand was analyzed for the sake of comparison, and the results are included in Table 3.

Relative to the results of the oil samples in Table 2, the extracted C 15+ fractions of the oil sands show somewhat lower saturated hydrocarbon contents and correspondingly higher NSO and asphaltene contents. Normalization of the C 15+ fraction without the saturated hydrocarbons

T A B L E 3 .

Composition of Oil Extracted from Oil Sands.

	Big Sandy	Allen	Bourbon	Vernon	Athabasca
Depth, feet	1240	940	250	surface	surface
% Extractable Oil	5	6	5	1	22
C 15+ Oil Fraction					
% Sat. HC's	37	45	40	16	13
% Aro. HC's	25	29	30	7	33
% NSO's	18	8	8	24	17
% Asphaltenes	19	18	22	53	36
Sat/Aro	1.5	1.5	1.3	2.2	.4
Normalized C 15+ Oil Fraction					
% Aro. HC's	40	53	50	8	38
% NSO's	29	15	13	29	20
% Asphaltenes	30	33	37	63	41

shows a real increase in the non-hydrocarbon fraction, especially in the asphaltenes, when compared to the crude oil samples.

The saturated hydrocarbon fractions of the crude oils and the extracted oils were analyzed by gas chromatography, to characterize the distribution of n-paraffins, isoprenoids, and naphthenic hydrocarbons. The results are presented in Figures 3, 4, 5, and 6. The patterns from the Qunicy and Ft. Scott oils (Figures 3 and 4) are fairly typical patterns of most crude oils. The prominent, evenly spaced peaks represent a sequence of normal paraffins with carbon numbers ranging from 12 to 28. The three peaks that have been cross-hatchured are due to responses from branched paraffins (C 18 isoprenoid, pristane, and phytane). The large undifferentiated region below the base of peaks is proportional to the naphthene (cyclic-paraffin) content of the oil sample. Note that this large area under the curve remains fairly constant for all three of the oils, despite wide variation in the size of peaks above the naphthenes. The patterns obtained from the Bartlett oil and all of the oil sand extracts are quite different from the Qunicy and Ft. Scott oils. The normal paraffin and isoprenoid peaks are considerably diminished and in some cases entirely absent. The undifferentiated area under the curve has also been altered in a way as to suggest the loss of lower molecular weight naphthenic material.

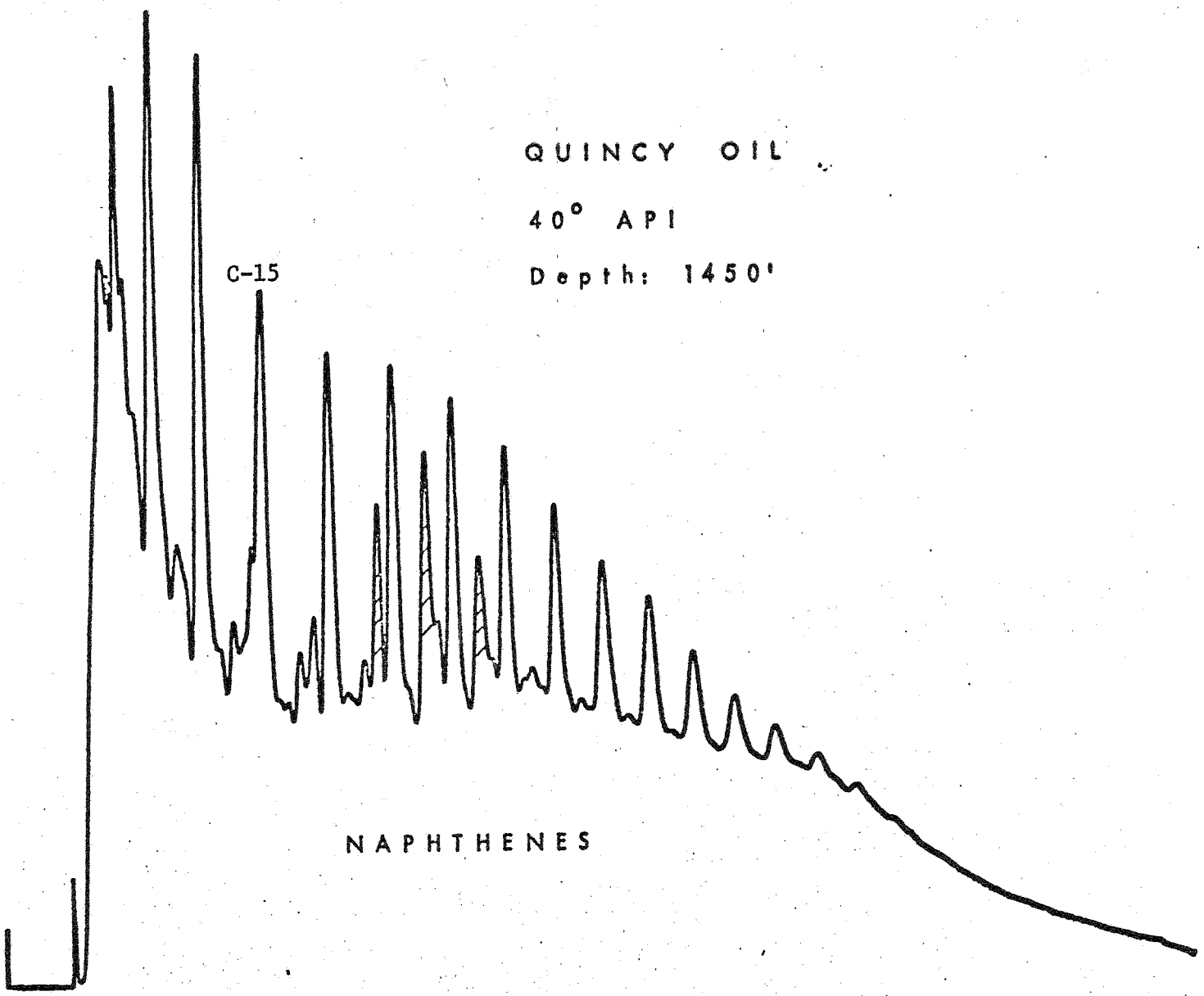


Figure 3. Gas Chromatogram of the Quincy Crude Oil.

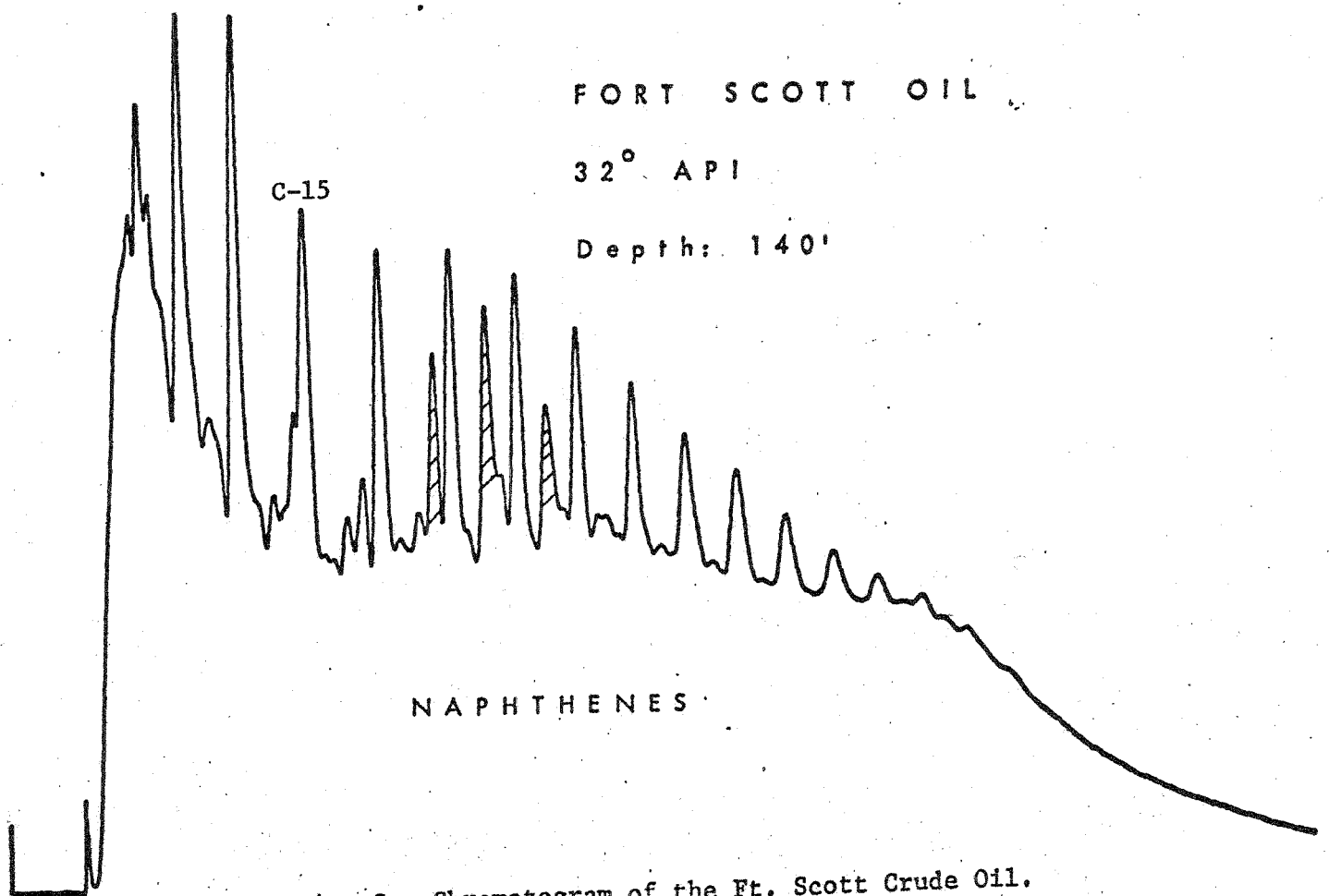


Figure 4. Gas Chromatogram of the Ft. Scott Crude Oil.

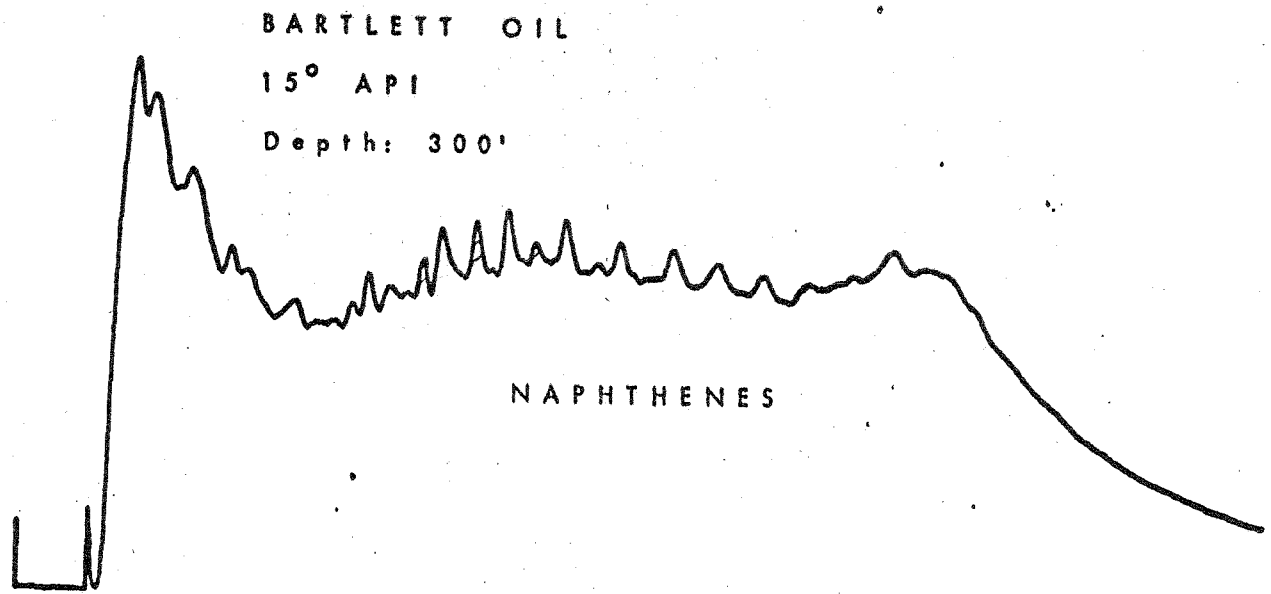


Figure 5a. Gas Chromatogram of the Bartlett Crude Oil.

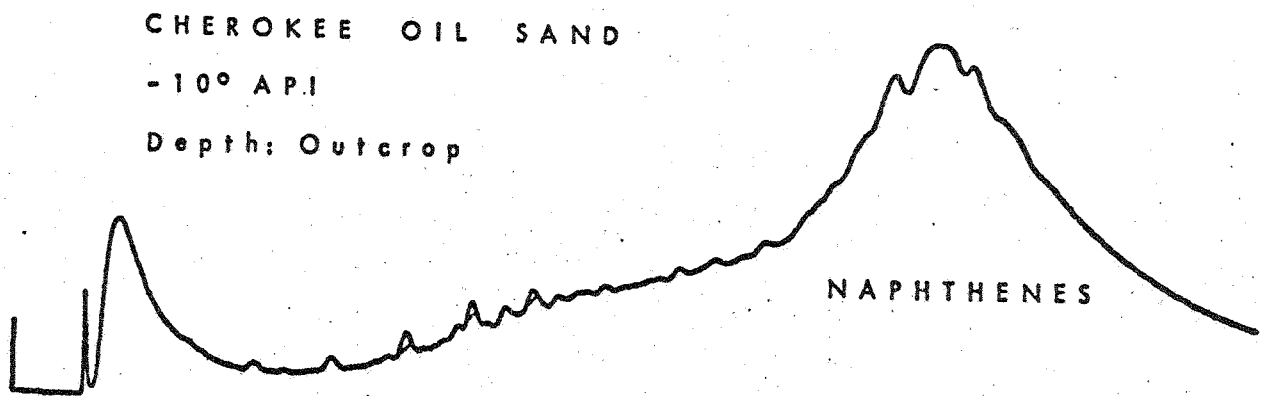


Figure 5b. Gas Chromatogram of the Cherokee Oil Sand.

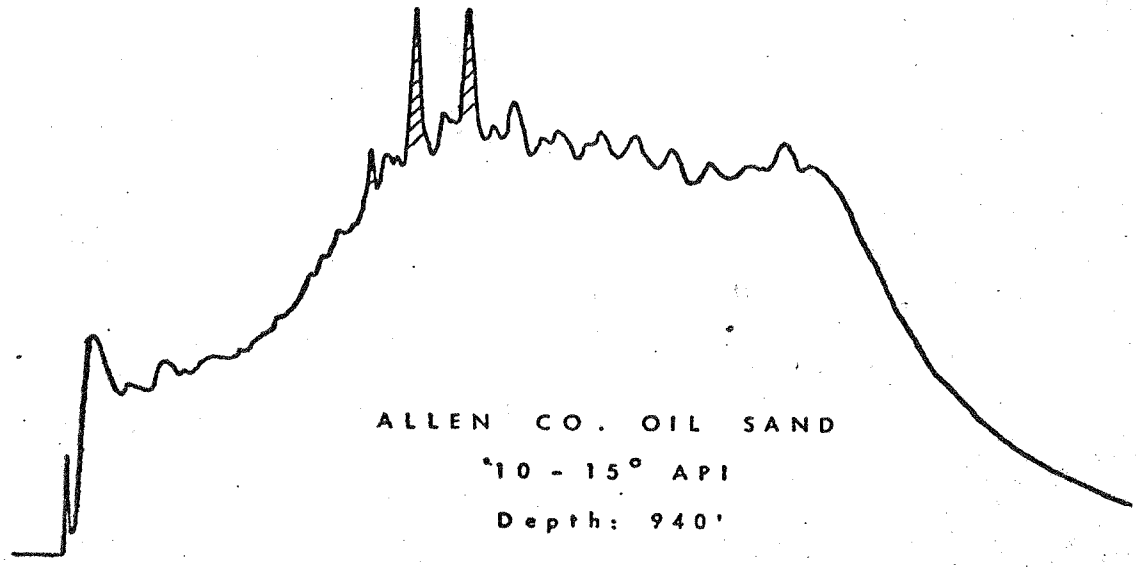


Figure 6a. Gas Chromatogram of the Allen Co. Oil Sand.

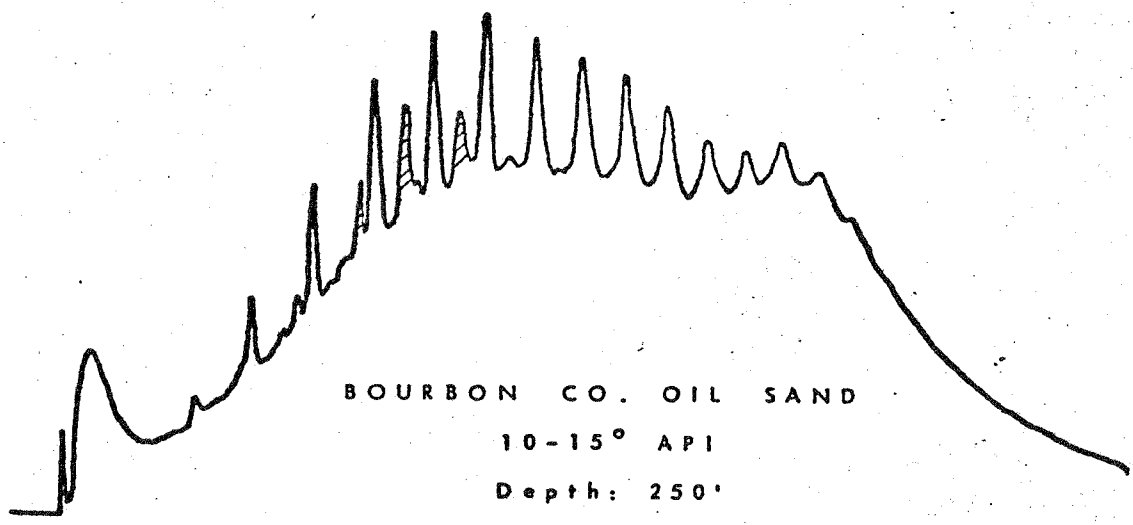


Figure 6b. Gas Chromatogram of the Bourbon Co. Oil Sand.

D I S C U S S I O N

The chemical quality and distribution of the Cherokee oils has been examined, and more detailed analyses of the hydrocarbon components of typical crudes and oil sands present in Cherokee reservoirs have been presented. The results of the hydrocarbon analyses make it possible to understand the variation in quality of the Cherokee crude oils in terms of modern concepts of petroleum generation, migration, and alteration.

Petroleum Generation.

The petroleum deposits of the Cherokee group have their origin in the remains of plants and animals (primarily phytoplankton and zooplankton) that lived in the varying paralic environments of deposition in this area of the Midcontinent. In the initial stages of accumulation and burial, much of the organic remains were broken down by bacterial action and chemical reactions, but some organic-rich muds enveloping the sand bodies developed, either because of rapid burial or because of anoxic sediment conditions which prevented the complete oxidation of the organic remains.

In such sediments, the organic matter is converted to "kerogen". Welte (1972) describes kerogen as a mixture of highly polymerized macromolecules with appreciable amounts of aliphatic chain structures and conjugated, variously

condensed ring systems of an aromatic nature. Philippi (1965) and Tissot et al. (1971) have presented evidence that petroleum hydrocarbons result primarily from the thermal degradation of kerogen. This degradation is a complex process involving a variety of reactions and yielding a variety of products which make up crude oil. However, the reactions appear to be strictly chemical in nature, and consequently, the degradation process is profoundly affected by the increased temperatures and pressures which result when sediment is buried. Pressure, because of its influence on gas-liquid equilibria, will affect the rate of generation of lower molecular weight hydrocarbons in particular. Temperature has a more far-reaching effect. The rate of a chemical reaction is affected exponentially by changes in temperature, commonly doubling for every increase of ten degrees Centigrade. Thus as an organic-rich sediment is buried to greater depths, and hence subjected to increasing temperatures, the rate of degration of kerogen - or the rate of generation of petroleum - will increase.

The temperature of geologic sediments depends upon their depth of burial and the geothermal gradient in that region. For petroleum generation reactions, the amount of petroleum produced would depend upon the length of time the kerogen was exposed to temperatures high enough to cause the reactions to proceed at significant rates.

"Length of time" and "significant rates" are correlative terms. A high reaction rate for a short period of time may result in the same amount of products as a low reaction rate occurring over a long period of time, provided the minimum temperatures necessary for the reaction to occur are reached. As a result, neither a fixed depth nor a fixed duration of the oil generation process exists.

However, it is possible to talk about a minimum temperature necessary for the generation of significant amounts of crude oil. Klemme (1971) in his study of giant oil fields and world oil basins concluded that the minimum temperature for petroleum generation in various types of basins, taking the element of time into account, varied from as low as 60°C to as high as 140°C. Welte (1972) also gives a minimum estimate of 50 to 60°C, calculated from empirical activation energies for the degradation of kerogen from several oil basins.

It seems likely that the Cherokee sediments have been exposed to temperatures of 50 to 60°C or higher for a geologically long period of time. Precise statements of temperatures or length of time are impossible because of a lack of precise history of depth of burial in the basin and uncertainty about paleothermal gradients (and hence duration of paleotemperatures) in the Midcontinent. Modern geothermal gradients in the Cherokee Basin are on the order of 0.8°C/100 feet to 1.2°C/100 feet, according

to the Geothermal Gradient Map for Region 15 prepared by the American Association of Petroleum Geologists in 1974. When an estimated surface temperature of 15°C is combined with a geothermal gradient of 1.0°C/100 feet, the resulting calculations show that the Cherokee source rocks would have been exposed to temperatures of 50 to 60°C if they had been buried to depths of 3500 to 4500 feet. Similarly, higher surface temperatures (as they might have been during the sub-tropical late Paleozoic and Mesozoic eras), and/or higher geothermal gradients, would have lead to the generation of oil at shallower depths. As previously noted in the "Geologic Framework" section, the Cherokee sediments may have had a depth of burial of 3000 feet by middle Permian times, and a maximum depth of burial of 3500' by the end of Cretaceous time. Allowing for a maximum thickness of 900 feet, the deepest Cherokee sediments would have been buried to a depth of about 4400 feet. This depth range would seem to place Cherokee sediments well within the thermal range necessary for the generation of crude oils.

From the initial time of burial of Cherokee sediments (approximately 300 million years ago), significant generation of petroleum probably did not occur until near the end of Permian time when depths of burial approached 3000 feet. The bulk of the Cherokee petroleum may have been generated during the next 150 million years, until the end of Creta-

ceous time (approximately 65 million years ago), at which time peak generation may have occurred for a relatively short period of time. Rates of oil generation must have slowed as the Cretaceous and Permian sediments were eroded away, and it is unlikely that the generation process is occurring at present rock temperatures.

The preceding discussion is intended to give a generalized account of the generation of petroleum of a fairly uniform quality throughout the basin, assuming the chemical characteristics of the organic material incorporated in the sediments was fairly uniform throughout the basin. However, a uniform oil quality also implies uniform thermal histories (i.e. depth of burial), and this was probably not the case, as will be discussed in the alteration section. At this point it will be assumed that the oil available for migration and accumulation was basically the type of oil throughout the basin.

Petroleum Migration.

In the Cherokee Basin, with the reservoir sand bodies apparently completely surrounded and isolated by oil-producing shales, migration pathways must have been quite limited and very similar throughout the basin. It seems unlikely that significant differences in the oil composition that exist today in Cherokee

crudes could be attributed to differences in migration processes and/or pathways. However, because migration is an important part of the petroleum evolution scheme, a brief description of current concepts of migration will be included here.

Primary migration is the movement of petroleum from source rocks into reservoir rocks. Secondary migration includes any movement of the oil in or from the reservoir rock. Most prominent concepts of oil migration involve some type of solution of oil in water (Hitchon, 1971; Price,1973). Actual mechanisms of migration are at best poorly understood, and are the subject of considable debate.

The controversies generally focus on: (1) the source of formation waters necessary to carry the oil (interstitual or interlayer), and (2) the mechanism of transport of petroleum hydrocarbons (molecular solution or micellar solution). The bulk of interstitual waters appear to be squeezed out of pore spaces relatively early in compaction of sediments, and there is some question as to whether or not enough pore waters are left in the rocks to mobilize the petroleum hydrocarbons by the time they are generated. Burst (1969) however, concluded that enough interlayer water is squeezed out of clays at moderate temperatures to provide a significant volume of fluid with which to mobilize hydrocarbons. Hydrocarbons

may be mobilized by some sort of micellar solution mechanism, but these explanations require the presence of natural surfactants in the oils, which may or may not be the case. Price (1973) indicates that petroleum hydrocarbons may be soluble enough at elevated temperatures to provide a significant mobilization process by molecular solution. Hydrocarbons in solution could be exsolved by either a decrease in temperature or increase in salinity of the water. The crude oil then separates as a distinct phase and continues to move in the porous reservoir rocks until it accumulates in a trap to form a pool.

Petroleum Alteration.

The petroleum reservoirs in the Cherokee Basin are generally sinuous sandstone bodies enclosed by silts and shales, and apparently were and are isolated from one another and from extra-basinal sources of oil. The basic naphthenic character of most oils in the Cherokee rocks is readily apparent from an examination of over 150 U.S.B.M. Routine Distillation Analyses, and it is reasonable to assume that the oils entering most, if not all, Cherokee reservoirs were similar in composition. The changes or alterations which produced the wide range of Cherokee oil quality must have taken place primarily in the reservoirs.

Before examining the alteration processes which

produced the range of characteristics displayed in the Cherokee oils, it will be useful to consider the quality of the oil which probably migrated from the source rocks to the reservoir rocks. Bailey et al. (1973) reported that the oil commonly entering reservoir rocks has an API gravity between 18 and 27 degrees and a sulfur content of less than 1.5%, and Winters and Williams (1969) found that unaltered oils from reservoirs commonly include a wide range of normal paraffins, isoprenoid hydrocarbons, and naphthenic hydrocarbons in the saturate fraction of the C 15+ boiling range of oils. All of the Cherokee crudes examined by the U.S. Bureau of Mines have sulfur contents considerably less than 1.5%, but all of the heavier oils (less than 25° API) examined in this study have only minor, if any at all, amounts of normal paraffins present. The medium quality oils, which have the full range of hydrocarbon components typical of unaltered oils, have a gravity range slightly higher than that found by Bailey et al. (1973) for oil available for migration. This could be a clue to the first type of alteration that may have occurred in the reservoir.

Crude oils may be thermally altered in a reservoir when they are subjected to higher temperatures, which generally result from deeper burial of the reservoir rock. It is similar to the thermal degration of kerogen that

occurs in source rocks, except that in the reservoir it is the heavier asphaltene and non-hydrocarbon components of the oil which break down to release hydrocarbons of lower molecular weight. The net effect of thermal alteration, at least initially, is an improvement in the quality of the oil, i.e., a higher API gravity. As noted by Evans et al. (1971), the end results of thermal alteration lead to the destruction of all heavier hydrocarbon components, leaving only dry or wet natural gas present in the reservoirs. Thus, thermal alteration may be the reason that the medium quality Cherokee oils show a slightly higher API gravity range than that of typical unaltered oils. Carried on to a slightly greater extent, thermal alteration would lead to the production of oils with gravities in the 35 to 42° API range, which are found at greater depths in the western part of the Cherokee Basin.

Many of the reservoirs in the central and eastern portions of the basin yield oil which is probably changed only slightly with respect to its chemical characteristics since its period of generation and migration into reservoirs at the time of maximum burial, even though the reservoirs are presently found at much shallower depths. Many of these reservoirs apparently remain rather tightly enclosed by surrounding sediments, with little opportunity for lighter gaseous hydrocarbons to escape or for ground-

waters to enter the reservoirs.

However, many of the shallow reservoirs in the same depth range contain low-quality heavy oils which are chacterized by a lack of light hydrocarbons, relatively high contents of non-hydrocarbons (NSO's and asphaltentes), and little, if any, heavy n-paraffins.

Evans et al. (1971) list two alteration processes, water-washing and bacterial oxidation of hydrocarbons, which could lead to the characteristics found in the heavy Cherokee crude oils. In addition to these two processes, a third should be mentioned, evaporation of light hydrocarbons. Each of these three processes are likely to have occurred, and are occurring, in belts of basin margins such as the eastern and central portions of the Cherokee Basin area in southeastern Kansas.

Water-washing and bacterial oxidation usually occur when meteroic waters find their way into a petroleum reservoir, along tension cracks, fault planes, or unconformities, or any combination of these porous zones. As noted by Bailey et al.(1973), both result in an oil of lower API gravity and higher sulfur contents.

Water-washing results from the fact that some types of hydrocarbons are actually slightly soluble in water at low temperatures. McAuliffe (1967) and Bailey et al.(1973) pointed out that light aromatic hydrocarbons (benzene and toulene) are fairly soluble in water, and that lighter

hydrocarbons are more soluble than heavier hydrocarbons; and that heavy normal paraffins are least soluble. Small as these solubilities may be, considerable quantities of oil may be dissolved from a petroleum reservoir if water undersaturated in hydrocarbons is in contact with petroleum for millions of years. Such a flow of surface water would be more likely to occur in shallow reservoirs, but deeper reservoirs might be affected in unusual circumstances. Bailey et al. (1973) reports evidence of water washing in a reservoir at a depth of 3900 feet.

Like water washing, bacterial oxidation frequently requires the introduction of surface water into a petroleum reservoir (as a transport medium). When bacteria are introduced into the reservoir, petroleum hydrocarbons are oxidized or dehydrogenated, with the nature of the resulting product depending on the nature of the hydrocarbon attacked. Normal paraffins of more than five carbon atoms are preferentially attacked by the bacteria, but as noted by Bailey et al. (1973), lighter aromatics and naphthenes can be attacked, once the normal paraffins have been consumed. This selective destruction or alteration of certain hydrocarbons produces a petroleum of lower API gravity, a sharply reduced normal paraffin content, and a higher sulfur content.

S U M M A R Y

The quality of crude oils of the Cherokee Basin in southeastern Kansas is highly variable and, although is gradational over a wide spectrum, can be generally classed into three major groups: light, medium, and heavy oils. In the western part of the Basin, Cherokee reservoirs produce a light oil (36 to 42° API gravity) from depths ranging from 1400 to more than 2600 feet. In the central and eastern parts of the Basin, some reservoirs produce a medium oil (25 to 35° API gravity) from depths of less than 1400 feet. Other reservoirs in the central and eastern part of the Basin contain a heavy oil (less than 25° API gravity) at depths of less than 1400 feet.

When the depositional environment and the post-depositional history of the Cherokee sediments is examined in light of modern concepts of petroleum evolution, it appears unlikely that the differences between these three groups of petroleum could arise from differences in petroleum generation or migration processes. The results of hydrocarbon group analyses indicate that the different quality of oils is due primarily to alteration processes that took place after the oils had accumulated in the reservoirs.

The medium quality oils were found to possess a wide range of normal paraffins, isoprenoids, and naphthenes that are typical of unaltered petroleum. However, these oils have a range of API gravities (25 to 35°) that is slightly

higher than what is considered by some geochemists to be that of unaltered petroleum (18 to 27°). An increased API gravity is one of the principal effects of thermal alteration which occurs when petroleum in a reservoir is subjected to an increase in temperature. Since the Cherokee reservoirs have been buried more deeply after most of the petroleum had accumulated in them, this factor of modest thermal alteration could account for the slightly higher gravity range of unaltered, medium quality oils.

The quality of the lighter oils (36 to 42° API) produced from the deeper reservoirs in the western part of the Basin is also most likely the result of thermal alteration. These deeper reservoirs have been subjected to somewhat higher temperatures, and so the oils in them is more extensively altered. Increased thermal alteration results in the breaking down of the heavier asphaltene and non-hydrocarbon components (as well as some of the heavier hydrocarbons) to form hydrocarbons of lower molecular weight. This alteration thus produces oils with higher API gravities and lower contents of asphaltenes, non-hydrocarbons, and sulfur. The lighter Cherokee oils show all of these qualities when compared to the medium oils.

The heavy oils have lower API gravities, lower light hydrocarbon contents, less normal paraffins, higher sulfur contents, and greatly increased asphaltene and non-hydrocarbon contents, compared to the other Cherokee crudes.

All of these effects are the result of a combination of water washing and bacterial alteration. These two types of alteration take place when surface waters enter a reservoir, dissolving some of the lighter hydrocarbons, and introducing bacteria which are capable of reducing sulfates, destroying lighter paraffins, and thus producing more asphaltenes and nonhydrocarbons.

Thus, reservoirs in the east and central part of the Cherokee Basin which have remained sealed off from surface (meteroic) waters still contain oil having a quality very similar to what they possessed at the time of their maximum burial. These are the reservoirs producing the medium quality oils today.

The deeper reservoirs in the western part of the Basin have also remained sealed off from surface waters. These reservoirs, too, contain oil very similar in quality to that which filled them at the time of maximum burial. The oils differ in quality from the medium oils only because of more extensive thermal alteration as a result of the higher temperatures at greater depths of burial.

Those reservoirs in the east and central part of the Basin which have been invaded by surface waters contain oils which have been extensively altered by water washing and bacterial alteration. These altered oils are the typical dark, viscous oils found in the relatively shallow reservoirs of the Cherokee Basin.

A P P E N D I X I

Sample Location and Depth

Sample	Type	County	Location	Depth
Quincy	oil	Woodson	28-25S-24E	1450'
Ft. Scott	oil	Bourbon	6-24S-24E	140'
Bartlett	oil	Labette	16-34S-20E	300'
Big Sandy	core	Woodson	26S-14E	1240'
Allen	core	Allen	9-25S-18E	940'
Bourbon	core	Bourbon	27-26S-25E	250'
Cherokee	outcrop	Vernon-Mo.	24-35N-33W	Outcrop
Athabasca	outcrop	McMurray, Alberta, Can.	----	Outcrop

A P P E N D I X I I

Analytical Procedures

The hydrocarbon group methods of analysis employed in this study of crude oils and oil sands are modifications of techniques described in a compilation by Davis and Bray, 1969 (Analyses of oil and cap rock from Challenger (Sigsbee) Knoll, in Initial Reports of the Deep Sea Drilling Project, v. 1, chp. 22: Washington, D.C., U.S. Gov't. Print. Off., p. 415-500).

1a) Topping of Crude Oil Samples.
In order to obtain a C 15+ oil fraction and to measure the light hydrocarbon content of the oil, a 150 mg sample was weighed into a tared 6-dram vial and placed in an oven at 45°C for 19 hours, and then reweighed.

1b) Extraction of Oil Sand Samples.
The oil sand samples were gently crushed to less than $\frac{1}{4}$-inch. A weighed portion of the sample was then placed in a small Soxhlet extraction apparatus along with 100 ml of redistilled reagent grade benzene. The extraction was continued for 24 hours at a cycle time of 20 minutes. Two to three grams of oil sand was usually sufficient to yield 100 to 150 mg of extract. This extraction procedure removes 95% + of the bitumen present in the sample.
The extract solution was then concentrated by distilling under vacuum at 40°C using a Buchler flash-evaporator. The concentrated extract solution was then transferred to a tared 6-dram vial and brought to constant weight under a stream of dry nitrogen, flowing through a disposable Pasteur pipette. The gas flow was adjusted to produce a small dimple in the surface of the solution. The vial and contents were weighed initially and at four-minute intervals until a weight loss of less than 2.0 milligrams was observed in a four minute interval.

2) Asphaltene Stripping
An asphaltene, or n-pentane insoluble, fraction was separated from both the topped crude oils and the oil sand extracts. Five ml of n-pentane were added to the 6-dram vial containing the topped oil or the benzene extract. The mixture was agitated thoroughly by brief immersion in an ultrasonic water bath. After mixing, the vial was allowed to stand at least four hours, before filtering through a $\frac{1}{2}$-inch cake of Hyflo Super Cel formed on a medium-porosity fritted-glass funnel.

The n-pentane soluble filtrate and washings were collected in a 25 ml Erlenmeyer flask, concentrated under a stream of nitrogen, transferred to a tared 2-dram vial, and brought to constant weight using two-minute weighing intervals.

The asphaltenes on the filter cake were washed into a small flask with benzene and benzene-methanol; the washing was continued until a colorless filtrate was produced. The solution was then concentrated under nitrogen, transferred to a tared 2-dram vial, and brought to constant weight using four-minute weighing intervals.

3) Hydrocarbon Group Separation.

The n-pentane soluble C 15+ oil fraction was then separated into saturated hydrocarbon, aromatic hydrocarbon, and NSO heterocyclic fractions by elution-column chromatography on silica gel and alumina by successive elutions with n-pentane, benzene, and 1:1 benzene-methanol.

The chromatographic columns were 8mm I.D. and 20cm in length. The lowere end was fitted with a Teflon stopcock, and the upper end had a 50 ml reservoir.

Two layers of adsorbents were used, each about nine centimeters thick. The lower layer was composed of activated silica gel (Davison, Grade 950, 60 - 200 mesh) to effect the separation of saturated hydrocarbons from aromatic hydrocarbons; the upper layer was activated alumina (Alcoa F-20, 80 - 200 mesh) which retained the NSO's. Both adsorbents were activated in a muffle furnace at 300°C for sixteen hours, and stored in an oven at 150°C.

The columns were packed by first filling them with about 15 ml of n-pentane, slowly adding five grams of silica gel, and stirring the silica gel to remove bubbles as it settled in the lower part of the column. After the lower part of the column was packed to a depth of nine centimeters with silica gel, the procedure was repeated with activated alumina to pack the upper half of the column; this procedure produced a uniform and reasonably bubble-free column. After being washed with 30 ml of n-pentane, the column was ready for use.

The deasphalted pentane-soluble oil extract was dissolved in a small amount of n-pentane and transferred to the top of the column. Three fractions were eluted: the saturated hydrocarbons with 25 ml of n-pentane, the aromatic hydrocarbons with 40 ml of benzene, and the NSO fraction with 30 ml of 1:1 benzene-methanol. Each fraction was collected in 50 ml boiling flasks, concentrated on the flash evaporator, transferred to 2-dram vials, and brought to constant weight as previously described.

4) Characterization of the Saturated Hydrocarbon Fraction

The C 15+ saturated hydrocarbon fraction was characterized by gas-chromatographic analysis, utilizing a eutectic salt column packing described by Hanneman, et al., 1960 (Anal. Chem., v. 32, p. 1386).

Normal operating conditions were as follows:

Helium flow rate:	15 ml/minute
Hydrogen flow rate:	15 "
Air flow rate:	250 "
Injector temperature:	225° C.
Detector temperature:	375° C.
Temperature program:	4 minutes @ 160° C. 160° to 340° C. at 6°/minute. 10 minutes @ 340°C.
Recorder chart speed:	0.2 inches/minute.

The instrument utilized in this study was a Varian Aerograph Series 1800 with flame ionization detectors, and an automatic linear temperature programmer. Ten-foot long, 1/8 I.D., stainless steel columns were packed with a eutectic mixture of lithium, sodium, and potassium nitrates coated on Chromosorb P. Only one column and detector were utilized in the analysis. The carrier gas was helium, and hydrogen and compressed air were supplied to the detectors.

The sample to be analyzed was dissolved in carbon disulfide, with a concentration ratio of 165 mg/ml. Four microliters of these solutions were injected into the gas chromatograph for analysis, and a ten inch recorder was used to produce a trace of the analysis.

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