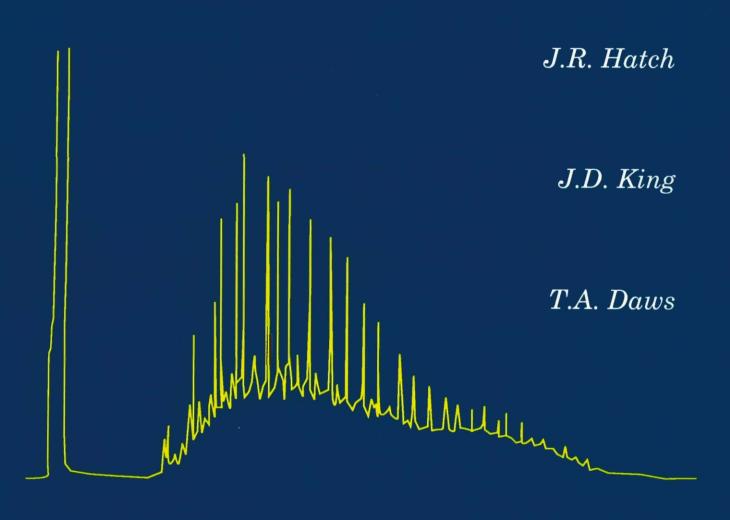
Geochemistry of Cherokee Group oils of southeastern Kansas and northeastern Oklahoma



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Geochemistry of Cherokee Group oils of southeastern Kansas and northeastern Oklahoma

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Abstract

We made organic carbon determinations, Rock-Eval pyrolysis analysis, and vitrinite reflectance measurements on 72 samples of organic-matter-rich (>1.0% total organic carbon) Middle Pennsylvanian (Desmoinesian) Cherokee Group and Marmaton Group shales and coals and on 13 samples of Upper Devonian-Kinderhookian Chattanooga Shale from southwestern Missouri, southeastern Kansas, and northeastern Oklahoma. These analyses show that the Cherokee Group and Marmaton Group offshore shales and coals and the Chattanooga Shale are thermally mature with respect to petroleum generation and still have good potential to generate oil and/or natural gas. In contrast, the organic matter in the Cherokee Group and Marmaton Group nearshore shales is hydrogen deficient and has little or no generating potential. Comparisons of saturated hydrocarbon, terpane and sterane distributions, pristane/phytane ratios, and carbon isotope compositions of saturated and aromatic hydrocarbon fractions from oils and rock extracts show that oils occurring in sandstone reservoirs of the Cherokee Group are similar to extracts from the Chattanooga Shale and are dissimilar to extracts of Cherokee Group and Marmaton Group offshore shales and coals. We conclude from these correlations that the Chattanooga Shale contains the source rocks for the Cherokee Group oils. These results imply that any porosity trends in Mississippian rocks above the Chattanooga Shale and/or in Paleozoic rocks immediately below it have the potential to be charged with the same oil found in Cherokee Group reservoirs. The excellent hydrocarbon-generating potential shown for the Middle Pennsylvanian offshore shales and coals suggests that these rocks, where thermally mature, may be sources for other midcontinent oils and/or natural gas.

Introduction

Rocks of the Middle Pennsylvanian (Desmoinesian) Cherokee Group in the midcontinent area of the United States are a complex mixture of coal cyclothem rock types that record deposition in marine, transitional marine, and nonmarine environments. In northeastern Oklahoma and southeastern Kansas oil is extracted from these rocks, primarily from traps along the basal Pennsylvanian unconformity and from stratigraphic traps in lenticular sandstone reservoirs [i.e., Burgess, Burbank, Bartlesville, Skinner, and Prue sands (drillers' terms)]. The apparent isolated character of many of these sandstone reservoirs has led previous researchers (McCoy and Keyte, 1934; Clark, 1934; Bass, 1936; Weirich, 1953; Baker, 1962; Baker and Ferguson, 1964; Hedberg, 1964; Baker et al., 1969) to suggest that the surrounding nonreservoir rocks are source rocks for the petroleum.

Modern studies that correlate Cherokee Group oils with specific source rocks within the Middle Pennsylvanian section are lacking. More important, there has been little consideration of other lithologic units within the middle and upper Paleozoic section as possible source rocks of the Cherokee Group oils. In this paper we (1) characterize the organic geochemistry of the oils in Cherokee Group reservoirs; (2) characterize the thermal maturity of the organic matter, the hydrocarbon-generating potential, and the extract geochemistry of the organicmatter-rich rocks within the Middle Pennsylvanian section (Cherokee Group and overlying lower part of the Marmaton Group) and in the Late Devonian–Kinderhookian Chattanooga Shale; and (3) correlate the Cherokee Group oils with specific source rocks.

Previous geochemical studies

Baker (1962) was the first to study the organic geochemistry of Cherokee Group rocks and oils. He reported organic carbon contents, amount of extractable hydrocarbons, and saturated hydrocarbon/aromatic hydrocarbon ratios for various rocks within the Cherokee Group. He found that different rocks have distinct hydrocarbon compositions and that the saturated hydrocarbon/aromatic hydrocarbon ratios from the marine shales and limestones are similar to those of Cherokee Group oils. Baker (1962) indicated that all the nonreservoir rock types probably contribute to the Cherokee Group oil accumulations. Hunt (1979, p. 504), in discussing Baker's (1962) data, ques-

tioned whether the organic-lean rocks (such as underclays and greenish-gray shales) are significant contributors of petroleum. He pointed out that the most likely hydrocarbon source rock in the Cherokee Group is the marine black shale lithofacies (offshore shale). This lithofacies is volumetrically only a minor part of the section, however, and the lowest stratigraphic occurrence of it is above many of the principal producing sands.

Other studies of the organic geochemistry of Cherokee Group rocks and oils in the midcontinent area were conducted by Baker and Ferguson (1964), James (1970), James and Baker (1972), Hatch et al. (1984), Hatch and Leventhal (1981, 1982, 1985), Wenger and Baker (1986), and Coveney et al. (1987). Baker and Ferguson (1964) compared δ^{13} C of hydrocarbons (saturated + aromatic hydrocarbon) separated from 24 Cherokee Group oils with δ^{13} C of hydrocarbons extracted from a composite section of Cherokee Group rocks in Greenwood County, Kansas. Mean δ^{13} C for the 24 oils was $-28.0^{\circ}/_{\circ}$; for the extract of the composite section, δ^{13} C was $-26.3^{\circ}/_{\circ}$.

James (1970) conducted a regional study of a single black shale (Excello shale) in the upper part of the Cherokee Group. Citing the work of James (1970), James and Baker (1972) proposed that one of the major controls on regional variability in saturated hydrocarbon/aromatic hydrocarbon ratios from extracts of the Excello shale is differences in the relative proportion of marine and terrestrial organic matter.

Hatch et al. (1984) collected 247 samples of Cherokee Group and Marmaton Group rocks from cores and coal mines at 21 locations in southeastern Iowa, Missouri, southeastern Kansas, and northeastern Oklahoma. They list organic carbon contents and Rock-Eval pyrolysis results for the 247 samples, vitrinite reflectance values for 19 coal samples, extractable organic matter compositions for 77 samples, and carbon isotope compositions of saturated and aromatic hydrocarbon fractions for extracts from 18 rock samples and 6 Cherokee Group oils.

Hatch and Leventhal (1981, 1982, 1985) identified four different organic geochemical facies in the Cherokee Group and the overlying lower part of the Marmaton Group. The four facies, characterized by organic carbon content, hydrogen index (Rock-Eval pyrolysis), organic carbon isotope composition, extract geochemistry, and trace element content, reflect differences in organic matter source, relative amount of dissolved oxygen in the depositional environment, and degree of early postdepositional aerobic alteration of the organic matter.

Wenger and Baker (1986), using a variety of techniques, characterized the organic geochemistry and organic petrography of the Little Osage shale (Marmaton Group) and Excello shale (Cherokee Group) (plus transitional rock types) in two cores from southeastern Kansas and northeastern Oklahoma. They showed large and systematic variations in geochemical properties within the black shale units and related these variations to variable supplies of nutrients and humic detritus resulting from eustatic rise of sea level and rapid marine transgression over the continental craton.

Coveney et al. (1987) related metal contents in the marine black shales in the upper part of the Cherokee Group in Missouri and Kansas and in stratigraphically equivalent shales in Illinois and Indiana to type of organic matter (defined by Rock-Eval pyrolysis and pyrolysis gas chromatography) and proximity to the paleoshoreline.

Samples

Organic geochemical data for three groups of samples are summarized in this study:

- 1. Seventy-two core and strip-mine samples from the Middle Pennsylvanian Cherokee Group and lower part of the Marmaton Group, collected from 12 locations in southwestern Missouri, southeastern Kansas, and northeastern Oklahoma (Hatch et al., 1984, locations 8–18).
- 2. Thirteen core samples of Late Devonian-Kinder-hookian Chattanooga Shale from three locations in Greenwood and Wabaunsee counties, Kansas.
- 3. Eleven oils representing production from the major Cherokee Group sands and fields in southeastern Kansas and northeastern Oklahoma.

We list the locations and depth intervals of the sampled cores, strip mines, and oils in appendix 1 and show the locations in figure 1. We list the sample numbers, descriptions, and depth intervals for the 72 Cherokee Group and Marmaton Group samples and the 13 Chattanooga Shale samples in appendix 2. We selected rock samples on the basis of color (N1, N2, and N3 hues, GSA rock color chart).

The 72 Cherokee Group and Marmaton Group samples represent three lithofacies: offshore shale, coal, and some shale beds within the nearshore shale [nomen-

clature from Heckel (1977) and Ebanks et al. (1979)]. We determined lithofacies for the sampled intervals from lithology and stratigraphic position.

Organic-matter-rich rocks (N1, N2, and N3 hues, GSA rock color chart) make up a relatively small part of the Cherokee Group and Marmaton Group. For example, at locality 11 in northeastern Oklahoma, the Cherokee Group is 501 ft (153 m) thick. At this locality 77.5 ft (23.6 m) of nearshore shale, 13.1 ft (4.0 m) of coal, and 11.7 ft (3.6 m) of offshore shale (totaling about 20% of the section) qualify as organic matter rich. At this same locality the lower 185 ft (56.4 m) of the Marmaton Group contains no organic-matter-rich nearshore shale, 1.0 ft (0.30 m) of coal, and 11.7 ft (3.6 m) of offshore shale (totaling about 7.0% of the section).

Core samples of the Chattanooga Shale in southeastern Kansas and northeastern Oklahoma are scarce and, where they are available, represent only a fraction of the thickness of the formation. As examples, the samples of Chattanooga Shale (appendixes 1 and 2) collected for this study represent the basal 3 ft (0.9 m) (Davis A #2 well), the basal 12 ft (3.7 m) (Bock #1 well), and the basal 9 ft (2.7 m) (Stauffer #1 well) of the shale. In this part of eastern Kansas the Chattanooga Shale is between 50 ft and 100 ft (15 m and 30 m) thick (Adler et al., 1971, fig. 13).

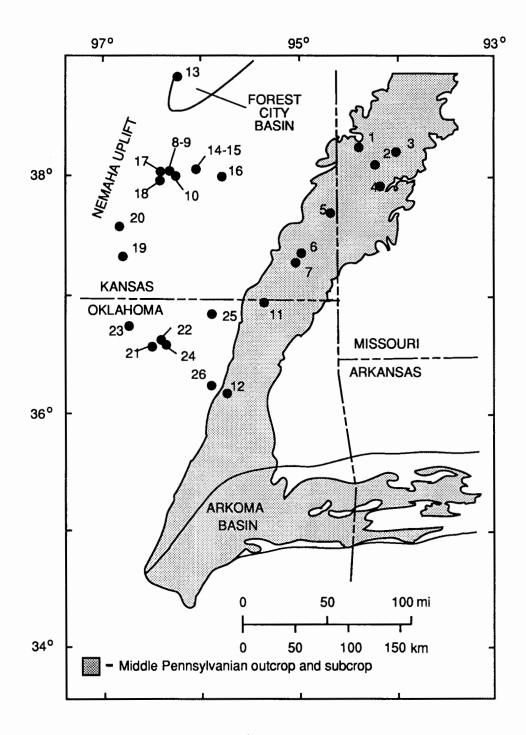


FIGURE 1—Locations of sampled Cherokee Group oil fields and sampled Cherokee Group, Marmaton Group, and Chattanooga Shale rocks in southwestern Missouri, southeastern Kansas, and northeastern Oklahoma. Locations are listed in appendix 1. Outcrop line is from King et al. (1974).

Methods

We determined total organic carbon (TOC) contents by a wet oxidation method slightly modified from Bush (1970). Procedures for measuring vitrinite reflectance (R_0 , oil immersion, random orientation) are described by Bostick and Alpern (1977).

For the Rock-Eval pyrolysis assays we used the instrument (Girdel, Inc.) and method of Espitalié et al. (1977). This method measures contents of volatile hydrocarbons (S_1 peak, mg HC/g rock), pyrolytic hydrocarbons (S_2 peak, mg HC/g rock), pyrolytic carbon dioxide (S_3 peak, mg CO₂/g rock), and temperature of maximum rate of pyrolytic hydrocarbon generation (T_{max}). S_1 , S_2 , and S_3 are combined or normalized by TOC to generate various indexes used for source rock evaluation, including genetic potential ($S_1 + S_2$, mg HC/g rock), hydrogen index (S_2 /TOC, mg HC/g TOC), and oxygen index (S_3 /TOC, mg CO₂/g TOC). Hydrogen index and oxygen index correlate with kerogen H/C and O/C ratios, respectively (Espitalié et al., 1977; Orr, 1983).

We extracted bitumens from powdered rock samples using a Soxhlet apparatus and chloroform for 24 hours. To remove sulfur, we refluxed with polished copper metal. We then concentrated the filtered extract solution at room temperature in a nitrogen atmosphere and diluted the solution with *n*-heptane to precipitate asphaltenes. We next separated a concentrate of the solution by using column chromatography on silica gel, eluting successively with heptane, benzene, and benzene-methanol (1:1 v/v) to collect the saturated hydrocarbon, aromatic hydrocarbon, and resin (NSO) fractions, respectively. We treated oil fractions in the same manner.

We used a Hewlett-Packard 5880 instrument for gas chromatography analyses of the saturated hydrocarbon fractions of oils and rock extracts. This instrument was equipped with a wall-coated open-tubular (WCOT)

column, 50 m \times 0.35 mm I.D., coated with SE54, and was temperature programmed from 50°C to 320°C at 4°C/min. The flame ionization detector temperature was 350°C; the injection port temperature was 245°C, with 1 μ L injected. We based the identification of peaks on the resultant chromatograms on relative retention time.

For gas-chromatography mass spectrometry analysis we used a Hewlett-Packard 5880 instrument directly coupled to a Kratos MS-30 mass spectrometer. The HP 5880 was equipped with a WCOT 50 m × 0.35 mm I.D. column coated with SE54 and temperature programmed from 80°C to 160°C at 10°C/min and then from 160°C to 340°C at 3°C/min. We operated the mass spectrometer ion source at 70 eV with a pressure of 10^{-6} torr at a temperature of 200°C. To determine relative distributions of terpanes (m/z = 191) and steranes (m/z = 217), we used multiple ion detection. This was accomplished by switching the accelerating potential to the specific mass at a constant magnetic field and scanning over the mass peak ± 250 mg/kg for 100 ms for each mass monitored.

We converted saturated and aromatic hydrocarbon fractions separated from oils and rock extracts to carbon dioxide in a high-vacuum combustion gas-transfer apparatus. We determined stable-carbon isotope ratios with a Finnigan MAT 251 isotope-ratio mass spectrometer. We directly compared the isotope compositions of carbon dioxide from the samples to working reference standards of carbon dioxide prepared from NBS limestone ($\delta^{13}C = 1.96$ % PDB). All ratios are reported as standard per-mil deviation relative to the Peedee belemnite standard (PDB):

 δ^{13} C°/ $_{\infty}$ = [(R sample/R standard) – 1] × 10⁻³, where R is the ratio of ¹³C to ¹²C.

Results and discussion

Source rock potential

Genetic potential $(S_1 + S_2, \text{mg HC/g sample})$ is a summary measure of hydrocarbon-generating potential and depends on organic matter amount, type, and thermal maturity (Espitalié et al., 1977; Tissot and Welte, 1978, p. 445–447). In this study we measured the amount of organic matter by total organic carbon content (wt %). We determined the type of organic matter by hydrogen index (mg HC/g TOC) and oxygen index (mg CO_/g TOC) and the organic matter thermal maturity by $T_{\text{max}}(^{\circ}\text{C})$ and vitrinite reflectance (% R_0).

The minimum organic carbon content necessary to generate and expel oil from a shale source rock lies between 0.4% and 1.4%, with the minimum probably closer to the higher of these two values (Ronov, 1958).

Organic carbon contents for 72 samples from the Cherokee Group and Marmaton Group and 13 samples from the Chattanooga Shale are listed in appendix 3 and summarized in table 1. The data in table 1 show that the organic carbon contents of the three lithofacies within the Cherokee Group and Marmaton Group [nearshore shales (\bar{x} = 2.9%, n = 19), offshore shales (\bar{x} = 13%, n = 24), and coals (\bar{x} = 60%, n = 29)] and the Chattanooga Shale (\bar{x} = 3.5%, n = 13) are all significantly higher than 1.4%, suggesting that each could be a source rock for oil and/or natural gas.

The type of organic matter (as shown by the hydrogen index and the oxygen index) is an indicator of the nature of the hydrocarbon (oil, gas, or both) that would most likely be generated. Type I organic matter generates primarily oil; type II generates both oil and gas, and type III gener-

TABLE 1—Organic geochemical analyses of Cherokee Group and Marmaton Group shale, coal, and oil samples and Chattanooga Shale samples.

	Cherokee C	Group and Marmator	Group		Cherokee
	Nearshore Shale	Coal	Offshore Shale	Chattanooga Shale	Group Oil
Organic carbon (%)	2.9 × 2.0°	60 ± 13	13 × 1.4°	3.5 ± 0.7	_
	(n = 19)	(n = 29)	(n = 24)	(n = 13)	
Genetic potential	$1.6 \times 3.0^{\circ}$	140 ± 47	$34 \times 1.6^{\circ}$	14 ± 3.7	-
(mg HC/g sample)*	(n = 19)	(n = 29)	(n = 24)	(n = 13)	
Hydrogen index ^b	$40 \times 2.1^{\circ}$	230 ± 52	$240 \times 1.2^{\circ}$	340 ± 50	_
(mg HC/g TOC)	(n = 19)	(n = 29)	(n = 24)	(n = 13)	
Pristane/phytane ratiod	3.9 ± 1.0	6.0 ± 1.9	1.7 ± 0.2	1.6 ± 0.1	1.6 ± 0.1
	(n = 8)	(n = 9)	(n = 15)	(n = 2)	(n = 11)
Saturated HC δ ¹³ C (°/∞)°	-26.6 ± 0.2	-27.3 ± 1.1	-28.4 ± 0.7	-29.2 ± 0.2	30.0 ± 0.5
	(n=2)	(n = 3)	(n = 4)	(n = 2)	(n = 7)
Aromatic HC δ ¹³ C (⁰/∞)°	-26.1 ± 0.1	-25.7 ± 0.8	-27.9 ± 0.6	-28.5 ± 0.2	-28.9 ± 0.4
,,,,	(n=2)	(n = 3)	(n = 4)	(n = 2)	(n = 7)

n = number of samples; -indicates no data.

ates primarily gas (Tissot and Welte, 1978, p. 447). The hydrogen and oxygen indexes for the 72 samples from the Cherokee Group and Marmaton Group and the 13 samples from the Chattanooga Shale are listed in appendix 2, plotted in fig. 2, and summarized in table 1. The curved lines in fig. 2 indicate approximate thermal evolution pathways for organic matter types I, II, and III. The hydrogen and oxygen indexes of organic matter in the Chattanooga Shale and in the Cherokee Group and Marmaton Group coals and offshore shale lithofacies plot between type II and type III evolutionary pathways, suggesting that each has the capability to generate oil and natural gas. Organic matter in the nearshore shale lithofacies is degraded type III, indicating that organic matter in these shales has little generating capacity.

The main zone of oil generation (oil window) occurs over the vitrinite reflectance range (R_0) from 0.5% to 1.3%, which corresponds to $T_{\rm max}$ values from 430°C to 460°C (Tissot and Welte, 1978, p. 450–455). Vitrinite reflectance values for eight coal samples from the Cherokee Group and Marmaton Group (table 2) range from 0.53% to 0.80%; T_{max} values for 72 shale and coal samples from the Cherokee Group and Marmaton Group range from 430°C to 453°C (appendix 3). These measurements show that organic matter in Cherokee Group and Marmaton Group rocks is thermally mature with respect to petroleum generation in southwestern Missouri, southeastem Kansas, and northeastern Oklahoma. The data presented by Hatch et al. (1984, tables 3 and 4) indicate a higher level of organic matter thermal maturity in the more deeply buried Cherokee Group and Marmaton Group rocks in Osage County, Oklahoma. There, the T_{max} values for

organic matter in 42 samples of coal and shale from three cores range from 444°C to 474°C, and the vitrinite reflectance values for three coal samples range from 0.87% to 0.97%.

Organic matter in samples of the Chattanooga Shale from Wabaunsee and Greenwood counties, Kansas, is thermally mature with respect to petroleum generation, as indicated by $T_{\rm max}$ values that range from 434°C to 445°C (appendix 3). South of Greenwood County in southeastern Kansas and northeastern Oklahoma, organic matter in the Chattanooga Shale is assumed to be thermally mature because organic matter in the overlying Middle Pennsylvanian shales and coals is thermally mature.

Tissot and Welte (1978, p. 447) suggest the following classification of genetic potential $(S_1 + S_2, \text{ mg HC/g sample})$:

<2 mg/g: Little or no source rock potential 2-6 mg/g: Moderate source rock potential >6 mg/g: Good source rock potential

Based on this classification, the data summarized in table 1 show that the Cherokee Group and Marmaton Group coals $(\bar{x} = 140 \text{ mg/g}, n = 29)$ and offshore shales $(\bar{x} = 34 \text{ mg/g}, n = 24)$ and the Chattanooga Shale $(\bar{x} = 14 \text{ mg/g}, n = 13)$ all have good potential to generate hydrocarbons. In contrast, most Cherokee Group and Marmaton Group nearshore shales $(\bar{x} = 1.6 \text{ mg/g}, n = 19)$ have little or no source rock potential. Because these rocks are thermally mature with respect to petroleum generation, some oil and/or natural gas has likely been generated. This implies that the genetic potential for these rocks was originally somewhat higher.

a. $S_1 + S_2$ (Rock-Eval pyrolysis).

b. S./organic carbon.

c. Geometric mean and deviation.

d. Pristane/phytane ratio is based on relative peak heights.

e. Relative to the PDB marine-carbonate standard.

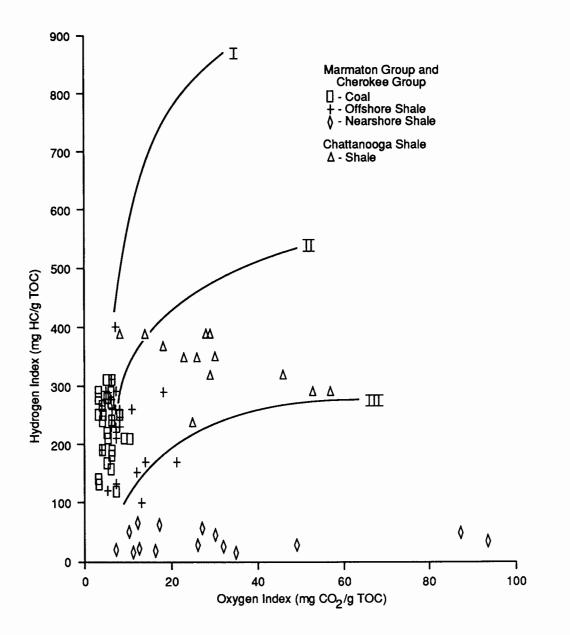


FIGURE 2—RELATIONSHIP OF HYDROGEN INDEX TO OXYGEN INDEX for 72 samples from the Cherokee Group and Marmaton Group and 13 samples of Chattanooga Shale from southwestern Missouri, southeastern Kansas, and northeastern Oklahoma. The curved lines (I, II, and III) indicate approximate evolution pathways for different end-member types of sedimentary organic matter.

TABLE 2—VITRINITE REFLECTANCE (R_0) for eight coal samples from the Cherokee Group and Marmaton Group.

Sample Number	v	itrinite Reflectai (% R _o)•	nce	Number of Measurements	Quality (PASLV + PGH) ^c
	Median	Range	Standard Deviation		
MC168-6	0.53	0.42-0.61	0.03	125	99699-911
D189091	0.65	0.54-0.75	0.03	125	97799-313
D196198	0.70	0.59-0.83	0.03	127	97699-214
889-72	0.68	0.55-0.79	0.05	139	87699-513
1513-13A	0.57	0.48-0.66	0.03	125	97699-213
1513-27	0.63	0.47-0.75	0.05	125	97799-313
1513-79	0.73	0.58-0.82	0.04	125	97799-313
1535-146	0.80	0.66-0.91	0.05	125	75599-512

Data from Hatch et al. (1984, table 4). Sample locations are listed in appendix 1, sample descriptions in appendix 2.

- a. Reflectance of vitrinite grains at random orientation, oil immersion objective.
- b. Range of values, first-cycle vitrinite constituent group.
- c. Operator subjective evaluation (scale 1-9 of increasing quality or abundance) of polish (P), abundance (A) (in the preparation), size (S), ease of picking "low-gray" (L) or first-cycle vitrinite, assurance that it is vitrinite (V), plus pyrite (P) in organic grains, organic groundmass (G), and "high-gray" (H) seen but not included in the measurements (inertinite in coals).

Oil-source rock correlation

Oil-source rock correlations are based on comparisons of the geochemistry of oils with bitumens extracted from potential source rocks. Bitumens and oils are most easily correlated by comparison of saturated hydrocarbon distributions, terpane (m/z = 191) and/or sterane (m/z = 191)217) distributions, and carbon isotope compositions of saturated and aromatic hydrocarbon fractions. The composition of bitumen reflects the composition of the organic matter in the rock. Organic matter composition is determined by a number of factors, including the relative amounts and compositions of the allochthonous and autochthonous organic matter fractions, the physical and chemical conditions of the depositional environment, the nature of early postdepositional biochemical degradation, and the thermal maturity of the organic matter. For oils these parameters are also affected by biodegradation in the petroleum reservoir and, possibly, distance of oil migration. Detailed discussions of the geologic and geochemical controls of bitumen and oil chemistry are beyond the scope of this study. For an extensive introduction to these topics, refer to texts by Tissot and Welte (1978, 1984) and Hunt (1979), and for an in-depth review of biomarkers, to the article by Mackenzie (1984).

We extracted bitumens from 32 of the 72 samples from the Cherokee Group and Marmaton Group and from 2 Chattanooga Shale samples. We list the total bitumen (mg/kg) contents for these samples in appendix 3. Figure 3 shows representative saturated hydrocarbon distributions from extracts of samples of Cherokee Group and Marmaton Group coals (fig. 3A), offshore shales (fig. 3B), nearshore shales (fig. 3C), the Chattanooga Shale (fig. 3D), and Cherokee Group oils (fig. 3E).

Saturated hydrocarbon distributions for coals (see fig. 3A) are significantly different from those of Cherokee

Group and Marmaton Group offshore and nearshore shales, the Chattanooga Shale, and Cherokee Group oils (see figs. 3B-E) in that pristane is the dominant compound, the pristane/phytane ratio is high $(\bar{x} = 6.0, n = 9)$ tables 1 and 3), and the C_{19} to C_{31} n-alkanes display an odd-carbon predominance. Distributions of the $n C_{15}^{+}$ saturated hydrocarbons of Cherokee Group and Marmaton Group offshore shales, the Chattanooga Shale, and Cherokee Group oils are similar and are characterized by a predominance of normal alkanes over isoprenoids (e.g., pristane), relatively low pristane/phytane ratios ($\bar{x} = 1.7$, n = 15; \overline{x} = 1.6, n = 2; and \overline{x} = 1.6, n = 11, respectively; table 1), and uniformly decreasing amounts of normal alkanes with increasing carbon number. Cherokee Group and Marmaton Group nearshore shales have higher pristane/ phytane ratios ($\bar{x} = 3.9$, n = 8) compared with offshore shales, the Chattanooga Shale, and Cherokee Group oils, and the C₂₅ to C₃₁ n-alkanes display an odd-carbon predominance. The saturated hydrocarbon distributions of Cherokee Group and Marmaton Group coals and nearshore shales are dissimilar to those of the Cherokee Group oils, indicating that these lithofacies are not source rocks for these oils.

Figure 4 shows representative terpane (m/z = 191) and sterane (m/z = 217) distributions from bitumens extracted from Cherokee Group and Marmaton Group coals (figs. 4A,B), offshore shales (figs. 4C,D), the Chattanooga Shale (figs. 4E,F), and Cherokee Group oils (figs. 4G,H). Terpane and sterane peaks are identified in table 4. Terpane and sterane distributions from Cherokee Group and Marmaton Group nearshore shales are not illustrated here because these shales have minimal potential to generate oil. Terpane distributions from coal (fig. 4A) differ significantly from those of Cherokee Group and Marmaton Group offshore shales (fig. 4C), the Chattanooga Shale

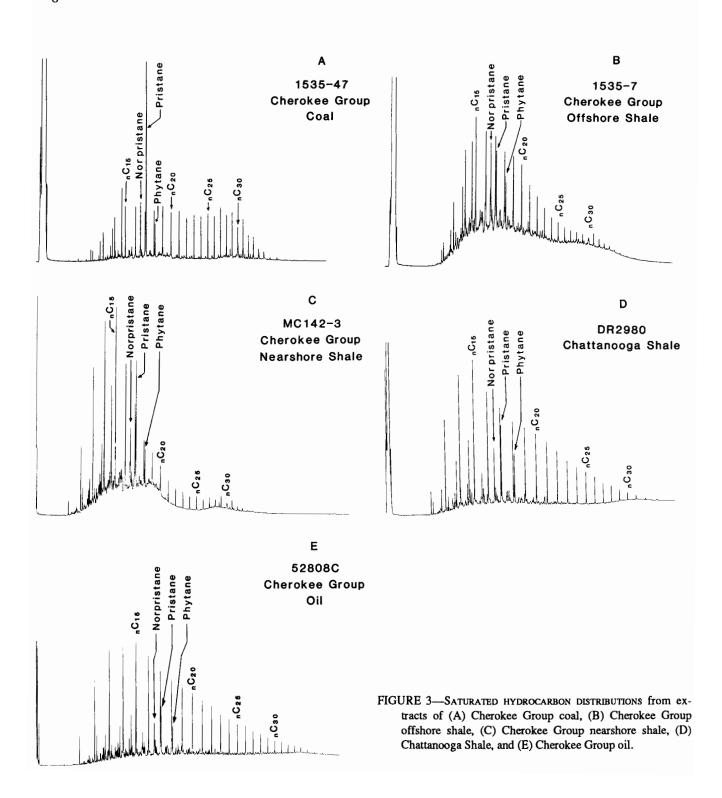


TABLE 3—PRISTANE/PHYTANE RATIOS for 11 Cherokee Group oils from southeastern Kansas and northeastern Oklahoma.

Sample Number	Pristane/Phytane*	
X-628	1.6	
58204C	1.6	
64188C	1.6	
58201C	1.6	
58208C	1.5	
58200C	1.6	
58203C	1.7	
58206C	1.7	
58209C	1.7	
64249C	1.6	
58210C	1.5	

Sample locations are listed in appendix 1.

(fig. 4E), and Cherokee Group oils (fig. 4G). Coal terpane distributions are characterized by low relative amounts of tricyclic compounds (peaks 1–4 and 6–8) compared with pentacyclic compounds (peaks 9–16) and high relative amounts of C_{19} and C_{20} tricyclic, C_{24} tetracyclic, and C_{27} - $17\alpha(H)$ -tris-norhopane. In contrast, terpane distributions from Cherokee Group and Marmaton Group offshore shales, Cherokee Group oils, and the Chattanooga Shale are characterized by relatively less abundant tricyclic compounds compared with pentacyclic compounds, low relative amounts of C_{19} tricyclic, C_{24} tetracyclic, and C_{27} - $17\alpha(H)$ -tris-norhopane, and high relative amounts of C_{23} , C_{26} , C_{28} , and C_{29} tricyclic compounds.

Sterane distributions differ significantly in the relative amounts of C_{27} -13 β ,17 α -diacholestanes (peaks 17 and 18) and C_{27} -14 α ,17 α -cholestanes (peaks 19 and 22). Sterane distributions from Cherokee Group and Marmaton Group coals (fig. 4B) are characterized by low relative amounts of C_{27} -13 β ,17 α -diacholestanes and C_{27} -14 α ,17 α -cholestanes; Cherokee Group and Marmaton Group offshore shales (fig. 4D) are characterized by intermediate amounts of C_{27} -13 β ,17 α -diacholestanes and high amounts of C_{27} -14 α ,17 α -cholestanes; and the Chattanooga Shale and the Cherokee Group oils (figs. 4F and 4H, respectively) are characterized by intermediate amounts of C_{27} -13 β ,17 α -diacholestanes and C_{27} -14 α ,17 α -cholestanes.

The carbon isotope compositions of the saturated and aromatic hydrocarbon fractions from oils and rock extracts are listed in table 5, summarized in table 1, and illustrated in figure 5. The carbon isotope values exhibit a range, with saturated hydrocarbon fractions from Cherokee Group and Marmaton Group coals the most enriched in 13 C ($\bar{x}\,\delta^{13}$ C $_{\rm sat}=-27.3$ °/∞, n=3), Cherokee Group and Marmaton Group offshore shales less enriched ($\bar{x}\,\delta^{13}$ C $_{\rm sat}=-28.4$ °/∞, n=4), and Chattanooga Shale and Cherokee Group oils least enriched ($\bar{x}\,\delta^{13}$ C $_{\rm sat}=-29.2$ °/∞, n=2; and $\bar{x}\,\delta^{13}$ C $_{\rm sat}=-30.0$ °/∞, n=6, respectively). Aromatic hydro-

TABLE 4—IDENTIFIED TERPANES AND STERANES.

Peak	Compound Name
Terpanes	
1	C ₁₉ tricyclic
2	C ₂₁ tricyclic
3	C ₂₃ tricyclic
4	C ₂₅ tricyclic
5	C ₂₄ tetracyclic
6	C ₂₆ tricyclics
7	C ₂₈ tricyclics
8	C ₂₀ tricyclics
9	$C_{27}^{-18\alpha(H)}$ -tris-norneohopane (TS)
10	C_{27}^{-18} (H)-tris-norhopane (TM)
11	C ₂₀ norhopane
12	$C_{30}^{-17\alpha(H),21\beta(H)-hopane}$
13	C_{31}^{-17} $\alpha(H)$,21 $\beta(H)$ -homohopane $(s+r)$
14	C_{32}^{-17} $\alpha(H)$,21 $\beta(H)$ -bis-homohopane (s + r)
15	C_{33}^{-17} $\alpha(H)$, 21 $\beta(H)$ -tris-homohopane (s + r)
16	C_{34}^{3} -17 α (H),21 β (H)-tetrakishomohopane (s + r)
Steranes	
17	C_{27} -13 β ,17 α -diacholestane (20S)
18	C_{27}^{-13} ,17 α -diacholestane (20R)
19	$C_{27}^{-14\alpha,17\alpha}$ -cholestane (20S)
20	C_{27}^{-14} ,17 β -cholestane (20R) + C_{29} -24-ethyl-
	13β,17α-diacholestane
21	C_{27} -14 β ,17 β -cholestane (20S)
22	C_{27}^{27} -14 α ,17 α -cholestane (20R)
23	C_{28}^{-1} -14 α ,17 α -24-methy-cholestane (20S)
24	C_{28}^{23} -14 α ,17 α -24-methyl-cholestane (20R)
25	C_{20}^{-14} -14 α ,17 α -24-ethyl-cholestane (20S)
26	$C_{\infty}^{-14\beta,17\beta-24}$ -ethyl-cholestane (20R)
27	C_{20}^2 -14 β ,17 β -24-ethyl-cholestane (20S)
28	C_{∞} -14 α ,17 α -24-ethyl-cholestane (20R)

carbon fractions show similar trends, with fractions from Cherokee Group and Marmaton Group coals the most enriched in 13 C (\$\bar{x} \delta^{13}\$C_{arom} = -25.8 \(^{9}\)/\[\infty_{\infty}, n = 3\), Cherokee Group and Marmaton Group offshore shales less enriched (\$\bar{x} \delta^{13}\$C_{arom} = -27.9 \(^{9}\)/\[\infty_{\infty}, n = 4\), and Chattanooga Shale and Cherokee Group oils the least enriched (\$\bar{x} \delta^{13}\$C_{arom} = -28.5 \(^{9}\)/\[\infty_{\infty}, n = 2\); and \$\$\bar{x} \delta^{13}\$C_{arom} = -28.9 \(^{9}\)/\[\infty_{\infty}, n = 6\), respectively).

Cherokee Group oils and extracts of the Chattanooga Shale have similar saturated hydrocarbon distributions, pristane/phytane ratios, and terpane and sterane distributions, suggesting that the Chattanooga Shale is the source rock for the oils. Saturated hydrocarbon distributions, pristane/phytane ratios, and terpane and sterane distributions from extracts of Cherokee Group and Marmaton Group coals are dissimilar to Cherokee Group oils. The primary geochemical mismatch between extracts of Cherokee Group and Marmaton Group offshore shales and Cherokee Group oils is the sterane distribution. In addition, the carbon isotope compositions of the saturated and aromatic hydrocarbon fractions from the Cherokee oils are closer to the isotope compositions of extracts of the

a. Pristane/phytane ratios calculated from relative peak heights.

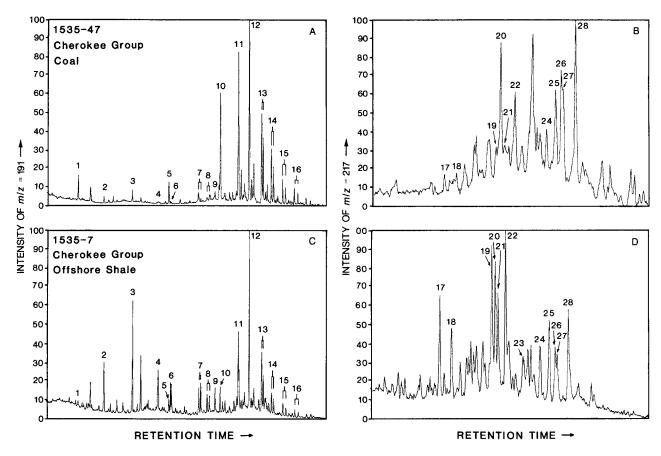
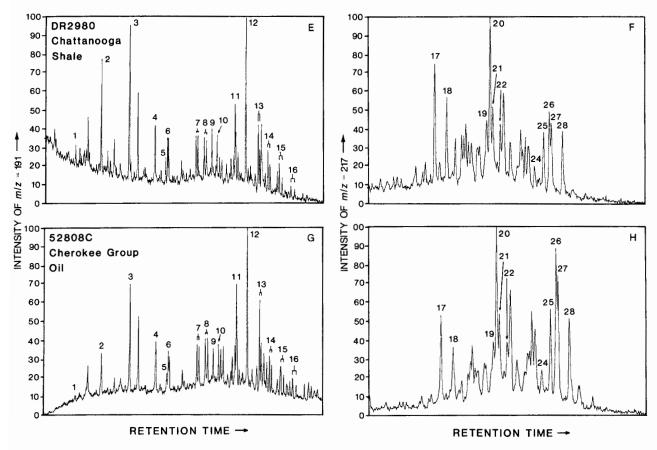


FIGURE 4—Terpane (m/z = 191) and sterane (m/z = 217) ion fragmentograms for (A,B) Cherokee Group coal, (C,D) Cherokee Group offshore shale, (E,F) Chattanooga Shale, and (G,H) Cherokee Group oil.

Chattanooga Shale than to those of extracts of Cherokee Group and Marmaton Group offshore shales and coals.

The correlation established between Cherokee Group oils and the Chattanooga Shale implies that, if continuous porosity trends and migration pathways exist in the Mississippian carbonates above and/or in the Paleozoic section immediately below the Chattanooga Shale in southeastern Kansas and northeastern Oklahoma and if

trapping conditions are present, the porosity can be charged with oil derived from the Chattanooga Shale. A second implication of this study is that, even though the Cherokee Group and Marmaton Group coals and offshore shales are not the source rocks of the Cherokee Group oils, these rocks have excellent remaining generation potential and may be source rocks for other midcontinent oils and/or natural gases.



(fig. 4, cont.)

Summary

- 1. Middle Pennsylvanian (Desmoinesian) Cherokee Group and Marmaton Group coals and offshore shales and Late Devonian–Kinderhookian Chattanooga Shale all have significant potential to be source rocks for oil and/or natural gas. Cherokee Group and Marmaton Group nearshore shales have little or no potential to generate oil and/or natural gas.
- 2. Organic matter in the Chattanooga Shale, Cherokee Group, and Marmaton Group in southwestern Missouri,
- southeastern Kansas, and northeastern Oklahoma is thermally mature with respect to oil generation.
- 3. The extract geochemistry of the Chattanooga Shale is similar to that of the Cherokee Group oils, whereas the extract geochemistries of the Cherokee Group and Marmaton Group offshore shales and coals are dissimilar. Therefore the Chattanooga Shale is the most probable source rock for the Cherokee Group oils.

TABLE 5— δ^{13} C ANALYSES OF SATURATED HYDROCARBON AND AROMATIC HYDROCARBON FRACTIONS from extracts from nine shales and coals from the Cherokee Group and Marmaton Group, extracts of two shale samples from the Chattanooga Shale, and seven Cherokee Group oils.

Sample Number	δ^{13} C for Saturated HC (°/ $_{\infty}$) ⁴	δ ¹³ C for Aromatic HC (°/∞)*
Cherokee Grou	up and Marmaton Group	
MC121-4	-26.6	-24.9
D189091	-28.6	-26.6
349-3	-27.4	-27.6
1535U-25	-28.7	-28.0
1535-12	-26.8	-26.0
1535-13A	-26.8	-25.6
1535-23	-26.5	-26.2
1535-25	-28.3	-27.4
1615-6	-29.0	-28.7
Chattanooga S	hale	
DR2980	-29.1	-28.4
STA2319	-29.3	-28.7
Cherokee Grou	up oils	
X-628	-29.6	-28.9
58204	-30.2	-29.4
58208	-30.3	-29.0
58200	-30.6	-29.2
58206	-29.2	-28.2
58209	-29.5	-28.7
64249	-30.4	-29.0

Cherokee Group oil and Cherokee Group and Marmaton Group extract data from Hatch et al. (1984, table 7). Sample locations are listed in appendix 1; sample descriptions in appendix 2. HC = hydrocarbons.

a. Relative to the PDB marine-carbonate standard.

ACKNOWLEDGMENTS—Special thanks go to George E. Claypool, who originally suggested the study and provided much encouragement. We would like to recognize the following organizations for their active support in the acquisition of core and oil samples: Marathon Oil Company, Littleton, Colorado; Missouri Department of Natural Resources, Division of Geology and Land Survey, Rolla, Missouri; and the Kansas Geological Survey, Lawrence, Kansas. Some of the geochemical analyses were provided by Sister Carlos M. Lubeck, Mark J.

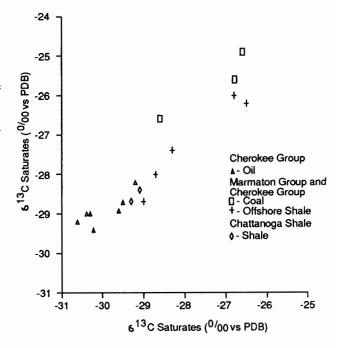


FIGURE 5— δ^{13} C of saturated and aromatic hydrocarbon fractions from Marmaton Group, Cherokee Group, and Chattanooga Shale rock extracts and Cherokee Group oils.

Pawlewicz, Charles N. Threlkeld, and April K. Vuletich. The illustrations were originally drafted by William J. Betterton and revised by Mark Schoneweis. Earlier drafts of this manuscript have benefited from reviews by Collin Barker, Wallace G. Dow, W. Lynn Watney, K. David Newell, Jerry L. Clayton, and Charles W. Holmes. Trade and company names are for descriptive purposes only and do not imply endorsement by the US Geological Survey or the Kansas Geological Survey.

Appendixes 1–3

Appendix 1

LOCATIONS AND SAMPLED INTERVALS for 72 samples from the Middle Pennsylvanian (Desmoinesian) Cherokee Group and Marmaton Group, 13 samples of Devonian-Kinderhookian Chattanooga Shale, and 11 samples of Cherokee Group oils.

Index Map Number	Core or Sample Number	Location	Depth Interval (Number of Samples or Producing Interval)
Cherokee Gro	oup and Marmaton Group		
1	MC 121	SW sec. 1, T. 40 N., R. 32 W., Bates County, Missouri	56.6-98.7 ft (5 core samples)
2	MC 142	SW sec. 29, T. 39 N., R. 30 W., Bates County, Missouri	85.0-88.0 ft (2 core samples)
3	M-7-65	NE sec. 30, T. 40 N., R. 27 W., Henry County, Missouri	strip mine (1 channel sample)
4	MC 168	SE sec. 35, T. 37 N., R. 30 W., Vernon County, Missouri	53.3-59.6 ft (4 core samples)
5	D189091	SE sec. 21, T. 26 S., R. 25 E., Bourbon County, Kansas	strip mine (1 channel sample)
6	D196198	SE sec. 2, T. 31 S., R. 25 E., Crawford County, Kansas	strip mine (1 channel sample)
7	PM-6	SE sec. 8, T. 32 S., R. 22 E., Cherokee County, Kansas	44.4–349.3 ft (6 core
8	871C, J. W. Martindell No. 52	NW sec. 31, T. 23 S., R. 10 E.,	samples) 2062–2097 ft (2 core
9	349C, J. W. Martindell No. 50	Greenwood County, Kansas SW sec. 31, T. 23 S., R. 10 E.,	samples) 2090–2289 ft (6 core samples)
10	889C, Teter No. 4	Greenwood County, Kansas NE sec. 6, T. 24 S., R. 10 E., Greenwood County, Kansas	2369-2401 ft (4 core samples)
11	1535C, Rexwinkle No. 1	SE sec. 30, T. 29 N., R. 18 E., Craig County, Oklahoma	95.3-766 ft (21 core samples)
12	1615C, Kelly No. 1	NW sec. 23, T. 20 N., R. 14 E., Rogers County, Oklahoma	187-1096 ft (19 core samples)
Chattanooga	Shale		
13	Davis A No. 2	SW sec. 33, T. 13 S., R. 10 E., Wabaunsee County, Kansas	2977-2980 ft (2 core samples)
14	ERDA Stauffer No. 1	NE sec. 20, T. 23 S., R. 12 E., Greenwood County, Kansas	2313–2322 ft (5 core samples)
15	ERDA Bock No. 1	NE sec. 15, T. 23 S., R. 12 E., Greenwood County, Kansas	2164-2176 ft (6 core samples)
Cherokee Gro	oup oils	•	
16	X-628, Headley "A" 1-9, Winterscheid field	sec. 29, T. 23 S., R. 14 E., Woodson County, Kansas	- (Bartlesville sand)
17	58204C, Cities Service	NW sec.15, T. 23 S., R. 9 E., Greenwood County, Kansas	2349 ft (Burbank sand)
18	64188C, Phillips Petroleum Cannon No. 14, Thrall field	NW sec. 12, T. 24 S., R. 9 E., Greenwood County, Kansas	- (Cherokee sand)
19	58201C, Texas Co. C. J. Gulick, Burden field	NE sec. 32, T. 31 S., R. 6 E., Cowley County, Kansas	2200 ft (Burbank sand)
20	58208C, Morrison Producing, Haverhill field	SW sec. 35, T. 28 S., R. 5 E., Butler County, Kansas	- (Burbank sand)
21	58200C, Texas Company No. 4, Burbank S. field	NE sec. 30, T. 25 N., R. 8 E., Osage County, Oklahoma	2470 ft (Burgess sand)
22	58203C, Nadel, Gussman and Sinclair Mayer No. 10, Simon Lebow field	SE sec.19, T. 25 N., R. 9 E., Osage County, Oklahoma	2300 ft (Mississippian chat)

(Appendix 1, cont.)

Index Map Number	Core or Sample Number	Location	Depth Interval (Number of Samples or Producing Interval)
23	58206C, General	SW sec. 24, T. 26 N., R. 4 E.,	3100 ft (Prue or
	American Soldani No. 1, Olsen field	Osage County, Oklahoma	Squirrel sand)
24	58209C, Layton No. 30 Pershing field	sec. 36, T. 25 N., R. 9 E., Osage County, Oklahoma	2001 ft (Bartlesville sand)
25	64249, SW Bartlesville unit	T. 26–28 N., R. 12–14 E., Washington County, Oklahoma	- (Bartlesville sand)
26	58210C, Sunray Midcontinent, H. Spybuck, Sperry field	NW sec. 24, T. 21 N., R. 12 E., Tulsa County, Oklahoma	1217 ft (Burgess sand)

Data on Cherokee Group oils and Cherokee Group and Marmaton Group rocks from Hatch et al. (1984, tables 2 and 1, respectively). – indicates no data.

Appendix 2

Sample numbers, Lithologies, Lithofacies, and depth intervals or thickness for 72 rock samples from the Middle Pennsylvanian, Cherokee, and Marmaton groups, and 13 rock samples from the Late Devonian-Kinderhookian Chattanooga Shale, southwestern Missouri, southeastern Kansas, and northeastern Oklahoma.

Sample Number	Lithology	Lithofacies*	Depth Interval or Thickness (ft)	Notes
Cherokee Group ar	nd Marmaton Group			
MC121-2	Shale, N2, phosphatic	Offshore shale	62.3-63.1	Anna shale
MC121-3	Shale, N2	Offshore shale	63.6–65.1	
MC121-4	Coal	Nearshore shale	73.3–73.8	Lexington coal
MC121-5	Shale, N3, fossiliferous	Nearshore shale	76.8–81.2	•
MC121-7	Coal	Nearshore shale	83.7-83.9	
MC142-3	Shale, N2	Nearshore shale	85.0-88.0	
MC142-4	Coal	Nearshore shale	88.0-89.4	Robinson Branch coal
M7-65	Shale, N2, phosphatic	Offshore shale	0.5	Seahorne shale
MC168-4	Shale, N3	Nearshore shale	53.3-59.6	
MC168-5	Shale, N2, phosphatic	Offshore shale	60.7-62.4	
MC168-6	Coal	Nearshore shale	62.6–64.1	
MC168-7	Shale, N3	Nearshore shale	80.0–86.5	
D189091	Coal	Nearshore shale	1.2	Mulky coal
D196198	Coal	Nearshore shale	1.5	Bevier coal
6-1	Shale, N2-N1	Offshore shale	44.4–49.6	Verdigris shale
6-2	Coal	Nearshore shale	52.0–52.7	Croweburg coal
6-12	Shale	Nearshore shale	150.7–152.3	0.0
6-13	Coal	Nearshore shale	152.3–153.0	Tebo coal
6-27	Shale	Nearshore shale	346.7–348.5	1000 0000
6-28	Coal	Nearshore shale	348.5–349.3	
871-3	Coal	Nearshore shale	2062.0–2062.9	
871-12	Shale, N2, phosphatic	Offshore shale	2095.7–2097.0	Excello shale
349-3	Shale, N2	Offshore shale	2095.1-2096.1	Excello shale
349-17	Shale, N2	Nearshore shale	2121.7–2122.7	Executo situito
349-38	Coal	Nearshore shale	2213.0–2213.1	
349-46	Shale, N2-N3	Offshore shale	2225.0–2226.4	Verdigris shale
349-57	Shale, N2, phosphatic	Offshore shale	2252.8–2253.9	v Claigils shale
349-69	Shale, N2	Offshore shale	2288.7–2289.3	
889-44	Shale, N3	Offshore shale	2368.7–2374.3	
889-61	Coal	Nearshore shale	2391.2–2392.1	
889-71	Shale, N3, fossiliferous		2400.0–2400.3	
889-72	Coal	Nearshore shale	2400.3–2400.3	
				Anna shale
1535u-5	Shale, N1-N2	Offshore shale Nearshore shale	95.3–97.1	
1535u-8	Coal		98.0–99.0	Lexington coal
1535u-23a	Shale, N2, calcareous	Offshore shale	200.7–200.8 and	Shaly partings in
1525 25	CL-1- NO	Off-111-	202.7–202.8	Higginsville limestone
1535u-25	Shale, N2	Offshore shale	229.6–235.5	Little Osage shale
1535-7	Shale, N2, phosphatic	Offshore shale	280.1–285.2	Excello shale
1535-12	Shale, N2-N3,	Offshore shale	304.0–306.7	
1505.10	calcareous, phosphatic		2071 2000	D
1535-13a	Coal	Nearshore shale	307.1–308.0	Bevier coal
1535-23	Shale, N2-N3,	Offshore shale	331.8–333.2	
	phosphatic			
1535-25	Shale, N2, phosphatic	Offshore shale	334.6–336.1	Verdigris shale
1535-27	Coal	Nearshore shale	342.3–344.0	Croweburg coal, 0.15 ft
1535-47	Coal	Nearshore shale	389.1-390.4	recovered
1535-66	Shale, N2, phosphatic	Offshore shale	440.7–441.7	Seahorne shale (?)
1535-69	Coal	Nearshore shale	445.0–446.0	Bottom 0.1 ft recovered
1535-78	Shale, N2	Nearshore shale	503.0-503.6	Doublin our It recovered
			202.0-202.0	

(Appendix 2, cont.)

Sample Number	Lithology	Lithofacies*	Depth Interval or Thickness (ft)	Notes
1535-107	Shale, N2-N3	Nearshore shale	588.9-600.0	Bottom 2.5 ft lost
1535-144	Shale, N3	Nearshore shale	685.4-690.7	
1535-146	Coal, shaly	Nearshore shale	691.5–692.5	Top 0.2 and bottom 0.3 ft sampled
1535-150	Coal	Nearshore shale	699.3-700.1	•
1535-159	Shale, N2-N3	Nearshore shale	711.9–725.5	
1535-187	Coal, shaly	Nearshore shale	765.4–765.7	
1615-3	Shale, N2, phosphatic	Offshore shale	186.9–189.4	Little Osage shale
1615-6	Shale, N2, phosphatic	Offshore shale	208.4-210.9	Excello shale
1615-12	Coal	Nearshore shale	221.3-221.9	
1615-53	Shale, N2-N3	Offshore shale	299.7-301.9	Verdigris shale
1615-56	Coal	Nearshore shale	320.0–321.7	Croweburg coal
1615-136	Shale, N3, phosphatic	Offshore shale	532.4-533.1	· · · · · · · · · · · · · · · · ·
1615-191	Shale, N2, phosphatic	Offshore shale	649.9–652.0	1615-191 and 1615-192 combined
1615-193	Shale, N2, fossiliferous	Nearshore shale	652.0-652.4	
1615-194	Coal	Nearshore shale	652.4–652.9	
1615-236	Shale, N3	Nearshore shale	766.9–772.0	
1615-237	Shale, N2, phosphatic	Offshore shale	772.0–772.4	
1615-264	Shale, N3	Nearshore shale	851.4–851.7	
1615-265	Shale, N2, phosphatic	Offshore shale	851.7–851.9	
1615-267	Coal	Nearshore shale	852.0–852.2	
1615-290	Shale, N2, calcareous	Offshore shale	890.9–891.6	
1615-292	Coal	Nearshore shale	893.4–894.3	
1615-341	Coal	Nearshore shale	1023.0–1024.4	
1615-382	Shale, N3, calcareous	Nearshore shale	1090.9–1095.7	
1615-384	Coal	Nearshore shale	1095.7–1096.0	
Chattanooga Shale				
DR2977	Shale, N2	-	2977.0–2977.2	Two samples basal
DR2980	Shale, N1	_	2980.0-2980.2	3.0 ft of shale
STA2313	Shale, N1	-	2313.0–2313.2	Five samples from
STA2315	Shale, N1	-	2315.0–2315.2	basal 9.0 ft of shale
STA2316	Shale, N1	-	2316.0-2316.2	
STA2318	Shale, N1	_	2318.0-2318.2	
STA2319	Shale, N1	_	2319.0-2319.2	
BOC2164	Shale, N1	_	2164.0-2164.2	Six samples from
BOC2166	Shale, N1	_	2166.0-2166.2	basal 12.0 ft of shale
BOC2168	Shale, N1	_	2168.0-2168.2	
BOC2170	Shale, N1	_	2170.0-2170.2	
BOC2172	Shale, N1	_	2172.0-2172.2	
BOC2174	Shale, N1	_	2174.0-2174.2	

Locations are listed in appendix 1. Cherokee and Marmaton Group data are from Hatch et al. (1984, table 1). 1 ft = 0.3048 m.

⁻ indicates no data or not applicable.

a. Lithofacies of Middle Pennsylvanian samples described by Heckel (1977) and Ebanks et al. (1979).

Appendix 3

Organic carbon content, Rock-Eval analysis, and extract composition for 72 rock samples from the Middle Pennsylvanian Cherokee Group and Marmaton Group and 13 rock samples from the Late Devonian-Kinderhookian Chattanooga Shale, southwestern Missouri, southeastern Kansas, and northeastern Oklahoma.

Sample Number	Organic Carbon (%)	Temperature of Maximum Yield (°C)b	Hydrogen Index (mg HC/g TOC) ^c	Oxygen Index (mg CO ₂ /g TOC) ^d	Genetic Potential (mg HC/g sample)*	Bitumen (mg/kg)	Pristane/ Phytane Ratio ^r
Cherokee Gro	oup and Mar	maton Group					
MC121-2	19.7	439	400	7	83	6700	1.4
MC121-3	9.9	441	220	7	23	2000	1.8
MC121-4	61.0	436	230	5	150	9400	6.7
MC121-5	1.7	436	17	16	0.36	_	-
MC121-7	50.4	441	250	8	120	_	_
MC142-3	6.0	433	21	12	1.6	_	3.3
MC142-4	76.6	435	210	9	160	_	-
M-7-65	20.1	441	290	18	61	5100	1.4
MC168-4	2.4	442	28	49	0.80	5100	4.4
MC168-5	18.0	443	230	8	44	4300	1.5
MC168-6	74.3	430	310	6	240	25,000	6.6
MC168-7	1.7	442	25	32	0.54		-
D189091	69.6	440	310	5	210	17,200	1.8
D196198	72.2	440	220	5	170	17,200	
6-1	9.4	444	190	4	20	_	_
6-2	40.9	438	250	4	100	-	-
6-12	8.5					-	-
		446	120	5	11	_	-
6-13	66.0	450	280	3	190	_	_
6-27	3.0	440	62	17	2.2	-	-
6-28	65.5	449	290	3	200	-	-
871-3	59.5	440	190	6	120	_	_
871-12	18.9	442	310	6	62	_	
349-3	21.6	440	280	6	64	6300	1.7
349-17	4.5	450	14	11	0.88	-	_
349-38	47.0	445	230	5	120	_	-
349-46	14.9	449	260	11	41	3800	1.9
349-57	8.1	446	170	14	15	2800	2.0
349-69	9.0	447	170	21	18	-	-
889-44	3.7	452	100	13	4.2	530	4.5
889-61	68.6	438	270	4	200	_	-
889-71	2.8	447	19	7	0.68	_	_
889-72	67.7	443	190	4	140	_	-
1535u-5	9.5	443	440	8	24	_	-
1535u-8	39.9	439	290	6	120	_	_
1535u-23a	7.6	441	270	4	24	_	_
1535u-25	11.0	445	230	6	27	3500	1.5
1535-7	14.8	447	260	8	40	3100	1.7
1535-12	4.7	449	130	7	7.0	1200	2.4
1535-13a	73.0	442	210	10	160	13,000	6.5
1535-23	7.2	444	120	5	10	1500	2.0
1535-25	14.6	448	290	7	45	5300	1.6
1535-25	35.3	445	160	6	57	5500	-
1535-27	65.9	443 447	240	6	170	7800	8.6
1535-47	7.9	437	150		13	7000	
1535-66 1535-69				12	160	_	_
	61.1	452	240	4		2500	- 52
1535-78	10.3	444	50	10	5.8	2500	5.2
1535-79	68.4	446	180	6	120	9300	7.5
1535-107	2.7	446	46	87	1.5	620	3.0

(Appendix 3, cont.)

Sample Number	Organic Carbon (%) ^a	Temperature of Maximum Yield (°C)b	Hydrogen Index (mg HC/g TOC) ^c	Oxygen Index (mg CO ₂ /g TOC) ^d	Genetic Potential (mg HC/g sample)•	Bitumen (mg/g)	Pristane/ Phytane Ratio ^f
1535-144	1.7	449	12	35	0.33	450	2.9
1535-146	33.4	445	130	3	47	2800	5.2
1535-150	55.6	453	120	7	73	_	_
1535-159	2.7	450	29	93	1.0	-	-
1535-187	42.4	453	210	5	95	-	-
1615-3	17.2	448	280	5	52	5500	1.6
1615-6	15.7	438	290	5	48	4300	1.6
1615-12	69.6	443	280	5	190	_	_
1615-53	12.4	444	260	6	34	4700	1.7
1615-56	76.1	452	170	5	130	5800	5.8
1615-136	7.3	443	260	11	21	-	_
1615-191	10.1	448	230	7	25	-	-
1615-193	3.9	453	65	12	3.1	_	-
1615-194	57.5	446	270	6	170	-	-
1615-236	1.2	445	26	26	0.45	_	_
1615-237	14.9	445	210	7	34	5800	2.0
1615-264	2.0	449	45	30	1.1	_	-
1615-265	12.5	448	260	7	34	_	-
1615-267	56.2	447	140	3	80	-	_
1615-290	21.0	448	240	6	55	3300	4.6
1615-292	62.7	447	250	3	160	7400	5.1
1615-341	66.7	454	240	4	160	-	-
1615-382	4.1	449	57	27	2.6	-	-
1615-384	44.1	448	270	4	120	-	-
Chattanooga	Shale						
DR2977	1.9	434	240	25	5.6	_	-
DR2980	3.4	438	390	8	15	4000	1.6
STA2313	4.1	443	320	29	15	-	_
STA2315	4.1	445	370	18	17	-	_
STA2316	3.1	442	290	57	10	-	-
STA2318	5.0	444	390	14	22	5300	1.6
STA2319	4.2	442	350	23	16	_	-
BOC2164	2.9	445	390	29	13	-	-
BOC2166	3.7	444	390	28	16		_
BOC2168	4.0	444	350	26	16	_	_
BOC2170	3.2	443	350	30	12	_	_
BOC2172	4.2	444	320	46	15	-	-
BOC2174	3.6	445	290	53	12	_	-

Locations listed in appendix 1; sample descriptions in appendix 2.

Cherokee Group and Marmaton Group data are from Hatch et al. (1984, tables 3 and 6).

HC = hydrocarbons; TOC = total organic carbon.

⁻ indicates no data.

a. Air-dried basis.

b. Temperature at which the yield of pyrolysis products (S_2) is at a maximum (T_{\max}) .

c. S₂/TOC. d. S₃/TOC. e. S₁ + S₂.

f. Ratios calculated from relative peak heights above base line.

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