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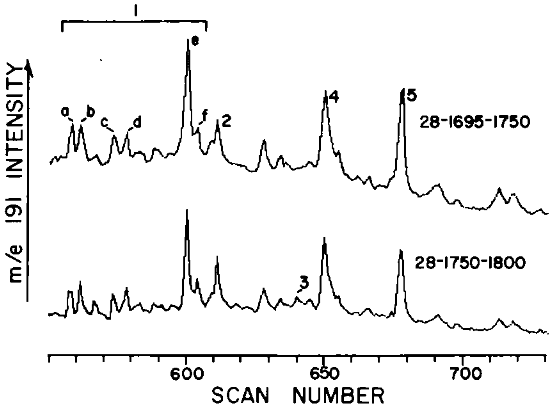
PETROLEUM OCCURRENCES AND SOURCE-ROCK POTENTIAL OF THE OUACHITA MOUNTAINS SOUTHEASTERN OKLAHOMA

JOSEPH A. CURIALE



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Title Page Illustration

Mass chromatograms (terpane) for Womble Formation samples. (See figure 44.)

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PETROLEUM OCCURRENCES AND SOURCE-ROCK POTENTIAL OF THE OUACHITA MOUNTAINS SOUTHEASTERN OKLAHOMA

JOSEPH A. CURIALE[1]

Abstract—Crude oils, solid bitumens, and potential oil-source rocks of the frontal and central Ouachita Mountains of southeastern Oklahoma were examined. The purposes of this study are to characterize the organic matter in each of these materials, and to correlate oils to potential source rocks in the Ouachita Mountains.

Four Ouachita Mountain oils and seven solid bitumens (grahamite and impsonite) were analyzed. The oils are paraffinic and range from 31.8 to 43.1 API gravity. Results indicate that the oils are thermally mature and generally unaltered. All four oils have a common source, as suggested by n-alkane, sterane, and hopane distributions, and stable-carbon–isotope ratios and vanadium/nickel ratios. A common source for the solid bitumens also is suggested, by isotope ratios and pyrolyzate characteristics. An origin by crude-oil biodegradation is suggested for these solids, on the basis of carbon-isotope ratios, elemental determinations, and sterane distributions of the solid-bitumen pyrolyzates.

Several stratigraphic intervals in the Ouachita Mountains possess adequate source potential for petroleum generation, as shown by their total organic carbon and extractable organic matter. Mississippian–Devonian rocks probably generated gas, whereas pre-Devonian rocks generated oil. The entire Paleozoic section is thermally mature enough to have generated oil, being about in the middle of the oil window. In general, the oil-source potential is greatest in Upper Ordovician (Polk Creek–Womble) rocks.

Oil–source-rock correlation techniques indicate that the oils examined from the frontal and central Ouachita Mountains most closely resemble a Silurian–Ordovician (Missouri Mountain–Polk Creek–Womble) source. This conclusion is supported by n-alkane, sterane, and isotope-ratio data. Listric reverse faults in the frontal Ouachitas might have served as migration conduits, connecting Silurian–Ordovician source rocks to Carboniferous reservoir rocks. A model is proposed whereby upward-migrating oil is gradually degraded as it nears the surface, yielding the near-surface solid-bitumen deposits. Further development of this model suggests that additional quantities of oil are yet to be discovered.

INTRODUCTION

Purpose

The Ouachita Mountains are in western Arkansas and southeastern Oklahoma (fig. 1), and represent the surface expression of the Ouachita Thrust Belt in these states. Petroleum occurrences in the Ouachita Mountains may be divided into three types: natural gas, liquid crude oil, and solid bitumen. This report concerns the occurrence of liquid oil and solid bitumen in the Ouachita Mountains of Oklahoma.

Primary objectives of this study are to (1) characterize oils and solid bitumens produced from rocks of the Ouachita facies in southeastern Oklahoma, (2) evaluate the potential of Ouachita rocks as hydrocarbon-source rocks, and (3) geochemically relate the oils and solid bitumens to specific stratigraphic intervals. Secondary objectives include an assessment of the thermal maturity of indigenous organic matter in rocks of the Ouachita facies, and a determination of the origin of the solid bitumen.

This study is limited stratigraphically to rocks of the Ouachita facies, which consists entirely of Paleozoic sandstones, shales, and cherts (fig. 2). Specifically, only rocks from the Mississippian Stanley Group, downsection to the Ordovician Womble Formation (inclusive), have been considered. Further, this study is limited to the frontal and central Ouachita Mountains (fig. 1), as defined by Cline (1968).

Study Area

The oils, solid bitumens, and rock samples were obtained from Atoka, Latimer, Le Flore, Pittsburg, and Pushmataha Counties in southeastern Oklahoma. The entire study area covers approximately 1,400 square miles; specific sample locations are listed in the Appendix. A total of 4 oils, 7 solid bitumens and 127 rock samples were analyzed in this study. The rock samples (cuttings) were composites of 50- to 100-foot intervals. All solid bitumens were collected from nine sites; oils

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[1] Union Oil Co. of California, Brea, California.

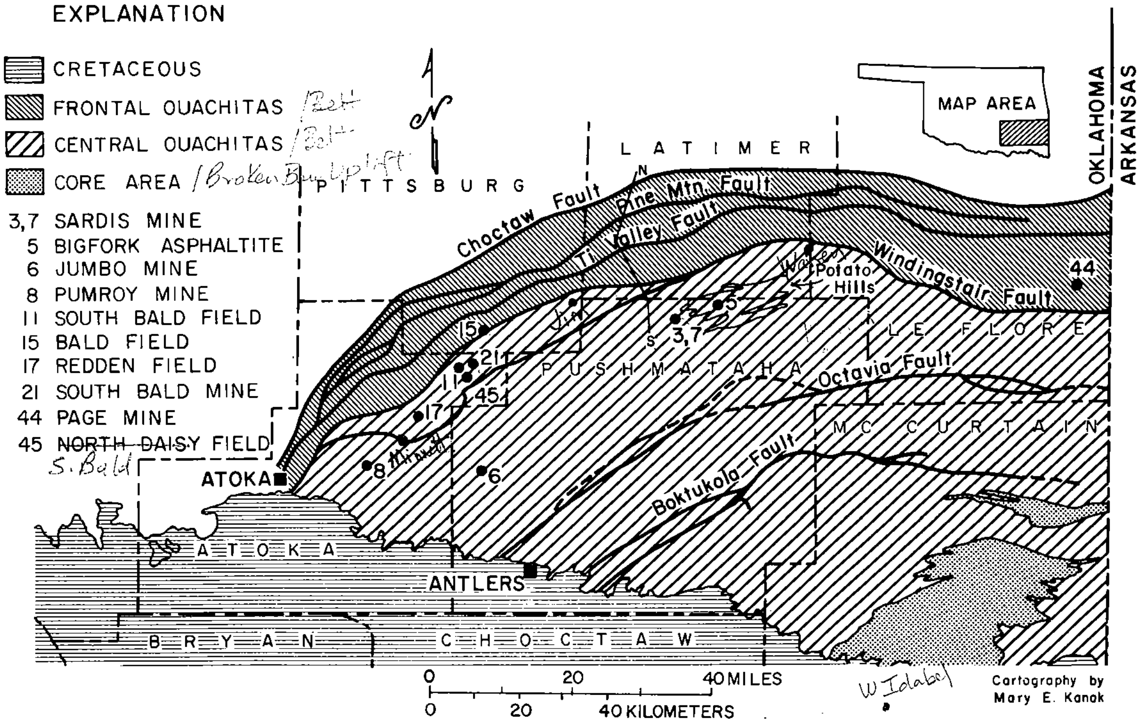

Figure 1. Map of Oklahoma Ouachita Mountain region. Adapted from Cline and Shelburne (1959). North–south cross section is shown in figure 3. Reproduced by permission of Pergamon Press.

were sampled from stock tanks or from flow lines leading to stock tanks. Specific information on samples sites and collection and preparation methods can be found in Curiale (1981). Oil and bitumen samples are designated by a single number; subsurface rock samples also are designated by a single number (corresponding to a specific well), followed by the subsurface interval in feet. Oils and solid bitumens are also discussed in terms of field or mine name. Figure 1 relates the sample number to field or mine and gives the geographic and physiographic location for each of the samples.

Regional Geology

The Ouachita Mountains of Oklahoma and Arkansas represent a major surface expression of the Ouachita Thrust Belt, which extends from southwestern Texas through eastern Mississippi. Several excellent discussions of the stratigraphic and structural characteristics of the Ouachitas are available (Cline and Shelburne, 1959; Cline, 1966; Keller and Cebull, 1973; Morris, 1974; Wickham and others, 1976; Wickham, 1978; and references therein). The reader is referred to these studies for detailed discussions of the history of the Ouachitas. The following brief review is drawn from these studies.

Earliest deposition in the Ouachita trough probably occurred in Ordovician time. Pre-Carboniferous strata include sandstones (for example, Blaylock), shales (for example, Womble, Polk Creek, Missouri Mountain), and cherts (for example, Arkansas Novaculite), all of which were deposited in what is now recognized as a "starved-trough" environment. Mississippian and Pennsylvanian flysch deposits subsequently filled the trough rapidly (for example, Stanley, Jackfork, Johns Valley, Atoka). Tectonic convergence occurred in mid-Pennsylvanian time, acting along an (approximately) east–west subduction zone whose dip direction is presently indeterminate. Cessation of convergence has left many southward-dipping listric reverse faults, which have been used to subdivide the Ouachita Mountains into frontal, central, and core zones (fig. 1). Deposition of post-Carboniferous sediments, and erosion of these as well as underlying Ouachita-facies rocks, have produced the east–west-lineated Ouachita physiography. Although this scenario is descriptive of the Ouachita Mountains, the history of other portions of the Ouachita Thrust Belt, particularly the Marathon Uplift of west Texas, is directly analogous.

The well-known thrust-belt pattern of faulting is easily recognized in figure 3, a north–south cross section through the Oklahoma Ouachita

SYS-TEM	OUACHITA MOUNTAINS	OIL (Field or Seep)	SOLID BITUMEN
PENN.	Atoka		
	Johns Valley		
	Jackfork	●*	●*
MISS.	Stanley	●*	●*
DEVONIAN	Arkansas Novaculite	●	●
SILURIAN	Missouri Mountain		●
	Blaylock[a]		
ORDOVICIAN	Polk Creek		
	Bigfork	●	●*
	Womble		
	Blakely		
	Mazarn		
	Crystal Mtn.		
	Collier		

Figure 2. Chart showing stratigraphic location of oils and solid bitumens in Ouachita Mountains. Asterisk indicates samples analyzed in this study. Letter *a* signifies that Blaylock Sandstone is locally missing in most of study area. Reproduced by permission of American Association of Petroleum Geologists.

Mountains (the line of section is shown in fig. 1). This section represents the structural configuration of the frontal and (northern) central Ouachita regions, showing both the intense folding and the widespread faulting. Almost all of the samples analyzed in this study were collected from within 50 miles of this line, along the strike.

The stratigraphic section of the Oklahoma portion of the Ouachita Mountains is shown in figure 2. Oils and solid bitumens were sampled as shown in this figure. Rock samples were obtained (subsurface and outcrop) from the Jackfork and Stanley Groups (flysch), the Arkansas Novaculite (chert, with significant shale and sandstone), the Missouri Mountain Shale, the Polk Creek Shale, the Bigfork Chert (with some shale), and the Womble Formation (black shale).

Previous Studies

Several references to the petroleum potential of the Ouachita Mountains have appeared in the literature (Honess, 1927; Howell and Lyons, 1959; Chenoweth, 1959, 1960; Jordan, 1964; Schramm and Caplan, 1971; Fay, 1976, 1982; Morris, 1977; Morrison, 1980a, 1980b). Although oil production from the study area has not been substantial, there have been enough commercial fields to demonstrate the presence of liquid petroleum. Nevertheless, no major studies of the chemical characteristics of the crude oil in the Ouachitas have been published. However, the chemistry of solid bitumens of the region (both asphaltite and pyrobitumen; see fig. 4) has been discussed in detail (Taff, 1909; Aurin, 1915; Miser and Purdue, 1918; Honess, 1927; Shelley, 1929; Ham, 1956). Excellent summaries of these studies, as well as reviews of past asphaltite and pyrobitumen mining activities, are provided by Fay (1976, 1982).

The most comprehensive studies concerning the origin of Ouachita solid bitumens are those of Miser and Purdue (1918) and Honess (1927). These workers considered both the Cretaceous rocks that overlap the Ouachita facies, and the Paleozoic rocks within the Ouachita facies, as being potential oil-source rocks. However, because Honess felt that "flints and shales" predominate below the Stanley Group in northern Pushmataha County and western Atoka County, he concluded that pre-Carboniferous rocks could not be the source beds for the petroleum in the frontal Ouachitas.

Subsequent references to oils, solid bitumens, and oil-source rocks in the Ouachita Mountains have consisted largely of supposition and geologic inference. This scarcity of geochemical data, and an increasing interest in the oil and gas potential of the Ouachita Mountains, have prompted this study.

Acknowledgments

I thank W. E. Harrison, who introduced me to organic geochemistry. Without his generous help and advice, this work would never have been completed. I also thank T. L. Thompson, R. O. Fay and C. J. Mankin, each of whom contributed to my interest in the Ouachitas and assisted in the project. Many others generously gave technical advice; these include P. Mommessin, A. Hood, W. Orr, S. Larter, E. Enwall, T. Karns, G. Smith, J. Wickham, B. Bernard, W. Seifert, and A. Fuex. Analytical assistance was generously given by K. Egan, M. Lambert, E. Sancaktar, R. Powell, and S. Weber. All of these individuals are gratefully acknowledged.

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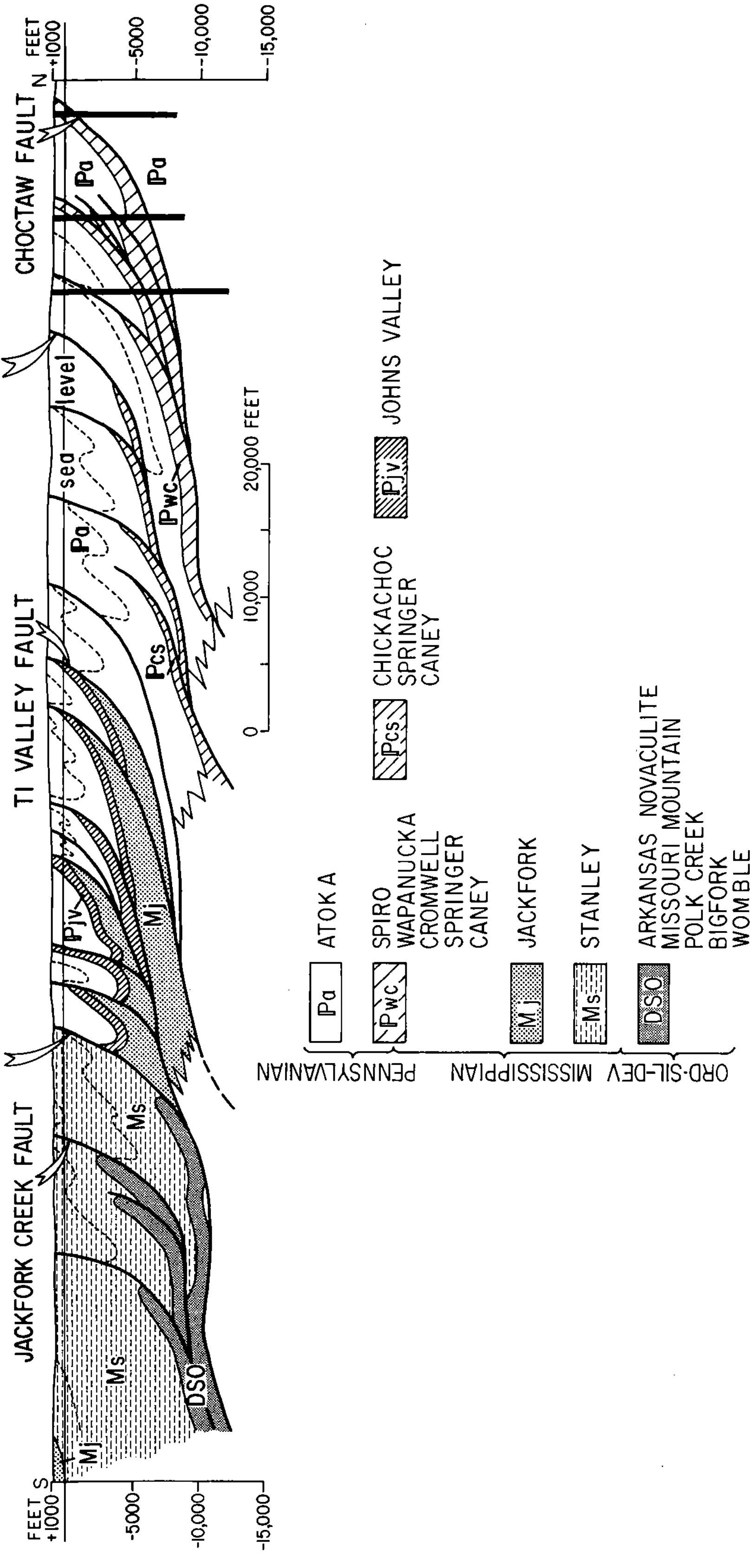

Figure 3. North–south cross section of Oklahoma Ouachita Mountains. Adapted from Berry and Trumbly (1968). No vertical exaggeration.

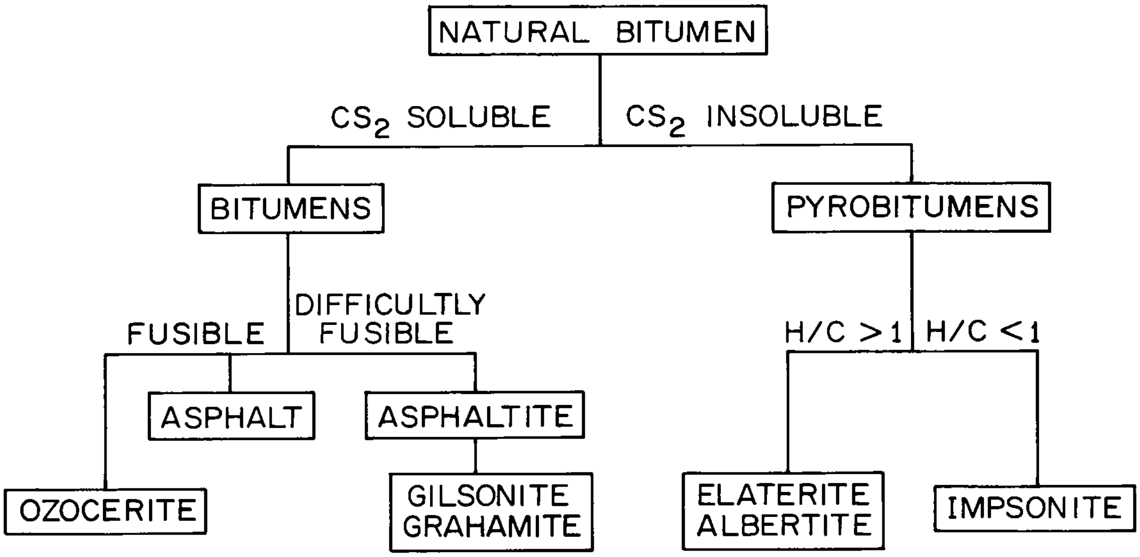

Figure 4. Classification chart for natural bitumens. Adapted from Hunt (1979).

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CRUDE-OIL CHARACTERISTICS

The four oils analyzed in this study were sampled at the fields indicated in figure 1. These fields, the South Bald, Bald, Redden, and North Daisy, are in the frontal and central Ouachitas and produce from the Jackfork and Stanley Groups (fig. 2; also see the Appendix). Specific gravities and API gravities are listed in table 1. These values are for untopped oils, at 60° C. Loss on topping is also indicated in table 1; most of the chemical analyses discussed below were conducted on untopped oils.

Table 2 lists results of elemental determinations for the oils, in raw weight percentage and also normalized to carbon content on the basis of atomic ratio (all analytical procedures as in Curiale, 1981). Few examples of whole-oil carbon and hydrogen elemental data are available in the literature (Colombo and Sironi, 1961; Rubinstein and others, 1977). Summarized determinations of nitrogen and sulfur (Tissot and Welte, 1978, p. 356–363) suggest that the oils analyzed for the present study are average with respect to concentrations of these elements. The nitrogen concentrations of the four oils listed in table 2 agree with the 0.10–percent (by weight) value reported by Costantinides and Arich (1967) for an average Midcontinent oil. The sulfur content of the oils also is considered normal, being within the lower mode of a bimodal distribution of 9,315 oil analyses published by Tissot and Welte (1978, p. 356). On this basis, the Ouachita oils are classified as low-sulfur crudes.

Three of the whole (unfractionated) oils of this study were analyzed for the trace metals, vanadium and nickel. Individual asphaltene fractions also were analyzed for these metals. Vanadium and nickel contents for the whole oils are 8.8–20.2 ppm and 2.5–7.0 ppm, respectively, and the V/Ni ratios are 2.15–3.59. Asphaltenes have vanadium

TABLE 1.—PHYSICAL PROPERTIES OF OUACHITA OILS

Oil	Specific Gravity (60°F)	API (60°F)	Topping Loss (%)	
South Bald (11)	0.8541	34.2	15.7	1N-15E-5
Bald (15)	0.8655	32.0	14.5	2N-15E-28
Redden (17)	0.8664	31.8	9.3	1S-14E-9
North-Daisy (45) Now S. Bald	0.8106	43.1	19.1	#1 Loman from F. Sellweger

TABLE 2.—WHOLE-OIL DATA FOR OUACHITA OILS

OIL	Elemental Analysis									Metal Analysis			Isotopic Analysis	
	%[a]					Atomic Ratios				V^{b}	Ni^{b}	V/Ni	$^{13}C^{c}$	$^{34}S^{d}$
	C	H	O	N	S	H/C	O/C	N/C	S/C	(ppm)	(ppm)	(w/w)	(ppt)	(ppt)
11 (S. Bald)	85.96	13.17	0.49	0.063	0.26	1.83	0.0043	0.0006	0.0011	8.8	2.5	3.59	-29.7	+17.8
15 (Bald)	85.70	12.97	0.48	0.125	0.52	1.80	0.0042	0.0013	0.0023	20.2	6.1	3.33	-29.8	+18.9
17 (Redden)	86.28	12.98	0.58	0.142	0.34	1.79	0.0050	0.0014	0.0015	15.0	7.0	2.15	-29.7	+14.3
45 (N. Daisy)	85.91	13.69	0.44	0.064	0.40	1.90	0.0038	0.0006	0.0017	-	-	-	-28.9	-

[a] Raw weight percentage.

[b] Precision = ± 15 %.

[c] Relative to PDB standard.

[d] Relative to troilite standard.

and nickel contents of 112.1–149.9 ppm and 63.3–123.0 ppm, respectively, with V/Ni ratios of 1.22–2.34. Results are listed in tables 2 and 3.

The whole-oil metal determinations show that the concentrations of vanadium and nickel fall within the typical ranges noted by Jones (1977) for these metals in crude oil. However, these values are significantly higher than those of other Paleozoic oils of Oklahoma (Bonham, 1956; Tissot and Welte, 1978, p. 364). In addition, vanadium/nickel ratios of these oils are also significantly higher than those of Carboniferous-reservoir oils in central Oklahoma. Of 51 Pennsylvanian and Lower Pennsylvanian oils of Oklahoma, analyzed by Bonham (1956), only two had V/Ni ratios greater than 0.50 (w/w). In addition, two Ordovician oils (Bromide production, Southwest Maysville Pool) exhibited ratios of 0.65 and 0.23. On the basis of metal content, the Ouachita oils appear to be distinct among Oklahoma crudes.

The metal concentrations in the asphaltene fraction, and the percentage of asphaltene in the whole oil (table 3), show that a large percentage of the nickel and vanadium is not contained in the asphaltene fraction in two of the three oils examined. The asphaltene fraction of oils from the Bald, South Bald, and Redden Fields contained only 16 to 31 percent of the total vanadium and 25 to 89 percent of the total nickel (tables 2, 3). These data indicate that vanadium and nickel are, in most cases, not concentrated in the asphaltene fraction of Ouachita oils. A further interesting consequence of these data concerns changes in V/Ni ratios with oil degradation. Because the V/Ni ratio is higher for the nonasphaltene compounds in these oils, the removal of these compounds (that is, biodegradation and devolatilization) will reduce the V/Ni ratio of the residual material.

Whole oils (untopped) were analyzed by ratio mass spectrometry to determine the carbon- and sulfur-isotope ratios of the material. In addition, the paraffinic and aromatic hydrocarbon; the nitrogen-, sulfur-, and oxygen-bearing (NSO) compound; and asphaltene fractions (table 3; fig. 5) were analyzed for their carbon-isotope ratios. Data are reported in tables 2 and 3. The notation used is standard. Reference isotope ratios for carbon and sulfur were the Peedee Formation belemnite (PDB) calcium carbonate standard for carbon, and the Canon Diablo troilite for sulfur

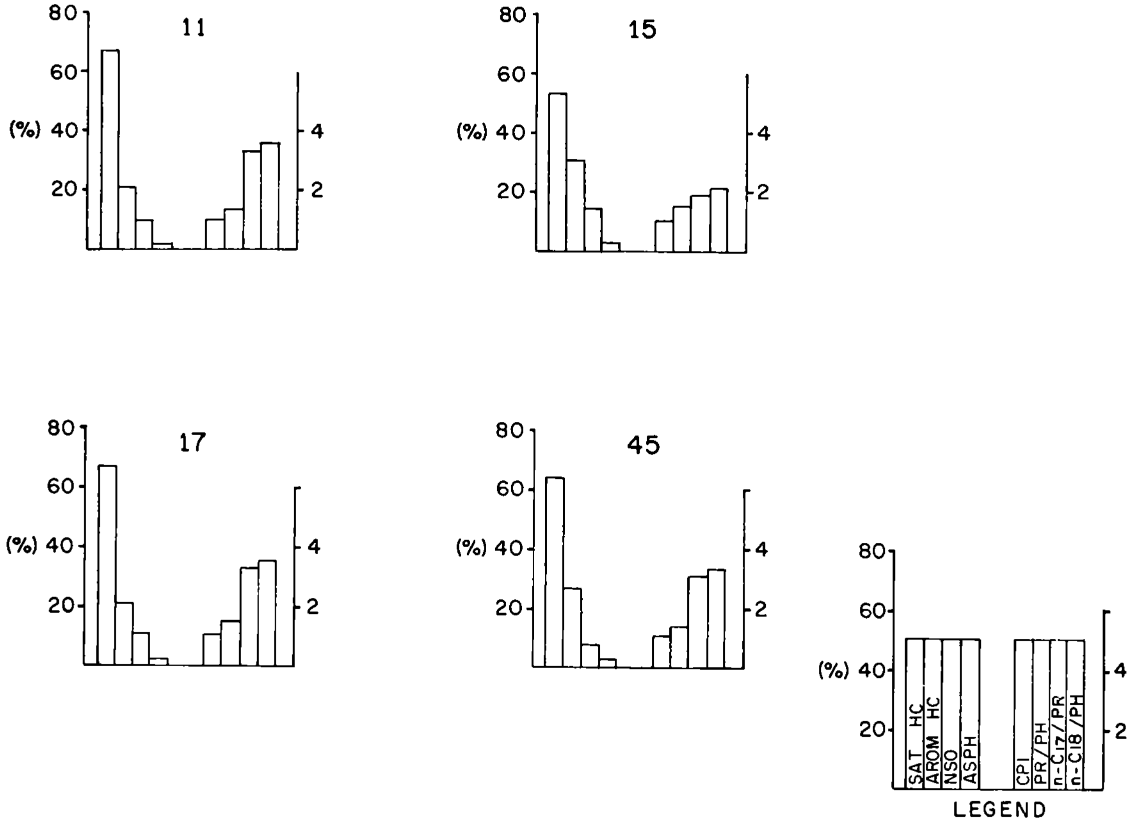

Figure 5. Graphic display of oil fractions and n-alkane/isoprenoid ratios. *PR*, pristane; *PH*, phytane; others as defined in text.

TABLE 3.—FRACTION DATA FOR OUACHITA OILS

OIL	Saturate Hydrocarbons							Arom HC		NSO		Asphaltenes				
	$\%^a$	$^{13}C^b$ (ppt)	$\frac{pr}{ph}$	$\frac{n\text{-}C_{17}}{pr}$	$\frac{n\text{-}C_{18}}{ph}$	CPI[c]	$\frac{Sat}{Arom}$	$\%^a$	$^{13}C^b$ (ppt)	$\%^a$	$^{13}C^b$ (ppt)	$\%^a$	$^{13}C^b$ (ppt)	V^d (ppm)	Ni^d (ppm)	V/Ni (w/w)
11 (S. Bald)	67.2	-28.7	1.38	3.25	3.60	1.02	3.15	21.3	-29.4	9.7	-28.4	1.8	-29.1	149.9	123.0	1.22
15 (Bald)	53.3	-29.7	1.44	1.89	2.10	1.01	1.76	30.2	-29.0	14.1	-29.5	2.4	-29.7	148.0	63.3	2.34
17 (Redden)	66.7	-29.5	1.46	3.34	3.51	1.03	3.19	20.9	-29.0	10.3	-29.8	2.1	-29.9	112.1	84.1	1.33
45 (N. Daisy)	63.8	-30.4	1.39	3.04	3.31	1.08	2.44	26.2	-29.7	7.5	-27.9	2.5	-28.9	-	-	-

[a] Raw weight percentage.

[b] Relative to PDB standard.

[c] Carbon Preference Index, calculated by the following formula, modified after Bray and Evans (1961) and Hunt (1973):

$$\text{CPI} = \tfrac{1}{2} \times \left(\frac{C_{23} + C_{25} + C_{27} + C_{29}}{C_{24} + C_{26} + C_{28} + C_{30}} + \frac{C_{23} + C_{25} + C_{27} + C_{29}}{C_{22} + C_{24} + C_{26} + C_{28}} \right)$$

[d] Precision = ± 20 %.

(Curiale, 1981). Values are cited as parts per thousand (ppt; o/oo).

The average carbon-isotope ratio for the four oils is −29.5 o/oo. Also, the spread among the different oils is very small. The ratio for these oils falls midway between oils of nonmarine (−34 to −30 o/oo) and marine (−30 to −21 o/oo) origin, according to Silverman and Epstein (1958) and Silverman (1967). One must be cautious, however, about assigning a marine or nonmarine origin to these oils on the basis solely of carbon-isotope ratio. Studies have shown that oils originating from, and kerogens isolated from, Cambrian–Ordovician rocks show very "light" (commonly less than −30 o/oo) carbon-isotope ratios (Welte, 1965; Welte and others, 1975a).

Several authors have reported sulfur-isotope ratios for crude oils (Thode and others, 1958; Thode and Monster, 1964; Monster, 1972; Mauger and others, 1973; Orr, 1974). The values from the present study, +14.3 to +18.9 o/oo, are relatively "heavy" for crude oils, being close to the value of +20 o/oo for present-day seawater sulfate.

In addition to whole-oil analysis, carbon-isotope ratios also were determined for each of the fractions of the four oils (table 3). These data are presented graphically as "isotope type curves" in figure 6 (Stahl, 1978). Most noteworthy about these data is the general lack of increasingly negative isotopic ratios as fraction polarity decreases, as was shown for Cenozoic and Mesozoic oils by Stahl (1978). According to Stahl's original isotope type-curve concept, this trend is detectable in the fraction order: asphaltenes, NSO compounds, aromatic hydrocarbons, paraffinic hydrocarbons (Stahl, 1978). This trend is discernible in oil 45. However, discounting the paraffinic hydrocarbon fraction, an opposite trend is observed in oils 15 and 17. Ostensibly, this can be attributed to biodegradation of the oils, which tends to pivot the isotope type curve around the aromatic point, to a greater slope (Stahl, 1980). Stahl suggested that this phenomenon is due to secondary formation of asphaltenes at the expense of the saturate-hydrocarbon fraction. However, although the steep slope of the isotope type curve for the oils of the present study suggests that biodegradation is involved, chromatographic analysis indicates that biodegradation has been minimal. A recent study of oils of the Bighorn Basin by Chung and others (1981) also has produced isotope type curves with steep slopes, although the oils in question show no effects of biodegradation. In addition, analysis of three Saskatchewan oils by Monster (1972) showed similar vertical type curves, presumably in nonbiodegraded oils. Further, one of the oils studied by Monster exhibited an aromatic fraction lighter than the saturate fraction, as observed for oil 11 of the present study. In most of these anomalous cases, the oils in question are Paleozoic in age; therefore, the use of such curves may be invalid for Paleozoic oils.

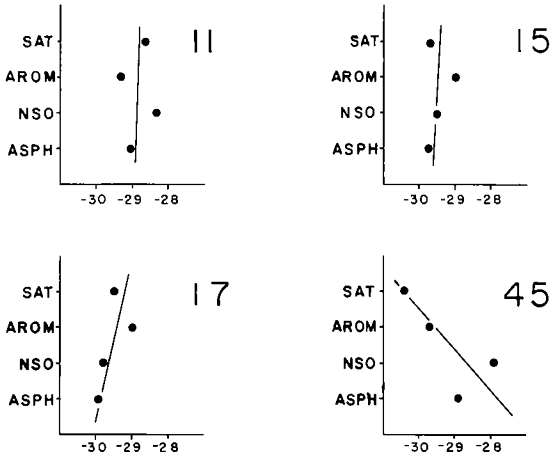

Figure 6. Isotope type curves for Ouachita oils. *SAT*, saturate (that is, aliphatic) hydrocarbons; *AROM*, aromatic hydrocarbons; *NSO*, nitrogen-, sulfur-, and oxygen-containing compounds; *ASPH*, asphaltenes. All carbon-isotope values in this figure and all other figures are relative to PDB standard.

Each of the whole untopped oils was examined by high-resolution gas chromatography, and the amount and distribution of n-alkanes and isoprenoid isoalkanes were estimated. The oils were subsequently fractionated (fig. 5), and the saturate-hydrocarbon fraction was analyzed by gas chromatography to determine whether n-alkanes were coeluting with compounds of the aromatic, NSO, or asphaltene fractions in whole-oil chromatograms. The n-alkanes were not coeluting with compounds from these fractions. Data reported on n-alkanes and isoprenoid isoalkane are from whole-oil gas chromatograms (Curiale, 1981). Figure 7 presents the chromatograms for each of the oils, and figures 8 and 9 show the n-alkane and isoprenoid isoalkane distributions for the oils. Because these analyses were conducted on untopped whole oils, minimal loss through volatilization is expected at the "light" end, as shown for oil 45 in figure 7.

Ratios of pristane/phytane (PR/PH), n-heptadecane/pristane (n-C17/PR), and n-octadecane/phytane (n-C18/PH) for each of the oils are listed in table 3. The initial isoprenoid isoalkane composition of an oil can vary depending on both maturity and organic matter source environment (Robinson and others, 1965; Tissot and others, 1971). Thus, correct interpretation of the above ratios will yield information about the origin of an unaltered oil. Tissot and Welte (1978) noted that pristane and phytane can result from deposition in either reducing or oxidizing environments. Further, the phytane content of an oil will tend to decrease with time and depth, from ther-

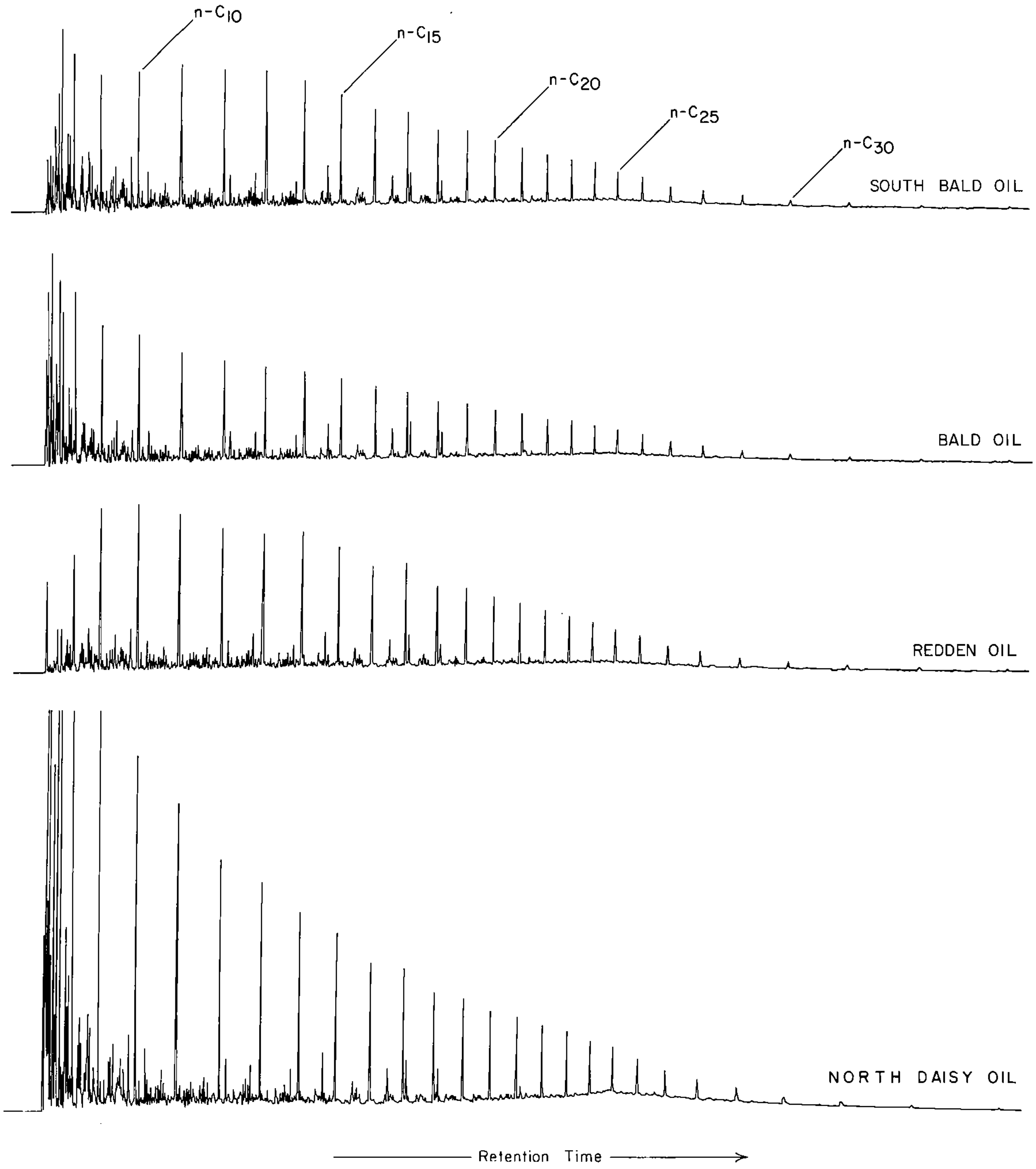

Figure 7. Gas chromatograms for Ouachita oils. Chromatograph conditions: 75°C (held 2 minutes); 10°C/minute ramp; 275°C (held 20 minutes). Injection temperature: 270°C. FID temperature: 300°C. Capillary head pressure: 20 psi. Other details in Curiale (1981).

mal cracking, producing increased amounts of the lower molecular weight isoprenoids (Robinson and others, 1965). Despite these many changes in isoprenoid content, the pristane/phytane ratio is a commonly determined parameter in coals, oils, and rock extracts, and has been determined for all samples in the present study, in anticipation of its usefulness as a correlation parameter (Welte and others, 1975b). For the oils listed in table 3, the pristane/phytane ratio ranges from 1.38 to 1.46. These values are relatively low, and suggest an oil produced from a clastic, marine rock sequence (Brooks and others, 1969; Powell and McKirdy, 1975).

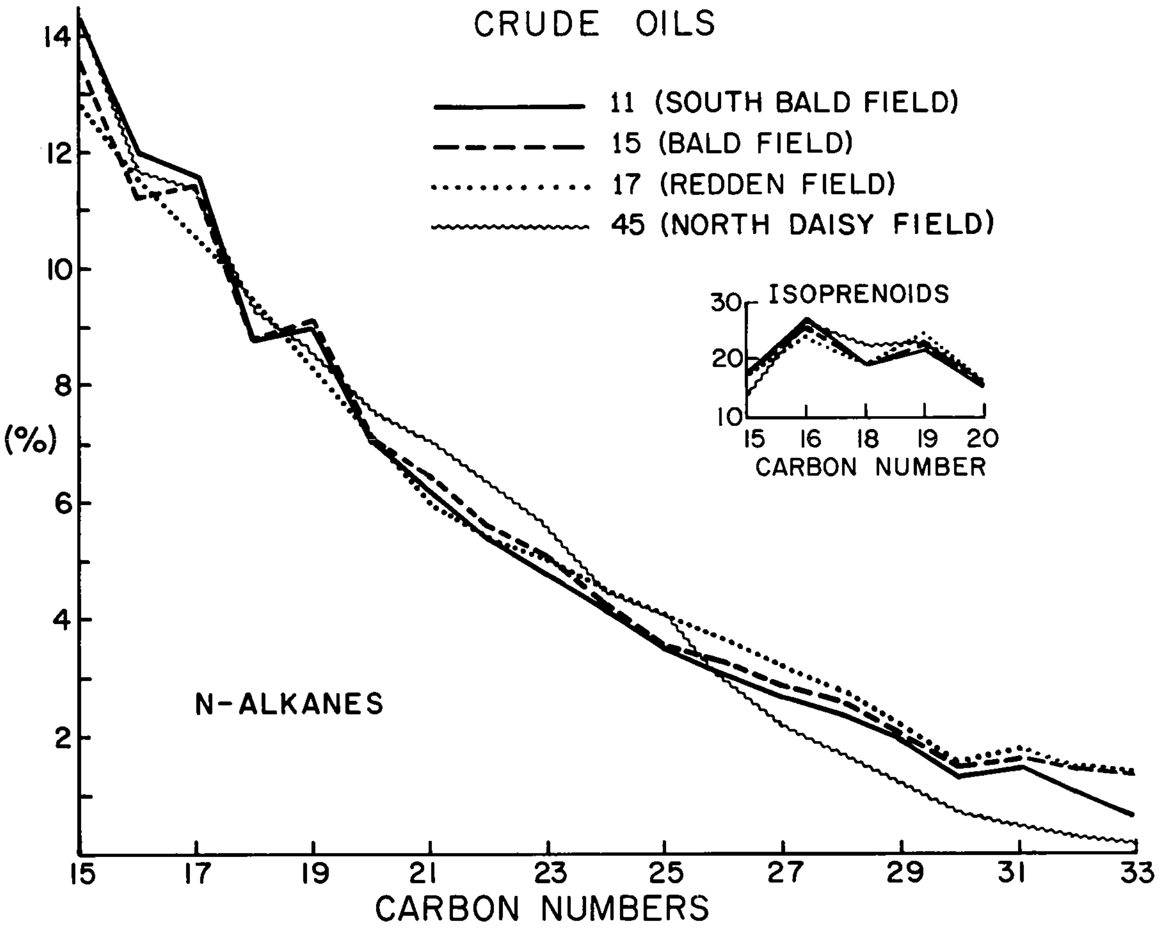

Figure 8. N-alkane and isoprenoid distributions in Ouachita oils. Depression of high carbon numbers in curve for oil 45 is attributed to use of peak height measurements rather than automatic area integration.

In addition to the pristane/phytane ratio, the ratios of n-heptadecane/pristane and n-octadecane/phytane also are listed in table 3, for each of the oils of this study. Interpretation of these ratios is subject to debate. A decrease in both ratios would suggest biodegradation of a mature oil, because microbial attack will preferentially remove n-alkanes (Deroo and others, 1974). However, Lijmbach (1975) suggested that, for an undegraded oil, the ratio of n-heptadecane/pristane is indicative of the environment of deposition: a high ratio (2.0 or higher) implies an aquatic origin, rather than a peaty or coastal environment. Data in table 3 indicate that the oils of the present study exhibit such a high ratio.

A better definition of the Ouachita oils as marine or nonmarine is provided by Philippi (1974), who used the n-alkane ratio (C21 + C22)/(C28 + C29) as a source indicator. Analysis of many oils worldwide indicated that ratios of 0.6 to 1.2 suggest a terrigenous source for the organic matter that produced the oil, whereas ratios of 1.5 to 5.0 suggest a marine source. Oils 11, 15, 17, and 45 from the Ouachitas have ratios of 2.6, 2.3, 2.6, and 4.7, respectively. These ratios all suggest a marine source.

A high ratio of n-heptadecane/pristane, in addition to being suggestive of depositional environment, may also provide information about the ultimate source organism of these hydrocarbons. Han and Calvin (1969) reported that normal heptadecane (n-C17) is the dominant compound among hydrocarbons in photosynthetic microorganisms. For example, n-C17 constituted an average of 85 percent of the major hydrocarbon in four species of blue-green algae. This predominance is missing in most nonphotosynthetic bacteria. In addition, Han and Calvin reported that isoprenoids are common metabolic products of photosynthetic bacteria, yet are absent in blue-green and green algae. These findings suggest a source-environment control on the n-heptadecane/pristane ratio of a crude oil.

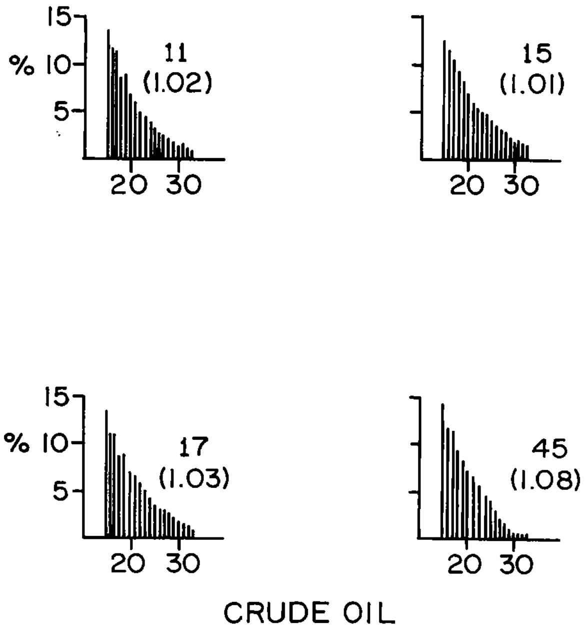

Figure 9. Histograms showing n-alkane distributions in Ouachita oils. Carbon-preference indices, as defined in table 3, are shown in parentheses.

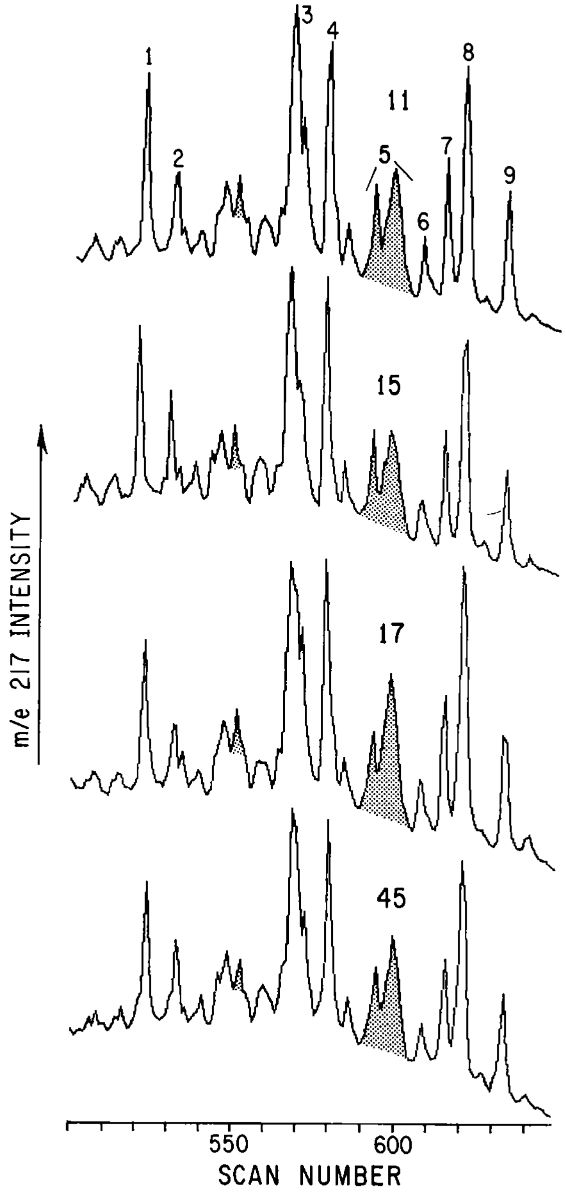

Figure 10. Mass chromatograms of m/e 217 for Ouachita oils. Differences between oils are shaded. Peak numbers correspond to assignments in table 4. GC–MS run conditions as in Curiale (1981). Reproduced by permission of Pergamon Press.

Sterane and Terpane Determinations

In addition to the previously discussed analyses, each of the four oils was analyzed qualitatively for steranes and terpanes by using combined gas chromatography–mass spectrometry to monitor parent ions and major-fragment ions (Curiale, 1981). Tentative identification of steranes was made on the basis of MAP software and published data (Gallegos, 1971; Ensminger and others, 1978; Seifert and Moldowan, 1978, 1979; Seifert and others, 1980). Distinction between diasteranes and regular steranes (Ensminger and others, 1978) was based on examination of the m/e–232 and m/e–259 mass chromatograms, displayed in MAP format with the ions of m/e 149, 151, 217, and 218 (Seifert and Moldowan, 1978).

Mass chromatograms for the m/e–217 ion for each of the four oils examined are presented in figure 10. Each peak or group of coeluting peaks is tentatively identified in table 4. In some cases, definite assignments of compounds are possible (for example, peaks 1, 2, 7, and 9 of fig. 10 and table 4). In general, however, coelution is the rule, and precise assignment is not possible. Consequently, compound names in table 4 represent those compounds that are probably present under a given peak, as determined from the mass spectra obtained across the peak.

In addition to general sterane m/e–217 mass chromatogram patterns, the molecular ion mass chromatograms for m/e 372, 386, and 400 were integrated over the sterane-elution region, and normalized. Results, in figure 11, indicate that most of the steranes present are ethylcholestanes, whereas methylcholestanes (C_{28}) are a minor component. The close structural similarities between steranes and sterols, suggesting diagenesis of the latter to produce the former, allow one to adapt recent conclusions concerning source environment of sterols to relative sterane distributions. For example, Huang and Meinschein (1976, 1979)

TABLE 4.—STERANE ASSIGNMENTS

Number[a]	Sterane Type[b]	Tentative Stereochemistry[c]	Name[d]
1	C_{27} (Rearranged)	5b, 13b, 14b, 17a, 20S	b, a-Diacholestane 20S
2	C_{27} (Rearranged)	5b, 13b, 14b, 17a, 20R	b, a-Diacholestane 20R
3	C_{27} (Regular)	5a/5b, 13b, 14a/14b, 17a/17b, 20R/20S	Coprostane 20R; Cholestane 20S; Isocholestane 20R/20S
	C_{28} (Rearranged)	5b, 13a, 14b, 17b, 20R/20S	24-Methyle-a, b-Diacholestane
	C_{29} (Rearranged)	5b, 13b, 14b, 17a, 20R	24-Ethyl-b, a-Diacholestane 20R
4	C_{27} (Regular)	5a, 13b, 14a, 17b, 20R	Cholestane 20R
	C_{29} (Rearranged)	5b, 13a, 14b, 17b, 20R/20S	24-Ethyl-a, b-Diacholestane
5	C_{28} (Regular)	5a/5b, 13b, 14a/14b, 17a/17b, 20R/20S	24-Methylcholestane 20S; 24-Methylcoprostane 20R; 24-Methylisocholestane 20R/20S
	C_{29} (Rearranged)	unknown	unknown
	---	---	unidentified hopane
6	C_{28} (Regular)	5a, 13b, 14a, 17a, 20R	24-Methylcholestane 20R (Erogostane)
	C_{29} (Rearranged)[e]	unknown	unknown
7	C_{29} (Regular)	5a, 13b, 14a, 17a, 20S	24-Ethylcholestane 20S
8	C_{29} (Regular)	5a, 13b, 14b, 17b, 20R/20S	24-Ethylisocholestane 20R/20S
		5b, 13b, 14a, 17a, 20R	24-Ethylcoprostane 20R
9	C_{29} (Regular)	5a, 13b, 14a, 17a, 20R	24-Ethylcholestane 20R (Sitostane)

[a] As listed in figure 10 and subsequent sterane figures.

[b] All regular steranes are 8b, 9a, 10b; all rearranged steranes are 8a, 9b, 10a.

[c] Slash (/) indicates configuration unknown; configuration at C_{24} is unresolved.

[d] From Seifert and Moldowan (1979); most possible coeluting steranes are listed.

[e] Tentative identification, based on interpretation of m/e-259 MAP.

suggested that sterol distributions in recent sediments can serve as "ecological indicators," that is, compounds typical of specific depositional environments. On this basis, the present data have interesting implications. If the sterane distributions in the Paleozoic oils of this study were actually sterol distributions in recent sediments, one would conclude that they were part of a nearshore depositional environment. To validate such a conclusion for a sterane distribution, the assumption must be made that diagenesis, subsequent catagenesis, and further migration and maturation of expelled oil do not alter the C_{27}, C_{28}, and C_{29} distribution of steroids in the system.

Terpane determinations were made by monitoring m/e 191 (major fragment) and m/e 370, 384,

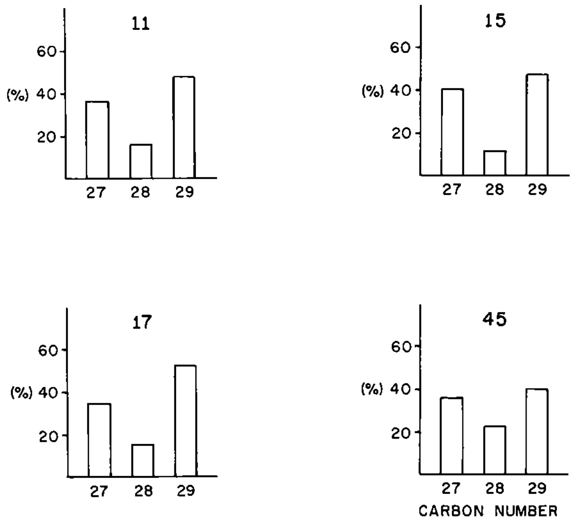

Figure 11. Distribution of C_{27}, C_{28}, and C_{29} steranes in oils. Obtained by integration of m/e 372, 386, and 400 mass chromatograms over elution range of common steranes (both rearranged and regular).

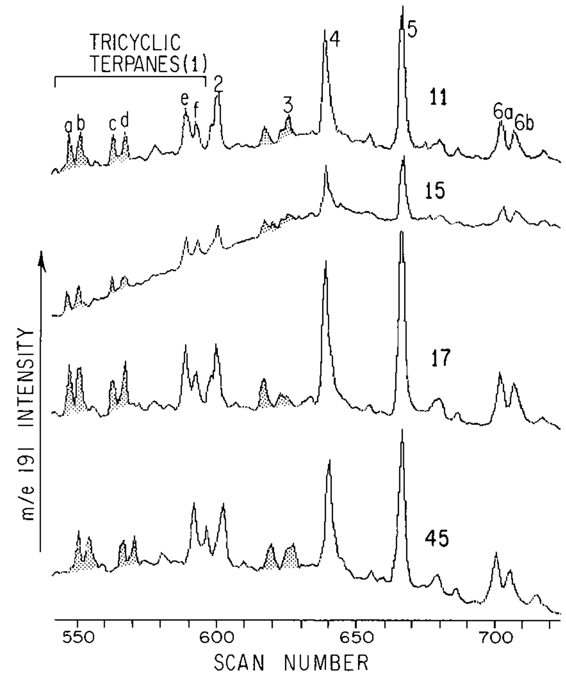

Figure 12. Mass chromatograms of m/e 191 for Ouachita oils. Differences between oils are shaded. Peak numbers correspond to assignments in table 5. Shaded peak eluting just before peak 3 has not been identified; mass spectral scan for this peak is obscured by peak 7 of steranes (see fig. 10), which is in much higher abundance.

398, 412, and 426 (molecular ions). Identifications were based largely on mass spectra published by Hills and Whitehead (1966), Whitehead (1973b), Kimble and others (1974a, 1974b), Seifert and others (1978), and Ekweozor and others (1979a, 1979b), and on elution order. Figure 12 shows m/e–191 mass chromatograms for the four oils studied, with numbers assigned to major peaks (all scans were terminated following elution of the C_{31} hopanes). Table 5 gives suggested peak assignments, by numbers corresponding to those in figure 12. The chromatograms shown are typical of mature oils.

In addition to scanning mass chromatograms of m/e 191 and the molecular ions, scans of m/e 205 and 177 were conducted to search for 17a(H), 21b(H) methylhopanes (discovered by Seifert and Moldowan, 1978), and demethylated hopanes. In the case of m/e 205, a MAP display of m/e 177, 191, and 205 (fig. 13) shows only minor 205 peaks, corresponding to fragments from norhopane (Hills and Whitehead, (1966), hopane (Whitehead, 1973b; Kimble and others, 1974a), and two epimers of homohopane (Seifert and Moldowan, 1979). These are peaks 4, 5, 6a, and 6 b of figure 12, respectively. On this basis, I conclude that the concentration of methylhopanes in these oils is insignificant.

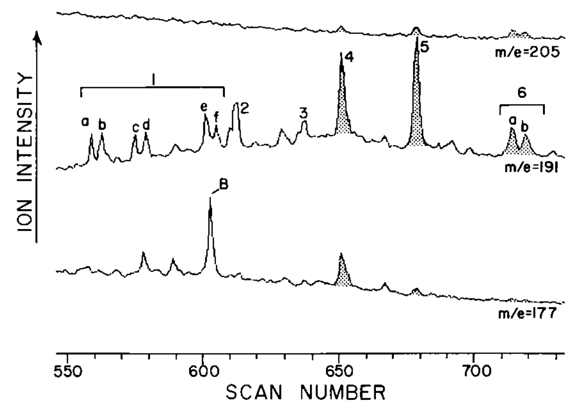

Figure 13. MAP of m/e 177, 191, and 205 for oil 11. C_{29}, C_{30}, and C_{31} hopane fragments are shaded. Peak numbers correspond to assignments in table 5.

The m/e–177 scan (MAP for crude-oil 11, fig. 13) shows the 177 fragment expected from 17a(H),21b(H)-30-norhopane (Hills and Whitehead, 1966), as well as a few other minor peaks eluting earlier. In addition, however, a large m/e–177 fragment is visible eluting prior to 18a(H)-22,29,20-trisnorhopane in all four of the oils. This compound, denoted B in figure 13, coelutes with the peak–5 group of steranes (fig. 10; table 4). A mass spectrum of compound B reveals the following: 163 (100 percent), 177 (67 percent), 341 (20 percent, 355 (6 percent), 370 (M+; 29 percent). Although identification of the compound is not

TABLE 5.—TERPANE ASSIGNMENTS

Number[a]	Assignment
1a-1f	Tricyclic Terpanes[b]
2 Ts	(Tentatively) 18a(H)-22,29,30-Trisnorhopane[c]
3	(Tentatively) 17a(H),18a(H),21b(H)-28,30-Bisnorhopane[d]
4	17a(H),21b(H)-30-Norhopane[e]
5	17a(H),21b(H)-Hopane[f]
6a,6b	17a(H),21b(H)-30-Homohopane (22S and 22R)[g]

[a] As listed in figure 22 and subsequent figures.

[b] These compounds are identified solely by analogy to elution orders published by Seifert and Moldowan (1979). Mass spectral data are limited for these compounds.

[c] Possibly triterpane H of Hills and Whitehead (1970); also see Pym and others (1975).

[d] Seifert and others (1978).

[e] Seifert and Moldowan (1979); Whitehead (1973b); Hydrocarbon D of Hills and Whitehead (1966).

[f] Whitehead (1973a); Kimble and others (1974a).

[g] Seifert and Moldowan (1979).

possible with only this information, it is informative to compare these data with unusual C_{27} triterpanes discussed in the literature. Seifert and Moldowan (1979) recently reported a ring-A/B–demethylated analog (C_{27}) of the C_{28}–hopane 17a(H), 21B(H)-28,30-bisnorhopane (Seifert and others, 1978), called demethylated 17a(H)-28-noradiantane. Careful measurement of the C_{27}–compound's fragments in the MAP diagram in figure 5 of Seifert and Moldowan (1979) suggests the following mass spectrum: 149 (37 percent), 163 (100 percent), 177 (81 percent). This compound has a larger 177 fragment than that of compound B of the Ouachita oils. In addition, the relative elution time of Seifert and Moldowan's ring-A/B–demethylated compound with respect to the regular hopanes is different from that of compound B, even after compensating for differences in GC phases. Finally, demethylated 17a(H)-28-noradiantane was found by Seifert and Moldowan (1979) in a heavily degraded crude oil, whereas the Ouachita oils show no evidence of strong biodegradation. However, it should be noted that the methylated analog of this compound was found in the undegraded oil analyzed by Seifert and others (1978), and also appears to be present in the Ouachita oils (see table 5).

Another report of an unusual C_{27} triterpane is that of Bjoroy and Rullkotter (1980). These authors report a 25,28,30-trisnormoretane in a Jurassic shale of the Norwegian continental shelf, with mass spectral data as follows: 163 (100 percent), 177 (84 percent), 341 (12 percent), 355 (3 percent), and 370 (48 percent). They assign a moretane, rather than a hopane, structure because the m/e–163 fragment is only slightly larger than the m/e–177 fragment (Van Dorssellaer, 1975, in Bjoroy and Rullkotter, 1980). If one subscribes to this argument, then the C_{27} triterpane of Seifert and Moldowan (1979), discussed earlier, also is a moretane, whereas compound B of the present study is a hopane. Nevertheless, neither the compound of Seifert and Moldowan (1979) nor that of Bjoroy and Rullkotter (1980) appears to be identical with compound B of the Ouachita oils. Unfortunately, in the absence of a model compound for coinjection, or data from proton NMR and X-ray, compound B remains an unknown.

Oil–Oil Correlations

Each of the physical and chemical characteristics discussed previously has been evaluated to determine if the four oils in this study belong to the same oil family, that is, if they originated in the same source rock or sequence.

The vanadium and nickel content of these oils (table 2) is 8.8–20.2 ppm and 2.1–7.0 ppm, respectively; the ratio of vanadium to nickel (w/w) is 2.15–3.59. Tissot and Welte (1978, p. 364) provided data for vanadium and nickel content of oils worldwide, in which the V/Ni ratio ranges from less than 0.05 to more than 10.0. Therefore, the range for oils of the present study is approximately 14 percent of the range for all oils. However, on a metal-by-metal basis, the range for vanadium in oils of this study is only 1 percent of that of worldwide oils, whereas the range for nickel is 4 percent. On this basis, the concentration levels of vanadium and nickel, and the V/Ni ratios of these oils, indicate that they belong to the same oil family.

The n-alkane distributions for the oils of the present study (fig. 9) suggest that at least three oils (11, 17, 45) correlate very well on this basis; the fourth (15) lacks only the minor predominance at n-heptadecane and n-nonadecane observed for the others. However, figure 14, an n-alkane–distribution–overlap diagram, suggests that all four are similar enough to be considered a single family. Table 2 shows that the ratio for carbon in Ouachita oils ranges only from −29.8 to −28.9 o/oo, providing futher evidence that these oils originated in the same rock or in rocks having very similar organic matter (Vredenburgh and Cheney, 1971). This conclusion cannot rest solely on the carbon-isotope data, however, because Williams (1974) showed that the two distinct oil families of the same basin can exhibit similar carbon-isotope values. However, the range of sulfur-isotope values for the three Ouachita oils analyzed (+14.3 to +18.9 o/oo; table 2) is also small enough for one again to conclude that these oils belong to the same family.

Mass chromatograms for the m/e–217 ion for the four oils are presented in figure 10. The sterane distributions are very similar in all four samples. Variations appear in the peak–5 group, and in minor peaks (diasteranes) between peaks 2 and 3, as shaded in figure 10. Assignments for peak 5 (table 4) indicate that this grouping consists mostly of C_{28} regular steranes. Oil 15, as shown in figure 11, possesses the least C_{28} structures, and thus peak 5 is smallest in oil 15 (fig. 10). Figure 12 presents the terpane chromatograms for each of the four oils examined. Differences in the oils (shaded) are mostly differences in peaks 1a–1f (tricyclic terpanes?); the hopanes (peaks 2–6) are identical, with the exception of the depletion of peak 3 in oil 17, which is presently unexplained. Nevertheless, similarity among the other hopanes suggests that the oils are of the same family.

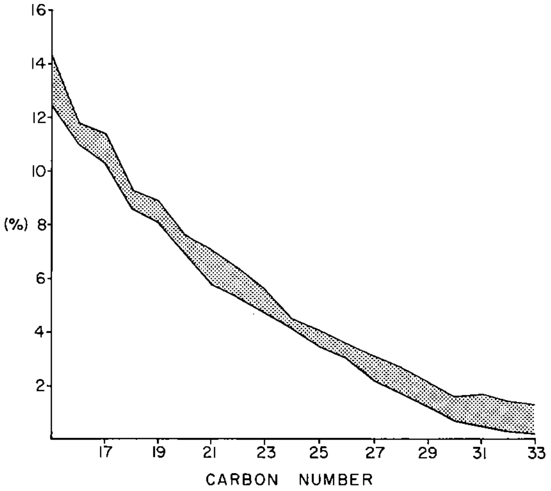

Figure 14. N-alkane–distribution overlap of Ouachita oils. All four oil distributions plot within the shaded region.

In summary, data presented here support the conclusion that all four Ouachita oils originated in one formation. Alternatively, they originated in a source sequence that contained very similar organic matter. This conclusion derives from examination of the whole oil (carbon and sulfur isotopes; elemental determinations; vanadium and nickel content) and the saturate-hydrocarbon fraction (n-alkane and isoprenoid distributions; sterane and hopane distributions).

SOLID-BITUMEN CHARACTERISTICS

Seven samples of grahamite and impsonite from six localities in the Oklahoma Ouachita Mountains were analyzed. One sample was collected from each of the following: Jumbo Mine, South Bald Field, Bigfork grahamite, Pumroy Mine, and Page Mine. Two samples were collected from the Sardis Mine. Figure 1 and the Appendix give sample locations. In addition, a sample of gilsonite (an asphaltite from the Uinta Basin) was analyzed for comparison.

Data on the physical characteristics of these eight samples are listed in table 6. Both analyses of whole solid bitumens and analyses of extracts

TABLE 6.—PHYSICAL PROPERTIES OF BITUMEN AND PYROBITUMEN

Sample Number	Deposit	Type	Specific Gravity	API	Luster	Solubility in Methylene Chloride (%)
3	Sardis	grahamite	1.18	-11.6	vitreous	28.8
5	Bigfork	grahamite	1.11	-	vitreous	21.1
6	Jumbo	grahamite	1.20	-13.6	dull	33.9
7	Sardis	grahamite	1.17	-10.6	dull	23.1
8	Pumroy	grahamite	1.15	-8.5	dull	44.8
21	South Bald	grahamite	1.08	-0.5	vitreous	34.5
44	Page	impsonite	1.30	-22.7	variable	1.3
Gilsonite	(Uinta Basin)	gilsonite	1.02	+7.2	vitreous	99.9+

(from dichloromethane) were made. Chemical analysis of the fractions of the extract (paraffinic and aromatic hydrocarbons, NSO compounds, and asphaltenes) was limited by the low yield of hydrocarbons and the negligible content of n-alkanes (see fig. 15 for extract chromatograms). This lack of n-alkanes in grahamite was also noted by Douglas and Grantham (1973). Consequently, fractionation data (presented in table 7) are primarily for use in a later discussion of the origin of the grahamite and impsonite. The remainder of the present discussion is generally confined to chemical analyses of whole grahamite, impsonite, and, for comparison, gilsonite. These data (table 7) will be discussed in the same general order as that followed for the crude oils of the previous section.

Elemental determinations for six grahamites (samples 3, 5, 6, 7, 8, 21), one impsonite (sample 44), and a gilsonite are listed in table 7 (also included are literature data of a second gilsonite, for comparison). Also, mineral matter may have contributed to the carbon, hydrogen, oxygen, nitrogen, and sulfur content of these solid bitumens, because as much as 25 percent of the weight of these bitumens is unaccounted for by these elements.

On the basis of H/C atomic ratios (table 7), samples 3, 5, 6, 7, 8, and 21 can be distinguished from sample 44. This last sample, the only impsonite analyzed, exhibits a distinctly low H/C atomic ratio, as would be expected for a material of such low solubility (table 6). The H/C ratio for impsonite of the present study (0.73) agrees very well with that for the Page impsonite (0.74), found by King and others (1963).

Figure 16 is a plot of nitrogen versus sulfur for various solid bitumens, adapted from Hunt (1979). Fields for the Ouachita grahamite and impsonite samples analyzed are distinctly different from the gilsonite sample from the Uinta Basin, particularly with respect to the much lower sulfur and somewhat higher nitrogen concentrations in the gilsonite. Therefore, although both gilsonite and grahamite are listed as asphaltites (fig. 4), they are quite different in terms of their elemental compositions.

The grahamite samples were also analyzed for sulfur, vanadium, and nickel. Results are listed in table 7; the ratio of vanadium to nickel (w/w) in whole grahamite also is reported. With the exception of data for sample 5, a correlation appears to exist between the V/Ni ratio and the S/C atomic ratio, as indicated in figure 17 (coefficient of correlation = 0.92; sample 5 excluded). Other workers have reported similar results with crude oils and tar-sand extracts. Radchenko and Sheshina (1955) and Hodgson and others (1963) suggested that a relationship exists between sulfur and vanadyl pigments in crude oils, and Brantaver and Dorrance (1978) showed that, for several tar-sand deposits in the United States, extracts having a high sulfur content generally have a V/Ni ratio greater than one. The results in table 7 and figure 17 suggest that this relation may hold for Ouachita grahamite as well.

Data for sample 5 in table 7 indicate that this sample does not conform to the relation suggested in figure 17 for the five other grahamites. Although the reason for this is unknown, consider that sample 5 is the only Ordovician-reservoir sample examined; all others come from reservoirs in Carboniferous rocks. Further, all other solid bitumens examined were sampled from large veins in shales which are as much as 25 feet thick, but sample 5 is from a small fracture in a chert. At present, no explanation is available for the lack of

TABLE 7.—CHEMICAL DATA FOR BITUMEN AND PYROBITUMEN

Sample Number	Elemental Analysis									Extract (%)				Metals			Isotopes	
	%[a]					Atomic Ratios				Sat HC	Arom HC	NSO	Asph	V[f] ppm	Ni[f] ppm	V/Ni (w/w)	^{13}C[b] (ppt)	^{34}S[c] (ppt)
	C	H	O	N	S	H/C	O/C	N/C	S/C									
3	61.59	7.76	2.63	0.992	1.24	1.50	0.0321	0.0138	0.0075	5.8	5.3	3.3	85.6	183	725	0.25	-29.8	+16.9
5	72.13	7.05	1.59	1.310	1.96	1.17	0.0166	0.0156	0.0102	-	-	-	-	540	200	2.70	-30.0	-
6	69.56	7.79	2.52	1.552	1.78	1.33	0.0272	0.0191	0.0096	3.9	7.8	7.7	80.6	399	402	0.99	-29.8	+15.5
7	67.60	8.13	3.91	1.011	1.32	1.43	0.0434	0.0128	0.0073	4.3	5.4	13.0	77.3	318	608	0.52	-29.7	+17.1
8	70.53	9.42	1.99	0.884	2.66	1.59	0.0212	0.0107	0.0141	-	-	-	-	583	370	1.58	-29.8	+18.8
21	85.42	8.24	1.20	1.396	2.93	1.15	0.0105	0.0140	0.0129	-	-	-	-	329	257	1.28	-30.2	+20.3
44	88.10	5.38	2.09	1.881	1.40	0.73	0.0178	0.0183	0.0060	32.6	29.0	23.5	14.0	-	-	-	-29.6	-
Gilsonite[d]	85.36	10.36	1.53	2.800	0.03	1.45	0.0135	0.0281	0.0001	-	-	-	-	-	-	-	-28.0	-
Gilsonite[e]	85.5	10.0	1.5	2.5	0.3	1.39	0.0132	0.0251	0.0013	-	-	-	-	-	-	-	-	-

[a] Raw weight percentage.

[b] Relative to PDB standard.

[c] Relative to troilite standard.

[d] This study.

[e] From Wen, et al., 1978.

[f] Precision (approximately) = ± 20 %.

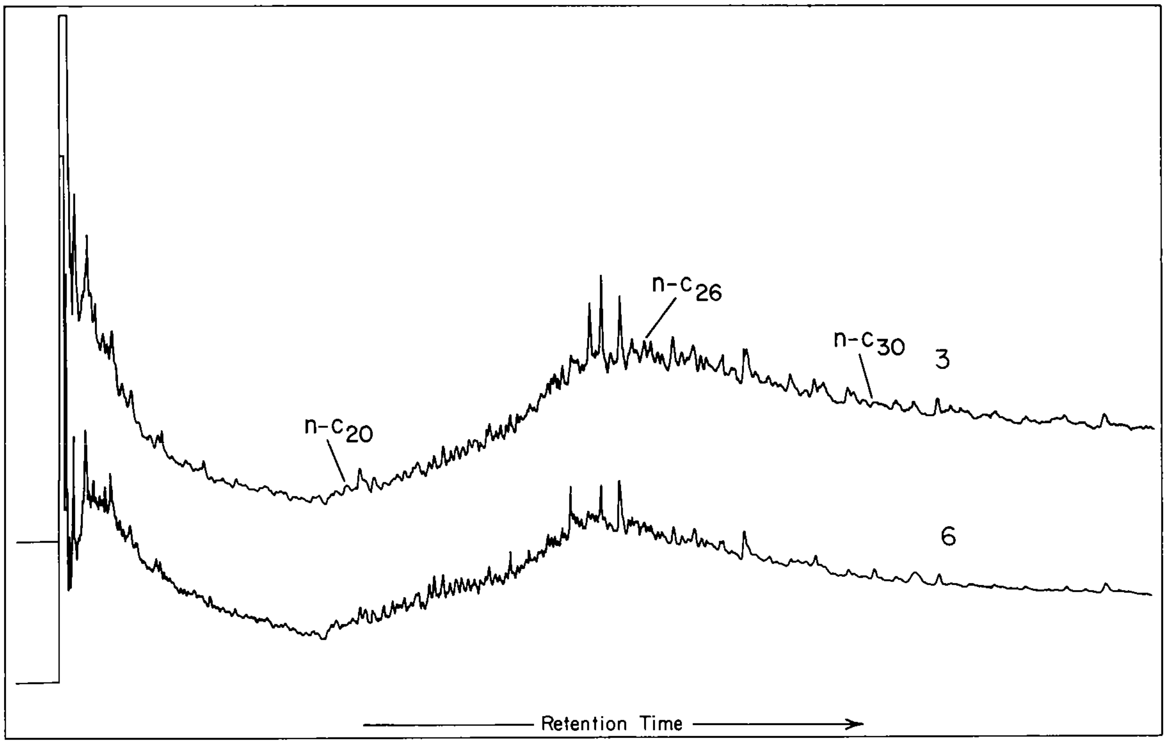

Figure 15. Gas chromatograms for typical asphaltite extracts. Relative retention times for three n-alkanes are as shown. Both samples were run in dichloromethane solution. Reproduced by permission of American Association of Petroleum Geologists.

a vanadium–sulfur relation in sample 5.

Table 7 also lists carbon- and sulfur-isotopic data for the grahamites and the impsonite and gilsonite of this study. Carbon-isotope ratios range from −30.2 to −29.6 o/oo; sulfur isotope ratios range from +15.5 to +20.3 o/oo. Both are very similar to the respective ratios determined for the oils.

Chemical Characteristics of Pyrolyzates of Solid Bitumens

In addition to routine analysis of the whole solid bitumen materials, each of the grahamite samples and the one impsonite were pyrolyzed, and the chemical characteristics of the pyrolyzates were studied. Pyrolysis experiments involved continuous-flow–high-temperature and closed-tube–low-temperature techniques. Details of these techniques are given in Curiale (1981).

High-Temperature Pyrolysis

Initially, each of the grahamites was pyrolyzed from 180°C to 570°C, at a program rate of 25°C/minute. The effluent was examined by high-resolution (capillary) gas chromatography. Two typical chromatograms are shown in figure 18, and indicate a homologous series of doublets. Such doublets have been noticed by many workers studying volatile products of high-temperature pyrolysis, and have been attributed to alkane–alkene pairs (Scrima and others, 1974; Martin, 1977; Sugimura and Tsuge, 1978). Of the doublets generated in this study, the early-eluting peak

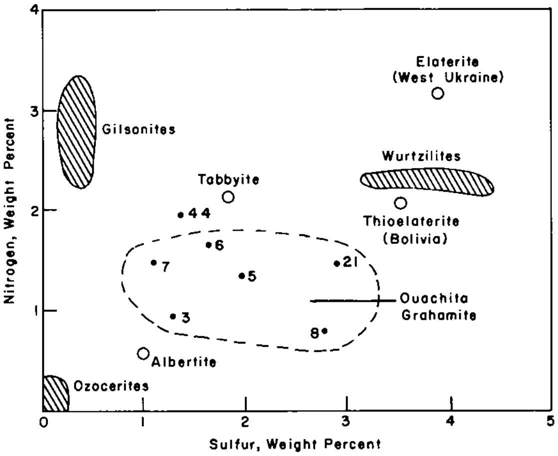

Figure 16. Content of nitrogen versus sulfur for solid bitumens. Data for non-Ouachita materials are from Hunt (1979). Grahamite and impsonite fields are as shown (impsonite = 44).

was identified as the alpha-olefin, and the late-eluting peak was identified as the corresponding (same carbon number) n-alkane. Determinations were made by coinjection with known standards.

Although yields were less than 10 percent by weight (of total solid bitumen), the pyrolyzate consisted predominantly of alkane and olefin components (fig. 18). An attempt to generate a quasi–n-alkane distribution (C_{15} to C_{31}), by combining the area of each alkane with that of its corresponding olefin, generated a distribution for each pyrolyzate that was similar to the distribution in a typical mature crude oil (fig. 19). The distributions show a predominance of the light components, with relatively high concentrations of C_{19} and C_{25} alkane–alkene pairs in some of the samples. Carbon-preference indices for the range 22 to 30 also are listed in figure 19, and indicate slight odd carbon preference in this range for most of the samples analyzed.

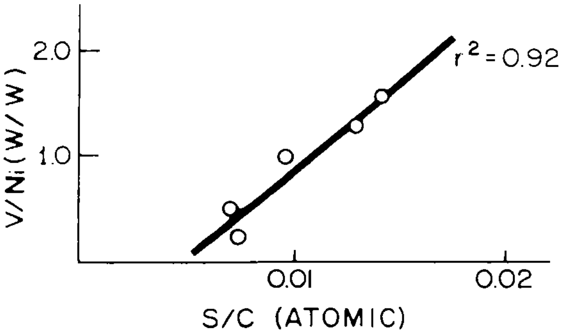

Figure 17. V/Ni (w/w) versus S/C (atomic) ratios for solid bitumens. Correlation coefficient for regression line (r squared) is as shown. Solid-bitumen sample 5 is not plotted.

The production of alkanes and alkenes on pyrolysis of grahamite and impsonite at high temperature is of interest owing to the conclusions possible concerning the chemical structure of these materials. The presence of long-chain hydrocarbons in the pyrolyzate suggests that these compounds were incorporated either as an occlusion in the material, or as a part of the asphaltite or pyrobitumen "molecule," in which case the high-molecular-weight alkanes would be chemically bound to the structure. However, exhaustive extraction in a soxhlet apparatus removed very little n-alkane or alpha-olefin material from any of these solid bitumens (see fig. 15), suggesting that these long-chain compounds do not exist in an easily removable form. Similar results were noted by Simm and Steedman (1980), who pyrolyzed crude-oil asphaltenes and produced n-alkanes with as many as 30 carbon atoms per molecule. Exhaustive extraction of the asphaltenes, in this case with diethyl ether, followed by pyrolysis,

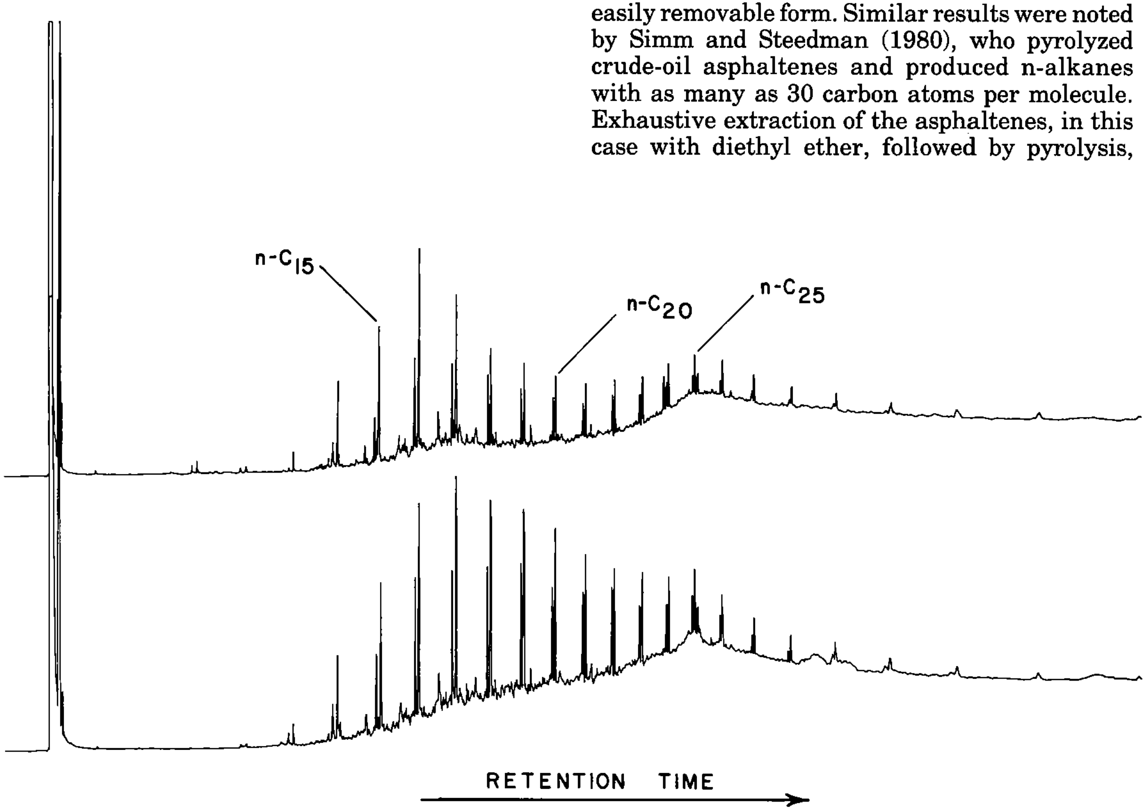

Figure 18. Gas chromatograms for typical high-temperature pyrolyzates. Conditions as in figure 7. Doublets represent alpha-olefin–n-alkane pairs, as discussed in text. Pyrolyzates are from sample 5 (top) and sample 7 (bottom).

yielded similar results. This suggested to the authors (p. 669) that "long alkyl chains are present in these asphaltene structures and are not due to residual absorbed resin."

Urov (1980), in a study of kerogen pyrolyzates, suggested that short-chain alkenes are actually products that have been thermally cleaved from kerogen side chains, at the bond that is beta to the kerogen nucleus. Because these straight-chain compounds cannot be conventionally extracted from the Ouachita bitumens, Urov's explanation is reasonable for these solid bitumens as well. The alkenes generated, as well as the n-alkanes, are thought to result from side-chain cracking, from the asphaltite or pyrobitumen framework.

Low-Temperature Pyrolysis

Although continuous-mode–high-temperature pyrolysis is adequate for determination of quasi–n-alkane distributions in pyrolyzates, formation of alkenes at temperatures above 350°C presents a problem in analysis for the biomarker components of the pyrolyzate. Consequently, a second method of pyrolysis was investigated. The method was applied to five of the bitumen samples, including the impsonite. Pyrolysis was conducted at a lower temperature for a longer time (300°C for 24 hours) in a closed system (Curiale, 1981). Examination of the pyrolyzate suggested that alkenes (specifically alpha-olefins) were absent, and that overall alkane yields were considerably lower than those obtained by continuous-mode pyrolysis (see gas chromatogram, fig. 20). This is a result of the pyrolysis interval, which is too short for a substantial conversion. Nevertheless, both steranes and triterpanes were evident in the closed-tube pyrolyzate. It must be emphasized, however, that these biomarkers represent the sum of those present in the solid-bitumen extract and those "created" by pyrolysis. The proportion of each type is unknown.

Sterane distributions of the five closed-tube pyrolyzates (CTPs) are shown in figure 21. The ratio of rearranged (dia-) steranes to regular steranes (shaded) increases in sample order 7, 5, 6, 3, 44, being greatest in the impsonite, sample 44. Changes within the diasteranes themselves, however, do not appear significant (for example, the ratio of peak 1 to peak 2, both representing C_{27} diasteranes, does not change appreciably from sample to sample). Each of these observations suggests biodegradation of a crude oil, as discussed later.

Figure 22 shows the distribution of (possible) tricyclic terpanes and hopanes for the CTPs. Three general observations can be made on these data. First, it is evident that the concentration of peaks 1a–1f is minimal in the pyrolyzates. Second, it is also evident that one of these peaks, peak 1e, rep-

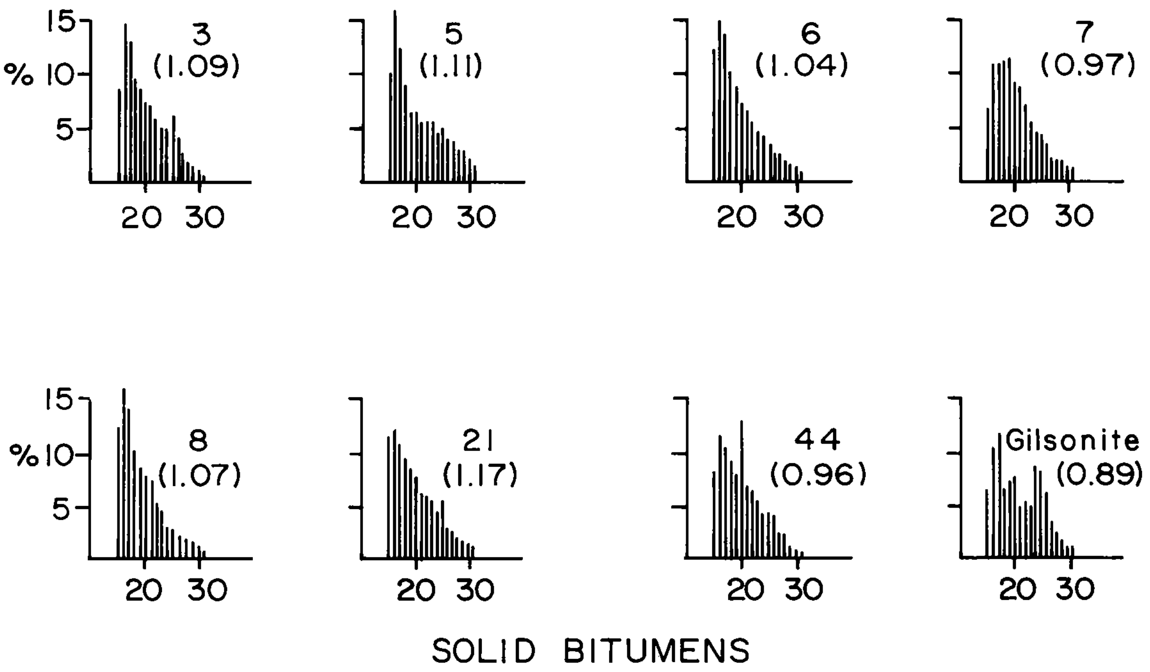

Figure 19. (Quasi–) n-alkane distributions in high-temperature pyrolyzates. Carbon-preference indices, as defined in table 3, are in parentheses.

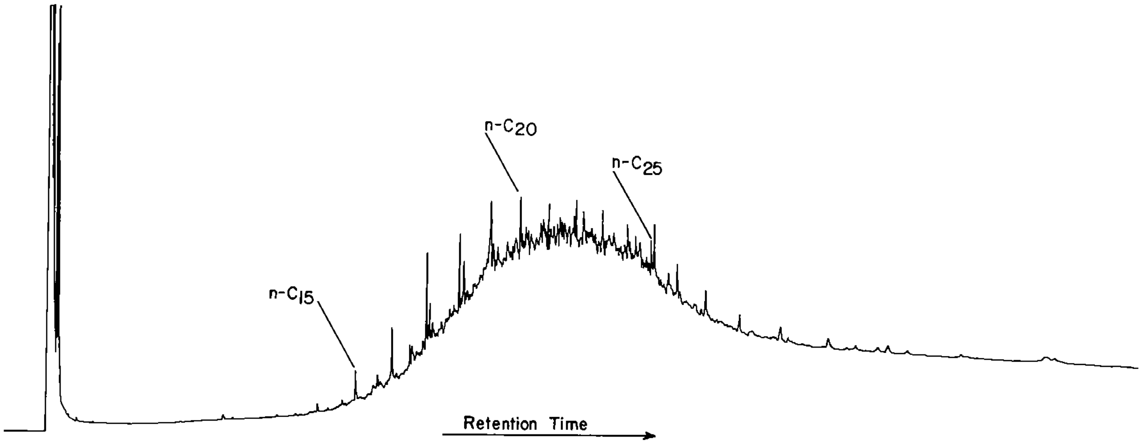

Figure 20. Gas chromatogram for typical low-temperature pyrolyzate. Closed-tube pyrolyzate 3 is shown. Conditions as in figure 7. Reproduced by permission of Pergamon Press.

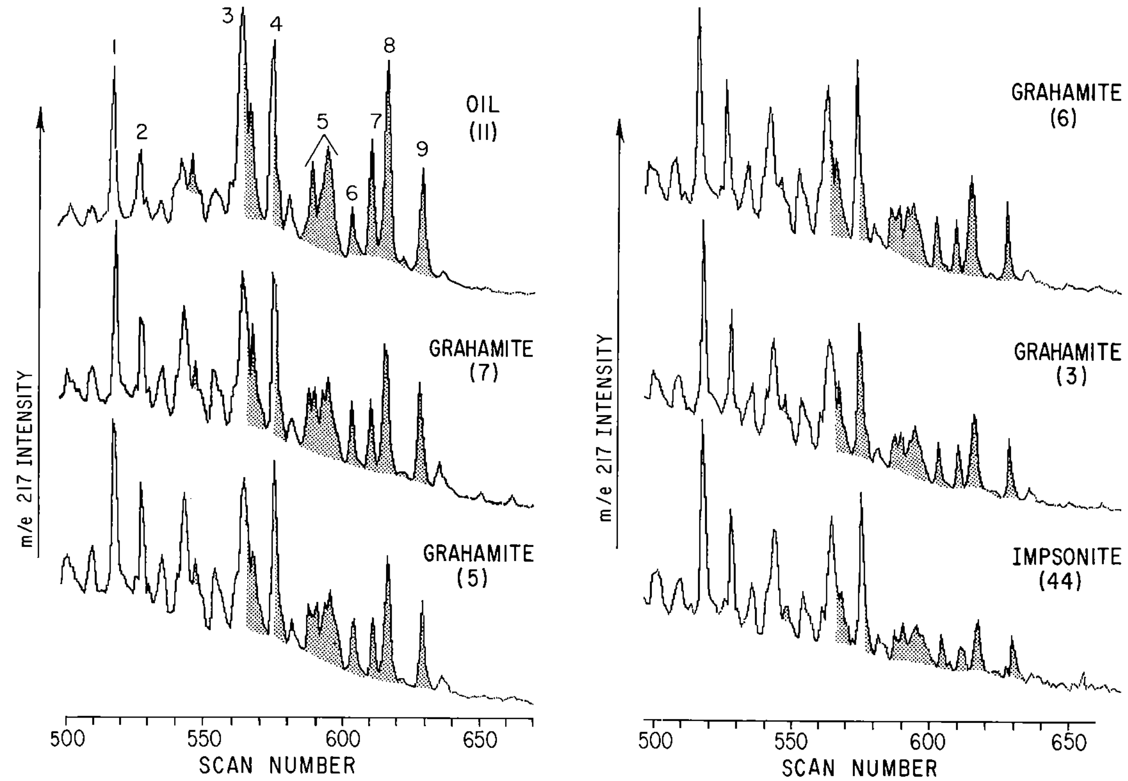

Figure 21. Mass chromatograms of m/e 217 for low-temperature pyrolyzates and oil 11. Regular steranes are shaded, although shading is not meant to indicate elution order or relative amount of each compound. See table 4 for peak identifications. Reproduced by permission of Pergamon Press.

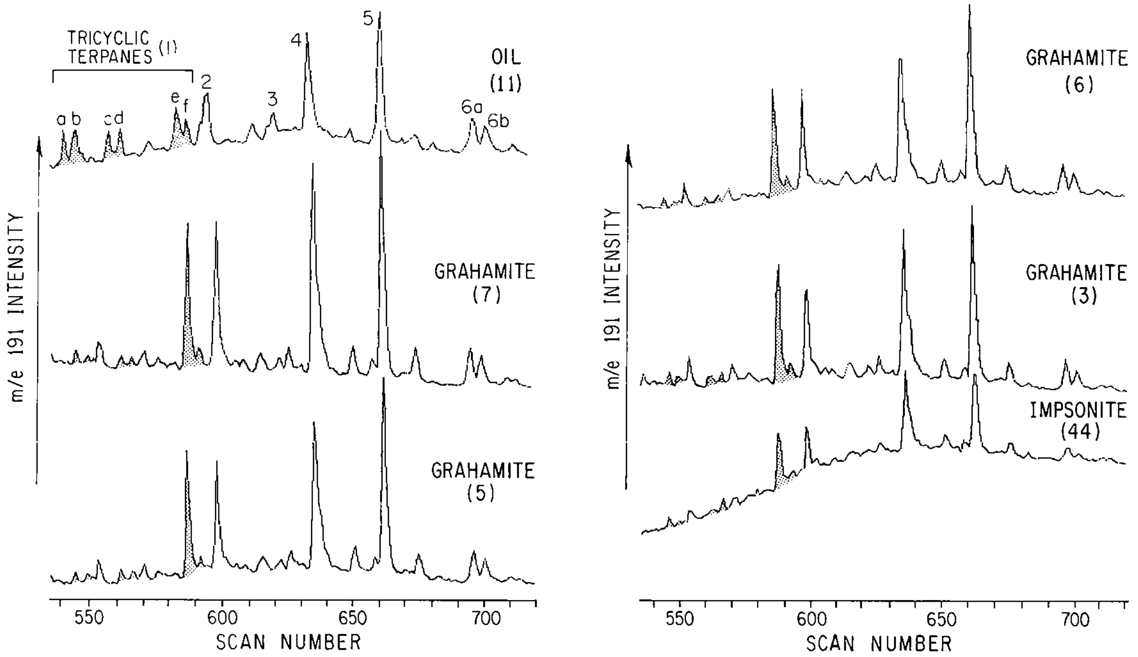

Figure 22. Mass chromatograms of m/e 191 for low-temperature pyrolyzates and oil 11. Peaks 1a–1f are shaded. See table 5 for peak identifications.

resents a significant portion of the m/e–191 mass chromatogram. Previously, peaks 1a–1f have been tentatively assigned to the tricyclic terpanes (table 5). The mass spectrum for peak 1e in pyrolyzate 5, however, shows strong fragment peaks (greater than 50 percent of the 191 base peak) at m/e 55, 69, and 365, suggesting coelution of a monoaromatic compound (Bendoraitis, 1973); such a compound was not detected in either the oils or the rock extracts, possibly because these were processed to remove aromatic compounds prior to analysis. Nevertheless, a base peak of 191 in this spectrum strongly suggests a prominent terpane component, probably a tricyclic terpane, indicating that this particular compound exists in much higher concentrations than the other tricyclic terpanes in the pyrolyzates of the solid bitumen examined. Third, whereas peaks 2, 3, 4, 5, and 6 (C_{27}, C_{28}, C_{29}, C_{30}, and C_{31} hopanes, respectively) are present in all of these samples, significant peaks eluting before and after peak 5 (C_{30} hopane) are present as well. These are labeled *A* and *C* in figure 22. Peaks A and C have been identified by their mass spectra (Whitehead, 1973a; Kimble and others, 1974a) as C_{29} and C_{30} moretanes [having 17b(H),21a(H) stereochemistry], previously observed in crude oils and kerogen pyrolyzates by Seifert (1978) and Seifert and Moldowan (1979). These components presumably were released by pyrolysis, although the mode of occurrence of these compounds in the original solid bitumen (that is, occluded or chemically bound) is unknown.

The m/e–177–ion chromatogram for the closed-tube pyrolyzates reveals unidentified peak B (fig. 13) in all five pyrolyzates. Unfortunately, the presence of this compound is greatly obscured by the large concentration of peak 1e (see above), which eluted just prior to peak B. Nevertheless, the m/e–370 molecular ion for compound B is clearly evident in the relevant mass spectra for each of the solid-bitumen pyrolyzates. Thus, in summary, peak 1e of the pyrolyzates appears to consist of three coeluting compounds: a tricyclic terpane (as found in the oils), the monoaromatic species discussed above, and the unidentified peak B (also found in all oils). Relative amounts of these compounds are impossible to determine by available data.

The preceding observations, particularly an increase in the diasterane/regular-sterane ratio, and the strong presence of a single "tricyclic terpane," suggest biodegradation of a crude oil. This possibility will be discussed in detail later in this report.

Solid Bitumen–Solid Bitumen Correlations

In addition to the previously discussed chemical analyses of the grahamite and impsonite, an attempt was made to correlate between each of these materials to determine whether the materials are cogenetic. Both carbon- and sulfur-isotopic ratios suggest that these solid materials are genetically related (table 7). The ranges of carbon and sulfur ratios of the samples (−30.2 to −29.6 o/oo, and +15.5 to +20.3 o/oo, respectively) are small in relation to ranges for these ratios in carbon- and sulfur-containing materials worldwide, indicating that the materials in question have a common source. Thus, gilsonite, although similar to grahamite and impsonite in carbon-isotope ratio (table 7; Silverman and Epstein, 1958), is distinguishable from the Ouachita materials by its sulfur-isotope ratio (Mauger and others, 1973).

Both the high-temperature–short-term and the low-temperature–long-term pyrolysis techniques are useful in relating the grahamites to one another and to the impsonite. All of the quasi–n-alkane distributions of the high-temperature pyrolyzates (fig. 19) of grahamites are similar, and yet they are distinct from the distribution of the gilsonite pyrolyzate. In addition, all sterane and particularly terpane distributions of the grahamite and impsonite closed-tube pyrolyzates bear a striking resemblance to one another (figs. 21, 22). The differences in the ratio of regular and rearranged steranes in these samples have been noted, although, as discussed later, they do not preclude cogenesis of these materials. In summary, I conclude from the isotopic composition and the distribution of specific compounds in the pyrolyzates that all Ouachita grahamites and impsonite examined in this study are genetically related.

SOURCE-ROCK POTENTIAL OF THE OUACHITA FACIES

Whole-Rock and Kerogen Studies

Samples of each formation or group, from the Stanley Group (Mississippian) to the Womble Formation (mid-Ordovician), were analyzed for their hydrocarbon-source potential. Initially, 115 subsurface and 11 outcrop samples were analyzed for total organic carbon (TOC) and total carbonate carbon (TCC). Results are presented in table 8 and in figures 23 and 24. Each stratigraphic interval studied has an average TOC value of greater than 0.76 percent. Relatively few samples of the Missouri Mountain Shale and Polk Creek Shale were analyzed for TOC content. Nevertheless, the TOC levels are certainly high enough to justify further study of all six formations as potential source rocks for oils and solid bitumens in the Ouachita Mountains.

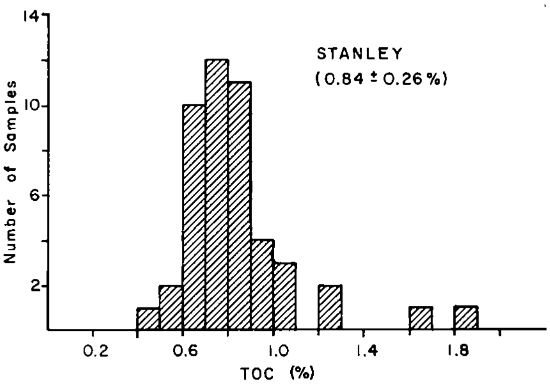

Figure 23. Total organic carbon histogram for Stanley Group samples. Only subsurface samples are plotted. Number in parentheses is average, with standard deviation.

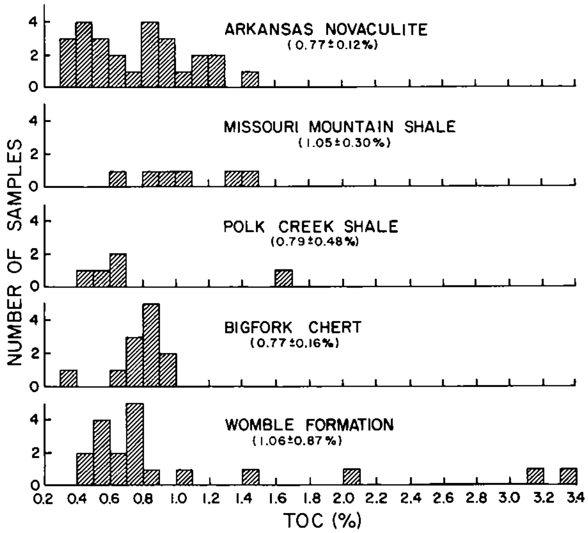

Figure 24. Total organic carbon histograms for Arkansas Novaculite through Womble Formation samples. See figure 23 for further information.

In addition to determinations of total organic carbon and total carbonate carbon, at least one sample of each formation and group was analyzed to determine the carbon-isotope ratio (table 9) of its total organic carbon (TOC). The range of ^{13}C values is −28.9 to −24.5 o/oo, suggesting a suite of organic matter types derived from both land and marine sources. Four Stanley Group and Arkansas Novaculite samples prepared for reflectance measurements show that almost all of the recognizable organic matter in the Mississippian and Devonian samples consists of the maceral vitrinite. Tissot and Welte (1978, p. 452) stated that "vitrinite is abundant in type-III kerogen, . . . moderately abundant in type-II kerogen, and mostly absent in type-I." On this basis, I suggest that the kerogen in the Mississippian and Devonian samples is predominantly of type III. Not enough data are available to classify kerogen types in the pre-Devonian samples.

Selected rock samples were demineralized after extraction of soluble organic matter, and the re-

TABLE 8.—TOTAL ORGANIC CARBON (TOC) AND TOTAL CARBONATE CARBON (TCC) IN OUACHITA ROCKS

Sample Number	Stratigraphic Interval	TOC (%)	TCC (%)
24-3400-3500	Stanley	0.89	a
-3500-3600		1.28	a
-3600-3700		1.89	a
-3700-3800		1.06	a
-3850-3900		0.81	a
-3900-4020		0.87	a
-4120-4140		1.21	a
-4140-4320		1.69	a
25-2980-3080		0.73	a
-3080-3180		0.76	a
-3180-3280		0.84	a
-3280-3300		0.70	a
-3300-3390		0.94	a
-3390-3445		1.08	a
-3445-3510		0.70	a
-3510-3555		0.92	a
-3555-3600		0.82	a
-3600-3650		0.74	a
-3650-3700		0.71	a
-3700-3745		0.88	a
-3745-3785		0.86	a
-3785-3855		0.69	a
-3855-3905		0.80	a
-3905-3950		0.68	a
-3950-4000		0.68	a
-4000-4050		0.83	a
-4050-4085		0.76	a
-4085-4135		0.67	a
-4135-4185		0.76	a
-4185-4235		0.69	a
-4235-4285		0.72	a
26-380-470		0.55	a
-510-600		0.85	a
-600-622		0.71	a
-627-661		0.68	a
-668-700		0.67	a
-700-757		0.64	0.39
-757-800		0.72	0.22
-801-843		0.96	a
-843-900		0.87	a
-910-939		0.63	a

TABLE 8.—*Continued*

Sample Number	Stratigraphic Interval	TOC (%)	TCC (%)
34-383-384	Stanley	0.93	a
-1440-1465		0.69	a
35-30-110		0.49	0.59
-110-200		0.58	a
-200-305		0.71	0.30
-305-365		1.04	a
OGS GCN 25[b]		0.83	a
OGS GCN 31[b]		0.25	a
40-6500-6600	Arkansas Novaculite	1.17	a
-6600-6700		1.42	a
-6700-6800		1.15	a
-6800-6900		0.91	a
-7000-7100		0.74	a
-7100-7200		0.86	a
-7200-7300		1.05	a
-7300-7400		1.27	a
-7400-7500		1.26	0.81
-7500-7600		0.87	1.80
-7600-7700		0.86	3.76
-7700-7800		0.80	3.24
-7800-7900		0.65	5.26
-7900-8000		0.53	6.27
-8000-8100		0.38	6.07
-8100-8200		0.52	5.60
-8200-8300		0.51	5.89
-8300-8400		0.49	5.66
-8400-8500		0.42	7.07
-8500-8600		0.33	5.11
-8600-8700		0.38	7.36
-8700-8800		0.48	4.79
-8800-8900		0.66	5.65
-8900-9000		0.41	6.88
-9000-9100		0.93	1.52
-9100-9200		0.93	0.67
OGS GCN 24[b]		14.56	a
29-800-850	Missouri Mountain	0.96	a
-850-900		1.06	a
31-9240-9295		1.42	a
-9295-9350		1.36	a
-9350-9400		0.81	a
-9415-9465		0.68	a
OGS GCN 17[b]		0.09	a
OGS GCN 21[b]		3.84	a

TABLE 8.—*Continued*

Sample Number	Stratigraphic Interval	TOC (%)	TCC (%)
28-700-800	Polk Creek	1.64	a
31-9565-9615		0.63	a
-9615-9665		0.47	0.87
-9665-9715		0.58	0.63
-9715-9765		0.63	0.52
OGS GCN 30[b]		6.51	a
40-9900-10000	Bigfork	0.87	a
-10000-10100		0.73	0.30
-10100-10200		0.66	0.43
-10200-10300		0.75	a
-10300-10400		0.85	a
-10400-10500		0.97	a
-10500-10600		0.93	a
-10600-10700		0.84	a
-10700-10800		0.83	a
-10800-10900		0.70	a
-10900-11000		0.35	a
-11000-11100		0.80	a
OGS GCN 22[b]		1.48	a
OGS GCN 32[b]		2.72	a
OGS GCN 36[b]		5.65	a
25-9856-9900	Womble	1.07	a
-9900-10000		0.88	a
-10000-10090		0.76	a
-10090-10190		0.78	a
-10190-10290		0.73	a
-10290-10400		0.71	a
-10400-10500		0.76	a
-10500-10600		0.69	a
27-2705-1750		0.48	a
-2750-2785		0.64	a
-2785-2830		0.50	a
-2830-2875		0.59	a
-2875-2925		0.56	a
-2925-2975		0.44	a
-2975-2995		0.50	a
28-1640-1695		3.35	a
-1695-1750		3.18	a
-1750-1800		1.40	a
-1800-1860		2.07	a
OGS GCN 28[b]		13.35	a
OGS GCN 35[b]		8.54	a

[a] Less than 0.1%.

[b] Outcrop sample.

Table 9.—Extractable Organic Matter (EOM) and Isotopic Data

Sample Number	Stratigraphic Interval	EOM (ppm)[a]	EOM/TOC (%)	^{13}C (°/oo)[b]		
				EOM	TOC	Kerogen
24-3600-3700	Stanley	6720	35.6	-34.6		
-4140-4320		3216	19.0	d	-26.5	-26.6
25-3390-3445		982	9.1	d	d	d
-4000-4050		670	8.1	d	d	d
26-510-600		862	10.1	d	d	d
-801-843		1469	15.3	d	d	d
OGS GCN 25[c]		1963	23.7	d	d	d
OGS GCN 31[c]		953	38.1	d	d	d
40-6500-6600	Arkansas Novaculite	922	7.9	d	d	d
-6600-6700		1183	8.3	d	d	-26.8
-6700-6800		1293	11.2	d	d	d
-6800-6900		558	6.1	d	d	d
-7100-7200		932	10.8	d	d	d
-7200-7300		616	5.9	d	-27.3	d
-7300-7400		629	5.0	d	d	d
-7400-7500		806	6.4	d	d	d
-7500-7600		960	11.0	d	d	d
-7600-7700		608	7.1	d	d	-27.1
-7700-7800		759	9.5	d	d	d
-7800-7900		d	d	d	-26.5	d
-8100-8200		681	13.1	d	d	-29.0
-8200-8300		298	5.8	d	d	d
-8400-8500		d	d	d	-26.6	d
-9000-9100		779	8.4	-41.2	d	d
-9100-9200		403	4.3	-29.3	d	-27.7
OGS GCN 24[c]		2501	1.7	d	d	d
29-800-850	Missouri Mountain	901	9.5	-32.4	d	d
-850-900		1098	10.4	d	d	-29.7
31-9240-9295		1096	7.7	d	d	-27.0
-9295-9350		553	4.1	d	d	d
-9350-9400		892	11.0	-31.0	d	d
-9415-9465		1308	19.2	d	-25.8	-27.3
OGS GCN 21[c]		2423	6.3	d	d	-29.1
28-700-800	Polk Creek	1126	6.9	d	d	d
31-9565-9615		353	5.6	-30.7	-24.8	d
-9615-9665		134	2.9	-34.5	d	d
-9665-9715		678	11.7	-31.5	d	-25.8
-9715-9765		295	4.7	d	d	d
OGS GCN 30[c]		2961	4.5	d	d	-29.9

TABLE 9.—*Continued*

Sample Number	Stratigraphic Interval	EOM (ppm)[a]	EOM/TOC (%)	^{13}C (ppt)[b]		
				EOM	TOC	Kerogen
40-9900-10000	Bigfork	671	7.7	d	d	-26.9
-10300-10400		467	5.5	d	-25.0	d
-10400-10500		495	5.1	-30.7	d	d
-10500-10600		682	7.3	d	d	-26.0
-10600-10700		1155	13.8	-30.4	-24.5	d
-10700-10800		577	7.0	d	d	d
-10900-11000		d	d	d	-24.9	d
-11000-11100		705	8.8	d	d	-25.5
OGS GCN 22[c]		479	3.2	d	d	d
OGS GCN 32[c]		558	2.1	d	d	d
OGS GCN 36[c]		1531	2.7	d	d	d
25-9856-9900	Womble	1634	15.3	-38.3	-26.0	d
-9900-10000		1516	17.2	d	-26.3	-26.8
-10000-10090		1768	23.3	-39.6	-26.2	d
-10400-10500		391	5.1	d	d	-26.3
28-1640-1695		2507	7.5	d	d	d
-1695-1750		2858	9.0	d	d	d
-1750-1800		3721	26.6	-31.0	-28.9	-29.7
-1800-1860		2127	10.3	d	d	d
OGS GCN 28[c]		4809	3.6	d	d	-28.2
OGS GCN 35[c]		5065	5.9	d	d	d

[a] Parts EOM per million parts rock.

[b] Parts per thousand, relative to PDB standard. Precision = ± 0.10.

[c] Outcrop sample.

[d] Not determined.

sultant kerogen concentrates were analyzed for carbon-isotope ratios. The carbon-isotope values for the kerogens (−29.7 to −25.5 o/oo) are similar to those for organic carbon in the whole rock (table 9). This is to be expected, because the bulk of organic matter in an ancient nonreservoir rock is kerogen (Tissot and Welte, 1978). In general, whole-rock organic carbon should be lighter than kerogen isolated from it, yet the opposite is observed here, in the four samples whose kerogen and total organic carbon isotope ratios were determined (see table 9). However, the isotopic ratios of extractable organic matter (EOM) in all cases are lighter than their corresponding kerogen or total whole-rock organic carbon, as would be expected (table 9). The unusual change in isotopic content, from TOC to kerogen, might be a function of the kerogen-concentration procedure. Alternatively, small amounts of carbonate material may have remained in the rock sample following acid washing. This would result in anomalously "heavy" carbon-isotope ratios in the TOC.

Bitumen Studies

Selected rock samples, chosen on the basis of TOC contents, were extracted (soxhlet) with dichloromethane to remove extractable organic matter (EOM). Yields of EOM as a fraction of the rock and as a percentage of total organic carbon (TOC) are listed in table 9, and are presented graphically in figure 25. Average values, in parts EOM per million parts rock, for the Stanley Group, Arkansas Novaculite, Missouri Mountain Shale, Polk Creek Shale, Bigfork Chert, and Womble Formation are 1,150, 871, 1,183, 925, 732, and 2,640, respectively. These values are all high enough to suggest that each of these stratigraphic intervals has hydrocarbon source-rock potential.

Also listed in table 9 are the carbon-isotope ratios for the EOMs, for 13 selected samples. As discussed above, these values (−41.2 to −29.3 o/oo) are isotopically lighter than those of their corresponding kerogen or total organic carbon (TOC), where comparisons are available.

Metal Determinations

In an attempt to establish characteristic metal concentrations for the EOM of each stratigraphic interval studied, vanadium and nickel were determined for at least one sample from each stratigraphic interval (table 10). The data suggest that the highest concentrations of vanadium (greater than or equal to 3.0 ppm of extract) occur in the Missouri Mountain Shale, Polk Creek Shale, and Bigfork Chert. Samples from pre-Devonian rocks are highest in nickel (all greater than or equal to 1.0 ppm of extract). The vanadium/nickel ratio (w/w) of the EOM appears to be highest in samples from Silurian and Upper Ordovician rocks.

Fractionation Data

At least three samples from each stratigraphic interval were chosen, on the basis of their high EOM/TOC ratios, for detailed analysis of extractable organic matter (table 11). Hydrocarbons typically constitute less than 50 percent of the total EOM of these samples. Table 11 lists hydrocarbon (HC) yield of the whole rock and of the total organic carbon of the rock (HC/TOC). Figure 26 shows the relation between HC yield and TOC (Baker, 1962). Various fields noted in figure 26 are from Hunt (1979, p. 266), and suggest that most of the samples in table 11 contain indigenous EOM. A single possible exception is sample 24–3600–3700, an unusually dark shale of the Stanley Group, which falls very close to that portion of the field designated "reservoir rock" by Hunt. As a result, this particular sample cannot be classified unambiguously as a rock whose organic matter is totally indigenous, and it was not used in calculating average EOM values for Stanley Group samples.

Philippi (1957) classified source-rock "quality" on the basis of parts hydrocarbon per million parts rock. A "fair" source rock thus contains more than

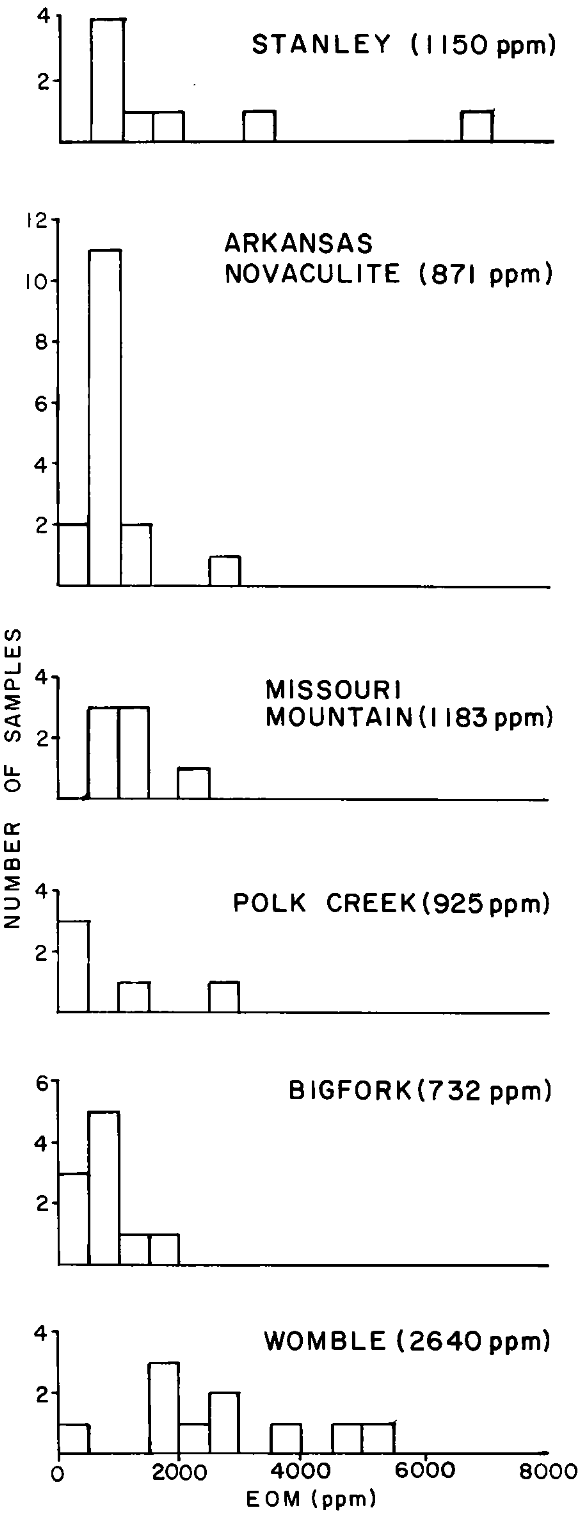

Figure 25. Extractable organic matter histograms for Stanley Group through Womble Formation samples. Numbers in parentheses are average EOM values. Average for Stanley samples excludes richest sample, owing to presence of nonindigenous organic matter (see text).

TABLE 10.—VANADIUM AND NICKEL CONTENT OF EXTRACTABLE ORGANIC MATTER

Sample Number	Stratigraphic Interval	V[c] (ppm of EOM)	Ni[c] (ppm of EOM)	V/Ni (w/w)
24-4140-4320	Stanley	0.4	0.3	1.3
40-7200-7300	Arkansas Novaculite	0.7	a	-
29-850-900	Missouri Mountain	4.2	1.3	3.2
31-9415-1465		6.9	2.8	2.5
31-9615-9665	Polk Creek	3.9	1.0	3.9
OGS GCN 30[b]		10.9	3.2	3.4
40-10500-10600	Bigfork	3.0	1.2	2.5
OGS GCN 22[b]		17.3	1.2	14.4
25-9900-10000	Womble	0.4	1.3	0.3
28-1750-1800		1.3	1.1	1.2

[a] Below detection limits.

[b] Outcrop samples.

[c] Precision (approximately) = ± 15%.

150 ppm HC, and a "good" source rock contains more than 500 ppm HC. By this measure, at least one sample from each formation in this study is a "fair" source rock, whereas "good" or better source rocks are restricted to the Stanley, Polk Creek, and Womble stratigraphic intervals.

The implications resulting from criteria such as total EOM and total HC in a rock can be better assessed if accompanied by a molecular description of the paraffinic hydrocarbon fraction of the EOM. Therefore, this fraction was investigated in detail by high-resolution gas chromatography (GC) and by computer-assisted gas chromatography–mass spectrometry (GCMS). Discussion will initially concern the n-alkane and isoprenoid isoalkane content of the paraffinic hydrocarbon fraction. Sterane and terpane distributions in some of the samples also will be discussed.

N-Alkane and Isoprenoid Data

N-alkane distributions for the Stanley Group, the Arkansas Novaculite through Bigfork Chert, and the Womble Formation are depicted in figures 27, 28, and 29, respectively. Different samples from the same formation and the same well exhibit similarities (for example, fig. 27, well 25; fig. 29, well 28). However, different samples from the same formation but different wells exhibit some differences (for example, fig. 29, wells 25, 28). In general, however, similarities are noted among samples from the same stratigraphic interval. For example, all Missouri Mountain Shale samples (fig. 28) show n-alkane–distribution maxima at n-C_{17}. Unfortunately, such similarities are not distinct enough to permit the use of n-alkane distributions as a unique characteristic of EOM of these stratigraphic intervals, which indicates significant vertical and lateral variations in organic matter.

Note the predominance of 22–carbon n-alkane in the EOM of all Arkansas Novaculite samples and of the two unweathered Bigfork Chert samples. The strong occurrence of n-C_{22} in these formations suggests a lithologic dependence. A predominance of n-C_{22} in rock extracts was noted

TABLE 11.—FRACTION DATA FOR EXTRACTABLE ORGANIC MATTER

Sample Number	Stratigraphic Interval	Fraction (%)				TOC	$\frac{HC^a}{rock}$	$\frac{HC^b}{TOC}$	$\frac{pris}{phyt}$	$\frac{n\text{-}C_{17}}{prist}$	$\frac{n\text{-}C_{18}}{phyt}$	CPI[c]
		Sat HC	Arom HC	NSO	Asph							
24-3600-3700	Stanley	34.2	26.6	34.2	5.2	1.89	4086	216.2	1.45	2.75	2.82	1.02
24-4140-4320[d]		12.3	23.5	30.9	33.2	1.69	1151	68.1	1.29	3.14	3.15	0.90
25-3390-3445[d]		38.1	17.4	28.8	14.7	1.08	545	50.5	2.03	2.27	2.29	1.01
25-4000-4050		37.2	12.0	23.9	20.2	0.83	332	40.0	1.08	2.78	3.03	1.09
26-510-600		25.9	16.5	26.3	31.3	0.85	365	42.9	1.40	2.40	2.29	1.06
26-801-843		32.3	22.2	32.1	13.4	0.96	801	83.4	0.67	1.90	1.55	1.10
OGS GCN 25		35.9	18.5	28.3	17.3	0.83	1068	128.7	1.30	3.18	3.18	1.04
OGS GCN 31		19.5	22.1	40.1	18.2	0.25	396	158.4	--	--	--	1.08
40-7200-7300[d]	Arkansas Novaculite	11.8	9.9	31.5	46.8	1.05	134	12.8	1.41	3.16	3.54	0.89
40-8200-8300[d]		17.0	16.1	34.0	32.9	0.51	99	19.4	0.88	3.20	3.13	1.14
40-9100-9200		18.2	19.2	35.5	27.1	0.93	151	16.2	1.46	3.59	3.22	1.19
29-850-900[d]	Missouri Mountain	13.7	14.5	51.7	20.0	1.06	310	29.2	1.15	2.36	1.97	1.06
31-9240-9295		14.7	16.1	59.8	9.4	1.42	338	23.8	1.76	2.64	2.36	1.10
31-9415-9465[d]		10.9	24.6	48.0	16.5	0.68	464	58.2	1.10	2.59	2.38	1.14
31-9615-9665[d]	Polk Creek	13.0	31.5	25.3	30.3	0.47	60	12.8	1.07	2.76	2.51	1.25
31-9715-9765		15.5	15.1	51.2	18.1	0.63	90	14.3	1.27	2.92	2.73	1.07
OGS GCN 30[d]		23.5	38.3	28.2	10.1	6.51	1830	28.1	1.24	3.24	3.06	1.04
40-9900-10000[d]	Bigfork	20.9	10.9	43.8	24.4	0.87	213	24.5	1.31	2.48	2.44	1.28
40-10500-10600[d]		6.6	8.4	57.3	27.6	0.93	102	11.0	1.24	3.09	3.37	1.38
OGS GCN 22		22.0	23.1	27.8	27.1	1.48	216	12.1	1.11	1.93	1.94	1.04
25-9900-10000	Womble	25.1	18.7	31.3	4.9	0.88	967	109.9	1.69	1.95	2.31	1.05
25-10400-10500		21.6	24.3	34.3	19.8	0.76	179	23.6	1.53	1.48	2.30	1.30
28-1640-1695		21.3	28.2	43.9	6.5	3.35	1241	37.0	1.58	6.43	8.06	1.05
28-1695-1750[d]		28.5	21.9	44.5	5.1	3.18	1440	45.3	1.33	5.41	5.72	0.94
28-1750-1800[d]		25.2	17.2	35.8	21.8	1.40	1578	112.7	1.43	4.45	4.86	1.08
28-1800-1860		26.2	17.2	51.0	5.6	2.07	923	44.6	1.38	4.58	5.28	0.99

[a] Parts hydrocarbon per million parts rock.
[b] Parts hydrocarbon per million parts total organic carbon.
[c] Calculated as for crude oils.
[d] Samples analyzed for sterane and hopane distributions.

by Schenck (1968), in rocks ranging in age from Miocene to Permian. This component was tentatively attributed to a specific organism containing n-C_{22} or to a structural precursor thereof. Schenck also suggested that, because an n-C_{22} predominance has never been documented in a crude oil, such a predominance in a rock extract implies immaturity of the rock. This conclusion appears to be unwarranted, at least in the present study, because several samples showing the n-C_{22} predominance are thermally mature (as documented later).

In addition to the distribution of various chemical fractions in the EOM of selected rock samples, table 11 also lists the carbon-preference index and three isoprenoid and n-alkane ratios: pristane/phytane, n-heptadecane/pristane, and n-octadecane/phytane. These parameters are combined in a single histogram for each sample, for the Stanley Group, the Arkansas Novaculite through Bigfork Chert, and the Womble Formation, in figures 30, 31, and 32, respectively. As with the n-alkane distributions, similarities are noticeable among samples from the same formation in the same well (for example, fig. 30, well 25; fig. 32, well 25). Also, in some cases all samples from a single formation exhibit similarities (for example, Missouri Mountain Shale, fig. 31). Other factors evident in figures 30–32 are as follows: (1) the Womble is the only formation that has an n-heptadecane/pristane and an n-octadecane/phytane ratio greater than 3.25 (see table 11); (2) the Stanley Group and the Womble Formation (figs. 30, 32) contain EOM with a paraffinic hydrocarbon/aromatic hydrocarbon ratio significantly greater than 1; (3) the asphaltene content is consistently greater than 24 percent in all samples of Arkansas Novaculite and Bigfork Chert;

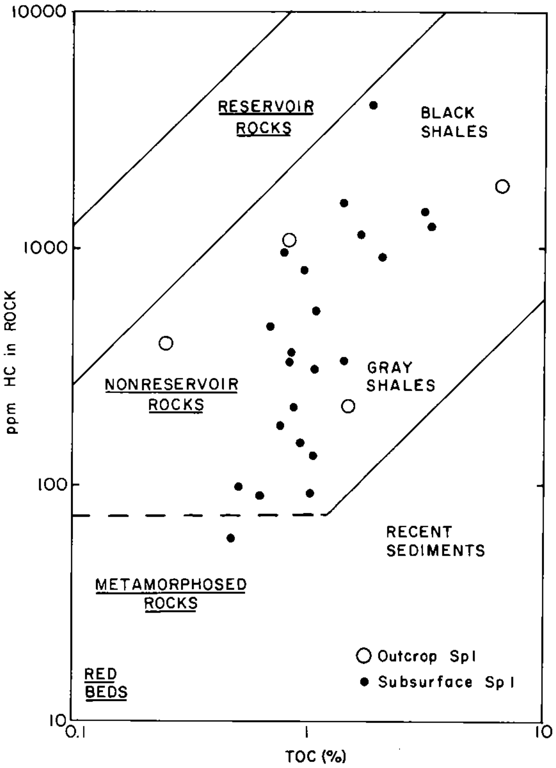

Figure 26. Graph of total hydrocarbon versus total organic carbon for selected rock samples. Plot format and fields are from Baker (1962) and Hunt (1979).

and (4) the NSO fraction typically makes up a higher percentage of EOM than either the hydrocarbon fractions or the asphaltene fraction. Observations 1 and 2 are probably functions of maturity level in these samples. Observation 3 is most likely a consequence of rock type, since both formations are siliceous. Observation 4, the dominance of the NSO fraction in many samples, is difficult to explain, although it is probable that this, too, is a function of the maturity of these samples.

Sterane and Hopane Data

The branched and cyclic fraction of the EOM of samples containing abundant paraffinic hydrocarbons was analyzed to determine the distribution of its steranes and terpanes. Unfortunately, because all samples were Paleozoic in age, sterane and terpane content was small. Two samples from each of the six stratigraphic intervals were analyzed (table 11). The characteristic ion fragments 217 and 191 were monitored for sterane and terpane content, respectively. These scans are shown in figures 33–38 (steranes) and figures 39–44 (terpanes). In addition, figure 45 presents the C_{27}, C_{28}, and C_{29} distributions of the steranes, as in the case of the oils.

Sterane and terpane mass chromatograms obtained from Stanley Group samples (24–4140–4320 and 25–3390–3445) are shown in figures 33 and 39, respectively. Figures 33 and 45 suggest

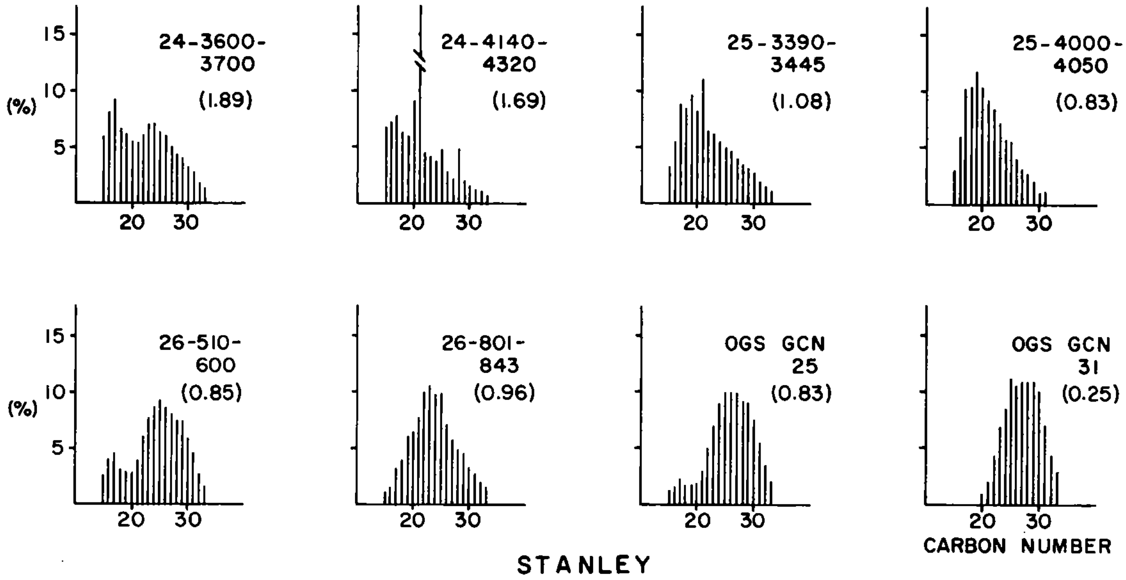

Figure 27. N-alkane distributions in Stanley Group samples. High "n-C21" concentration in sample 24–4140–4320 may be due to coelution of an unknown compound in saturate-hydrocarbon fraction. Total organic carbon values (%) are in parentheses.

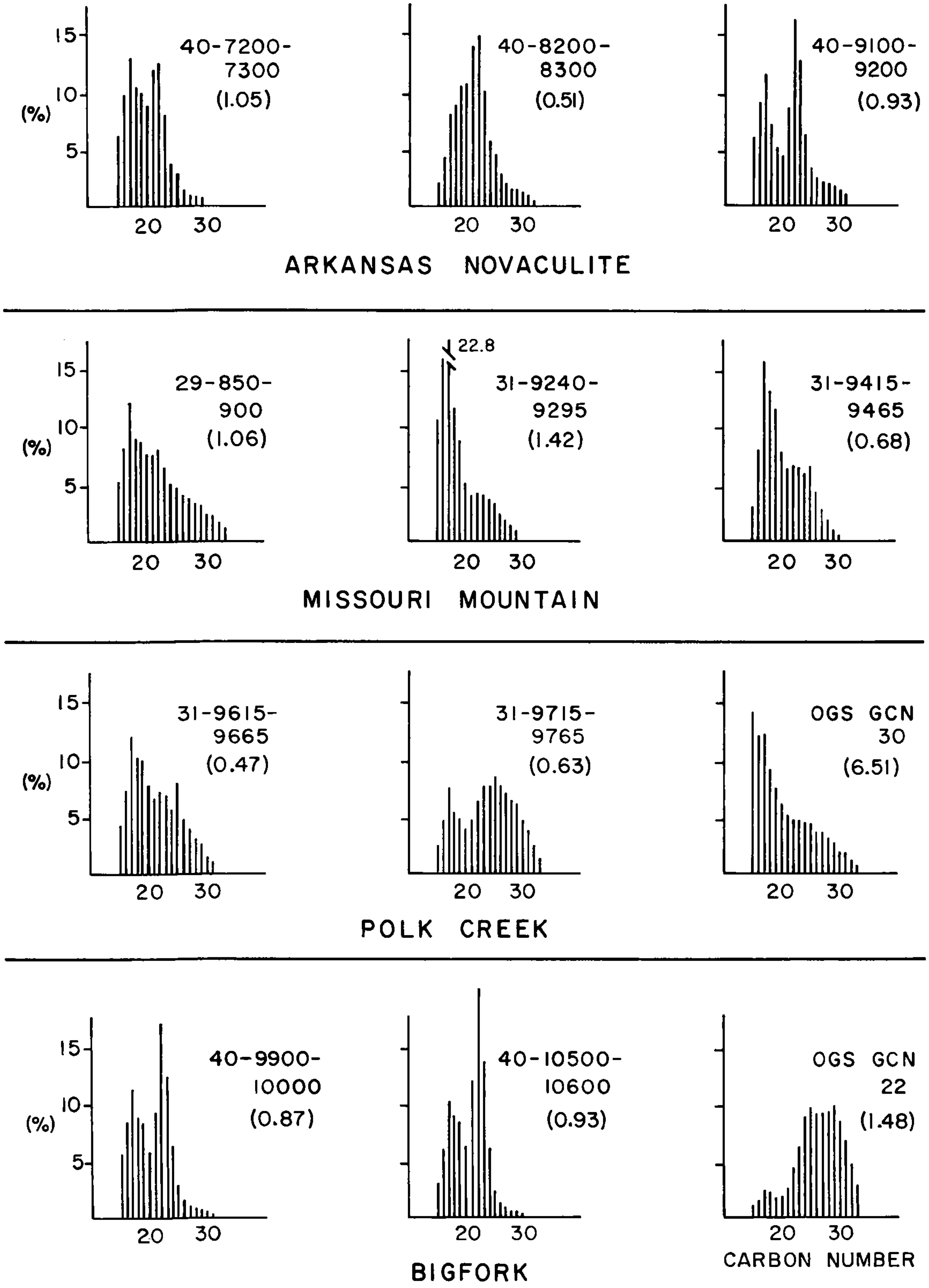

Figure 28. N-alkane distributions in Arkansas Novaculite through Bigfork Chert samples. Total organic carbon values (%) are in parentheses.

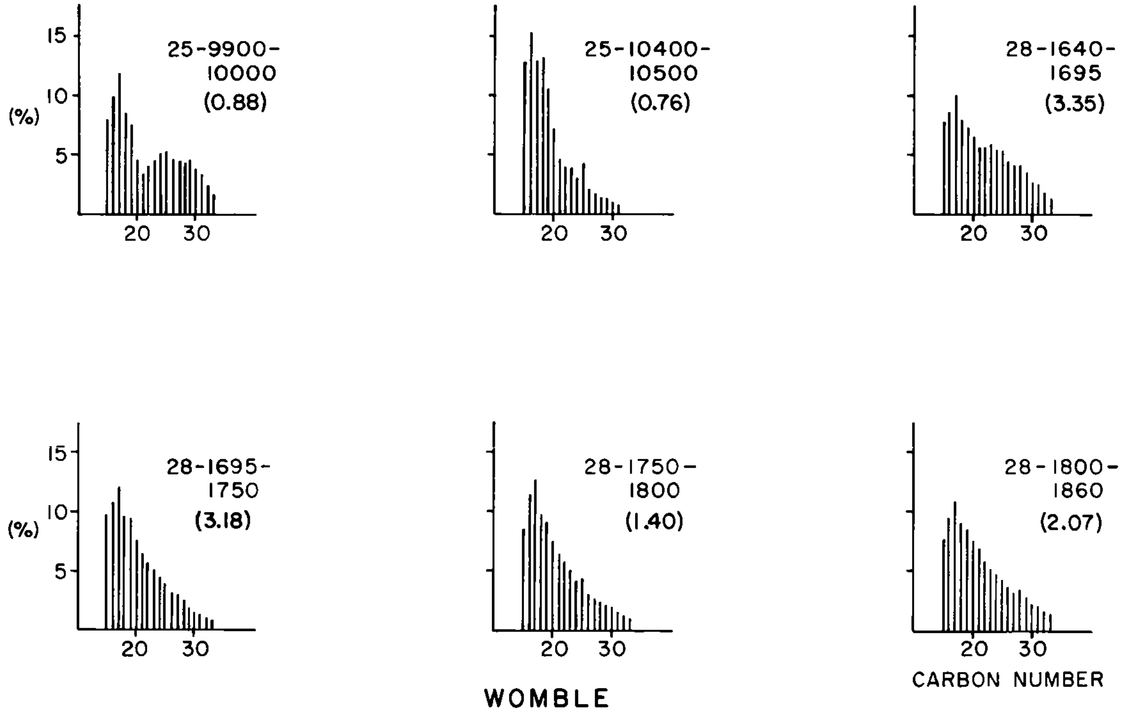

Figure 29. N-alkane distributions in Womble Formation samples. Total organic carbon values (%) are in parentheses.

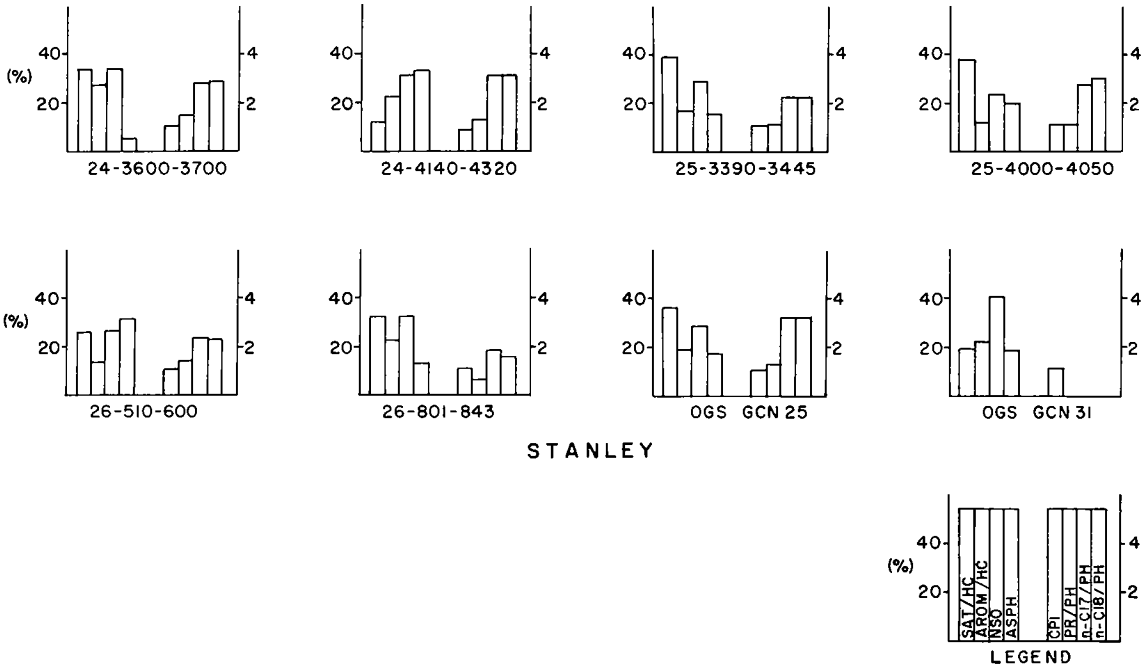

Figure 30. Graphic display of fraction distribution and n-alkane/isoprenoid ratios in Stanley Group samples.

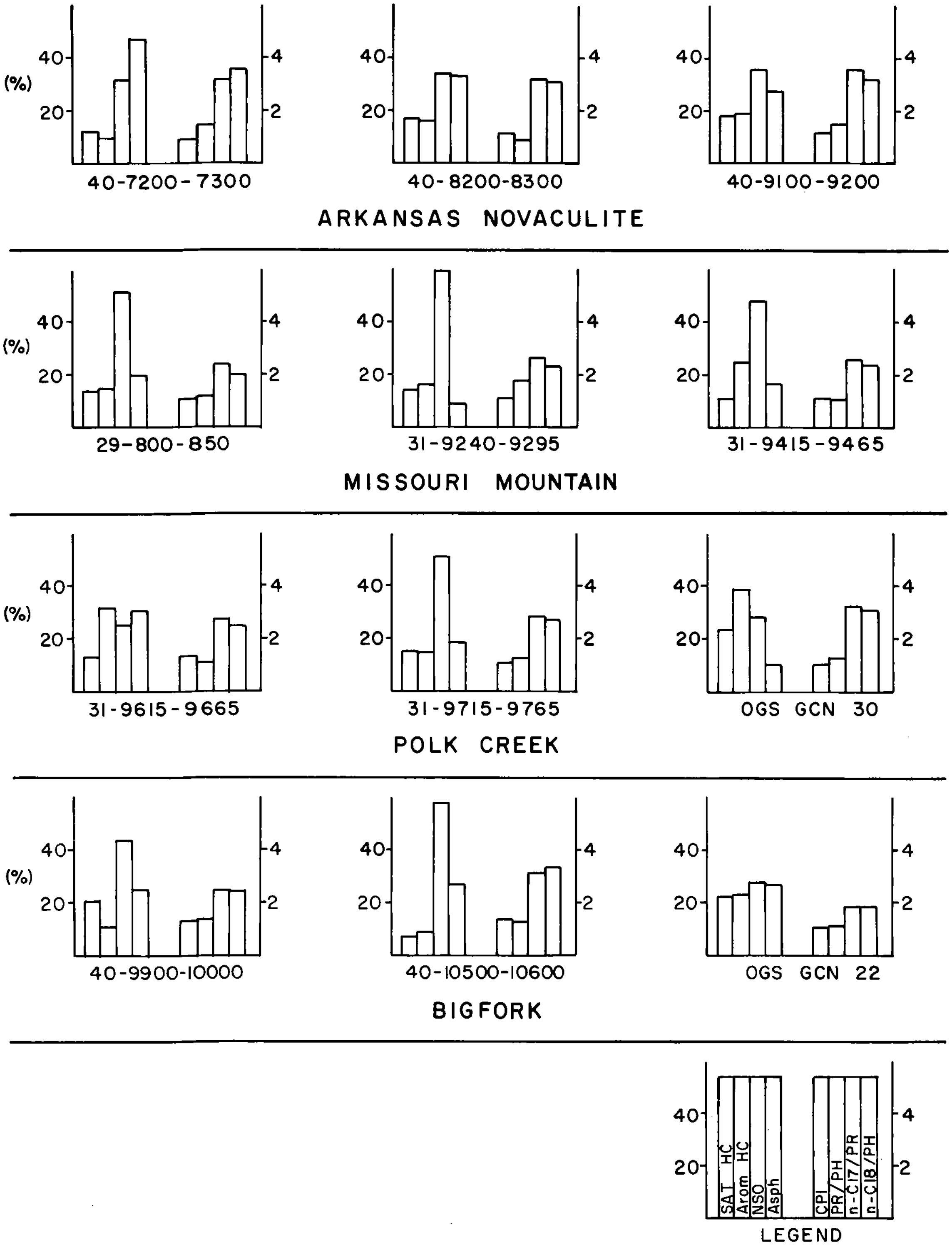

Figure 31. Graphic display of fraction distribution and n-alkane/isoprenoid ratios in Arkansas Novaculite through Bigfork Chert samples.

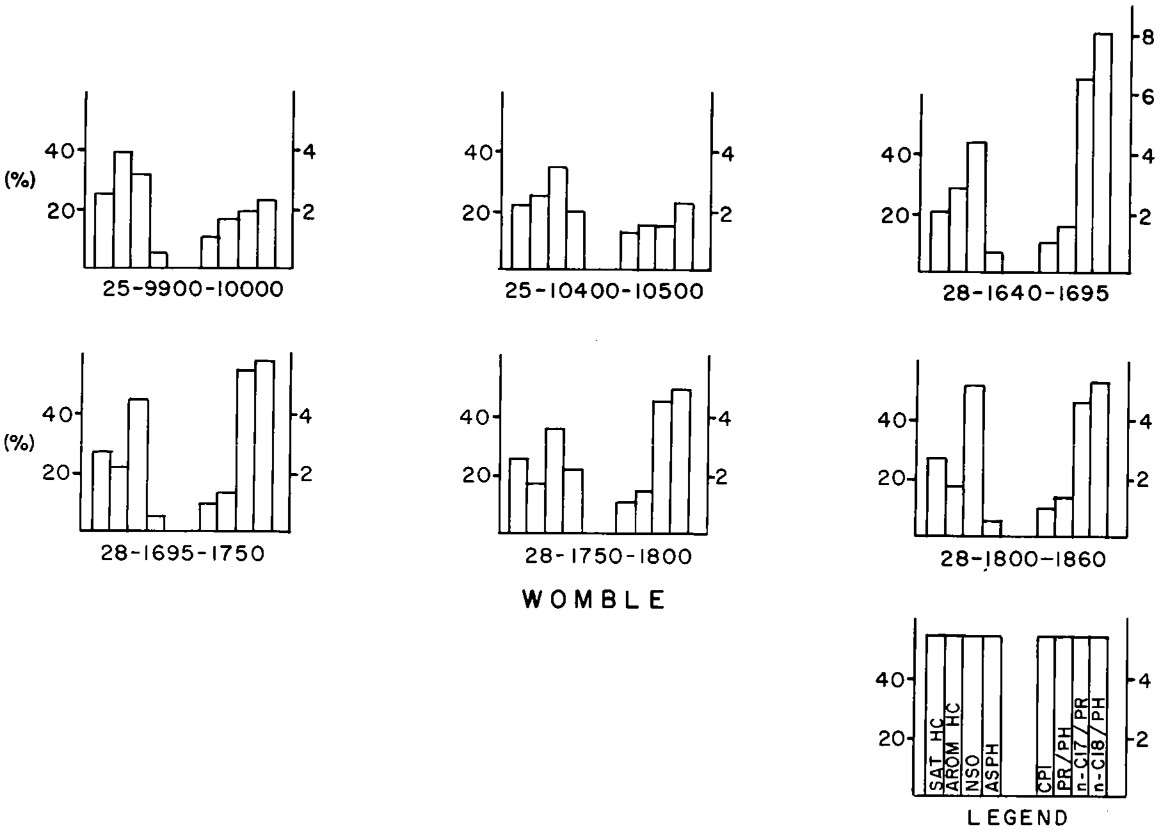

Figure 32. Graphic display of fraction distribution and n-alkane/isoprenoid ratios in Womble Formation samples.

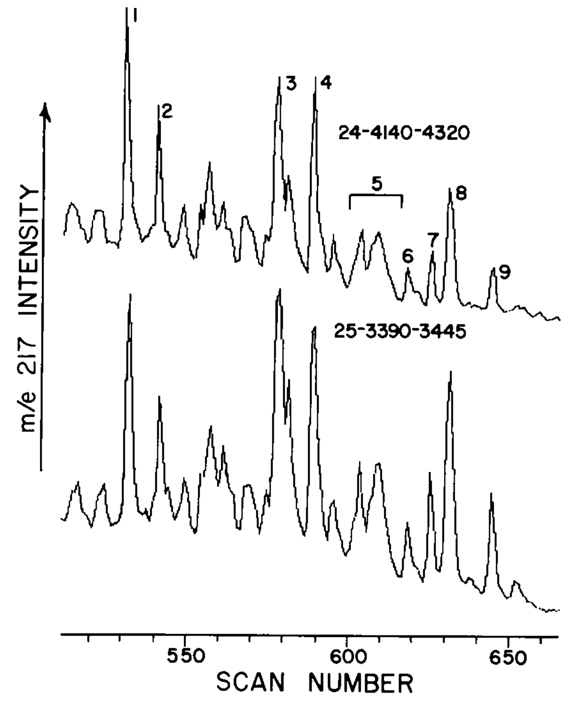

Figure 33. Mass chromatograms of m/e 217 for Stanley Group samples. See table 4 for peak identifications.

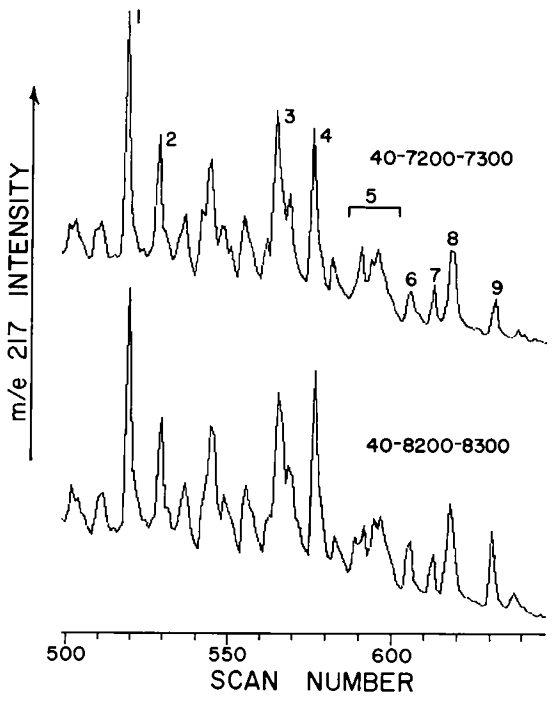

Figure 34. Mass chromatograms of m/e 217 for Arkansas Novaculite samples. See table 4 for peak identifications.

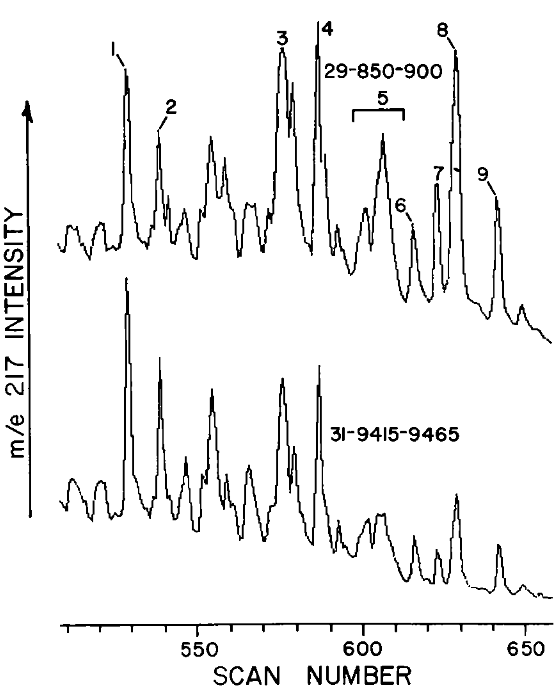

Figure 35. Mass chromatograms of m/e 217 for Missouri Mountain Shale samples. See table 4 for peak identifications.

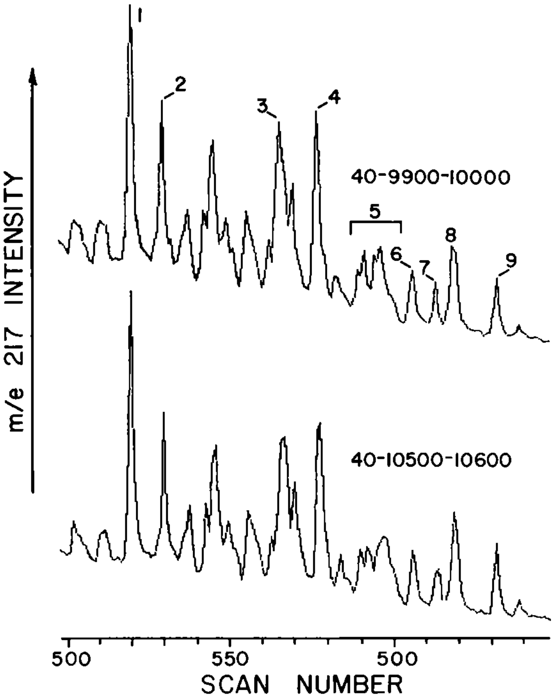

Figure 37. Mass chromatograms of m/e 217 for Bigfork Chert samples. See table 4 for peak identifications.

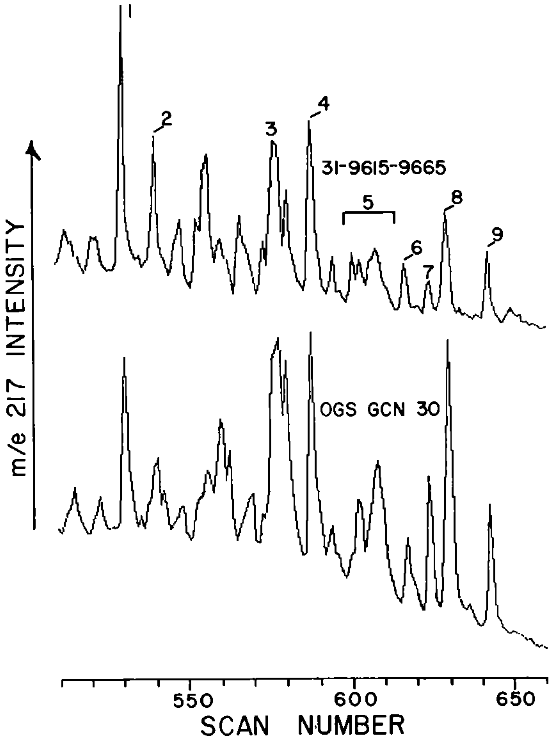

Figure 36. Mass chromatograms of m/e 217 for Polk Creek Shale samples. See table 4 for peak identifications.

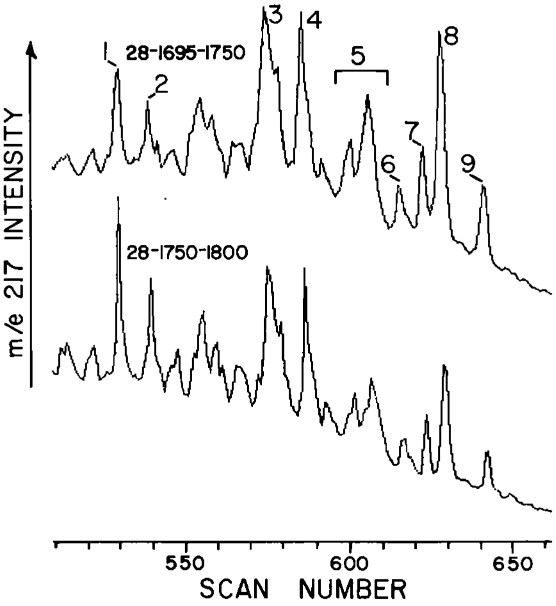

Figure 38. Mass chromatograms of m/e 217 for Womble Formation samples. See table 4 for peak identifications.

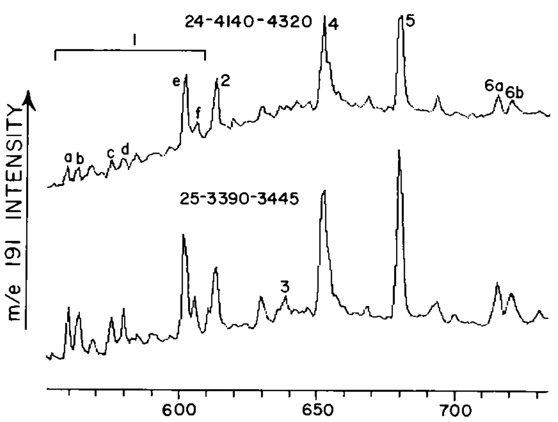

Figure 39. Mass chromatograms of m/e 191 for Stanley Group samples. See table 5 for peak identifications.

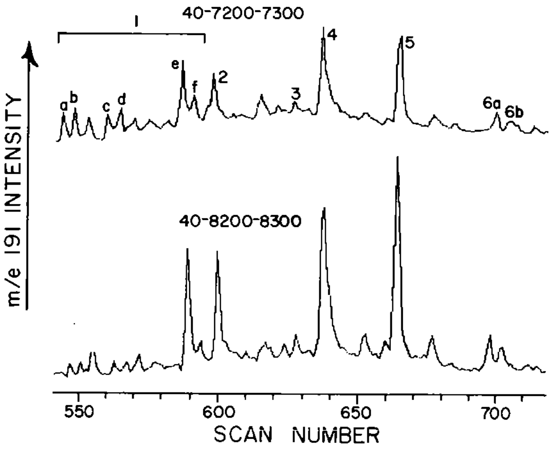

Figure 40. Mass chromatograms of m/e 191 for Arkansas Novaculite samples. See table 5 for peak identifications.

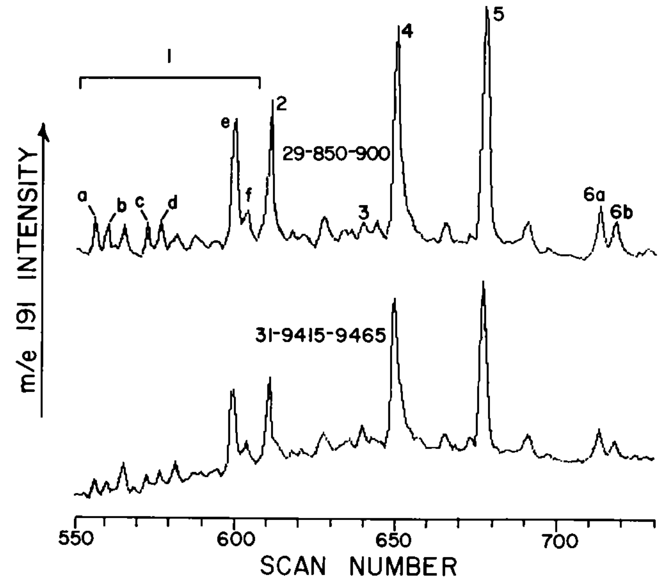

Figure 41. Mass chromatograms of m/e 191 for Missouri Mountain Shale samples. See table 5 for peak identifications.

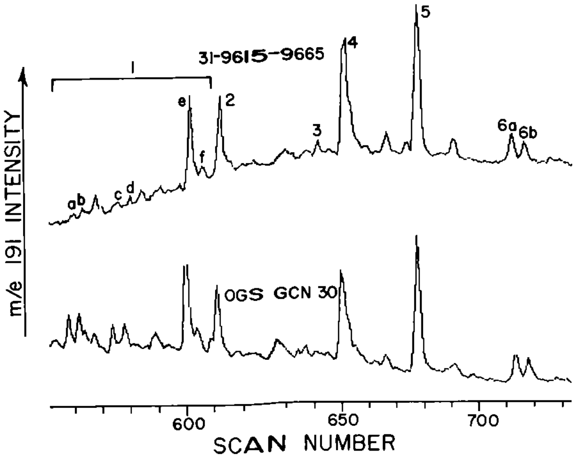

Figure 42. Mass chromatograms of m/e 191 for Polk Creek Shale samples. See table 5 for peak identifications.

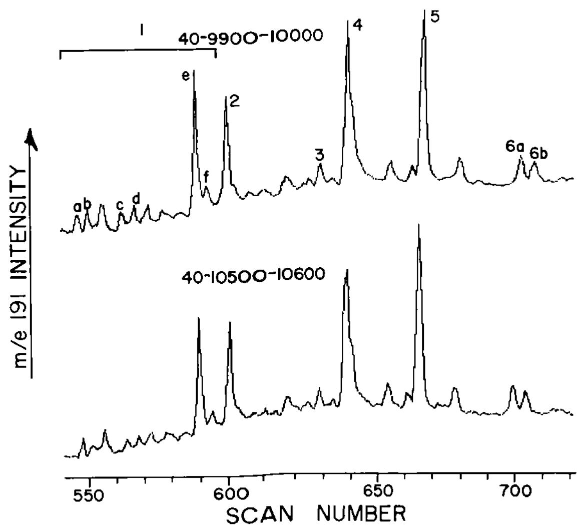

Figure 43. Mass chromatograms of m/e 191 for Bigfork Chert samples. See table 5 for peak identifications.

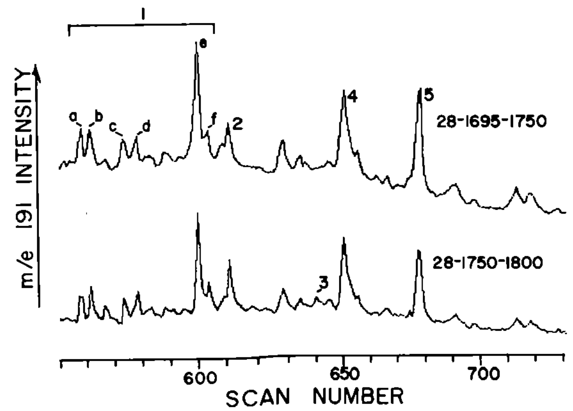

Figure 44. Mass chromatograms of m/e 191 for Womble Formation samples. See table 5 for peak identifications.

that, whereas the content of C_{28} steranes is low in both of these samples, the ratio of C_{29}/C_{27} steranes is higher in sample 25–3390–3445, where it approaches 1. Sample 25–3390–3445 shows relatively abundant "tricyclic terpanes" (peaks 1a–1f), as well as minor 17a(H),18a(H),21b(H)-28,30-bisnorhopane (fig. 39, peak 3). These components appear to be absent in sample 24–4140–4320. In addition, routine scanning of the m/e–177 ion (not shown in fig. 39) revealed unidentified compound B in Stanley sample 25–3390–3445. As discussed earlier, compound B was found to be a component of the crude oils. The presence of this unusual C_{27} triterpane in one of the Stanley samples, and in a quantity comparable to that found in the crude oils, suggests a source-rock–oil relationship between the Stanley Group and the oils of the Ouachitas. However, the completion reports for the well from which sample 25–3390–3445 was obtained imply another explanation. This well, the Max Pray 1 Ben Wyrick (D&A, 1958), encountered several oil-stained zones in the Stanley section. Specifically, dark-brown to black stains were noted in the 3,666–3,786–foot interval, and so-called "dead stains" were noted from 3,991 to 4,021 feet and from 4,031 to 4,056 feet. Further, in the interval closest to the sample in question, a drill-stem test from 3,676 to 3,786 feet recovered gas-cut mud, with a trace of oil. It seems clear, therefore, that the EOM of sample 25–3390–3445 cannot be safely classified as indigenous. The biomarker content of this sample has apparently been contaminated by migrated crude oil.

The sterane and terpane distributions of two Arkansas Novaculite samples are shown in figure 34 and figure 40, respectively. Both the sterane and the terpane distributions are very similar, with the major difference being fewer "tricyclic terpanes" (that is, peaks 1a–1f) in sample 40–8200–8300 (fig. 40). This suggests a similar depositional environment throughout this 1,000 feet of well 40. However, beds in this well are steeply dipping, indicating that much less than 1,000 feet of Arkansas Novaculite section is involved.

The sterane and terpane distributions for two samples of Missouri Mountain Shale, 29–850–900 and 31–9415–9465, were determined (figs. 35 and 41, respectively). Figure 35 indicates that both samples are high in diasteranes (peaks 1 and 2, and most unnumbered peaks between peaks 2 and 3; Seifert and Moldowan, 1979), particularly sample 31–9415–9465. Sample 29–850–900 has higher C_{28} and C_{29} (peaks 5 through 9) regular sterane concentration than does sample 31–9415–9465. This is evident in the histograms in figure 45. Despite these differences in the sterane distributions, figure 41 shows that the hopane distributions are similar for both samples, although tricyclic terpane concentrations differ. Sample 29–850–900 (above) also contains very minor amounts of unidentified compound B.

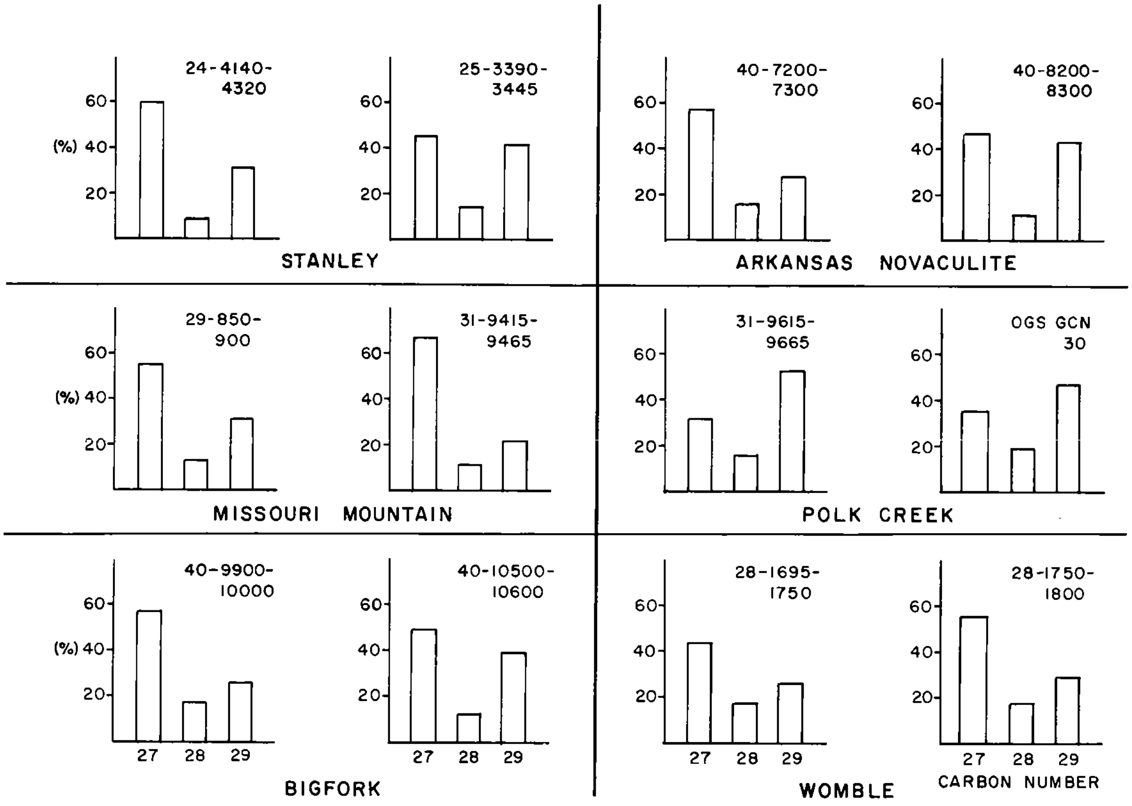

Figure 45. Distribution of steranes by carbon number in rock-EOM fraction. Obtained as described in figure 11.

The distributions of these biomarkers in the Polk Creek Shale, samples 31–9615–9665 and OGS GCN 30, are shown in figures 36 and 42. Figure 36 shows significant differences in the amount of C_{28} and C_{29} steranes present (see also fig. 45); the C_{29} steranes are minimal in sample 31–9615–9665. Figure 42 shows, however, that the hopane distributions in these samples are similar; peaks 1a–1f are in significant concentration in sample OGS GCN 30. Also, the m/e–177–ion chromatogram for sample OGS GCN 30 shows the unidentified peak B in relatively high concentration. This fact, along with the distribution of steranes shown in figure 36 for this sample, suggests a source-rock–oil relationship.

Sterane and terpane distributions in samples 40–990–10000 and 40–10500–10600 of the Bigfork Chert are shown in figures 37 and 43, respectively. Both of these samples are very similar, having sterane distributions that are dominantly marine in character (fig. 45). The hopane contents (fig. 43) also are similar.

Finally, the Womble Formation samples 28–1695–1750 and 28–1750–1800 were examined for steranes (fig. 38) and terpane (fig. 44). Figure 38 indicates that the diasterane and C_{27} and C_{28} regular-sterane distributions in these samples are similar, although significantly higher relative amounts of C_{29} regular steranes are present in 28–1695–1750. The terpane mass chromatograms (fig. 44) also are similar for the two samples, although a larger norhopane/hopane (peaks 4 and 5) ratio is evident for 28–1750–1800, whereas minor amounts of 17a(H),18a(H),21b(H)-28,30-bisnorhopane (peak 3) are present in this sample also. Examination of m/e–177 chromatograms for these samples reveals minor, although observable, quantities of the unidentified peak B, as observed in crude oils and in some samples of the Missouri Mountain and Polk Creek Shales.

Thermal-Maturity Studies of Frontal and Central Ouachita Rocks

Estimates of maturity level were made by a variety of methods: atomic H/C ratios, a palynomorph-color estimate of fixed carbon, reflectance of the kerogen "maceral" vitrinite, and carbon-preference index. Results of these assessments are listed in table 12. In addition, examination of the

TABLE 12.—MATURITY DATA FOR SELECTED ROCK SAMPLES

Sample Number	Stratigraphic Interval	H/C (atomic)	Fixed Carbon (%)	Vitrinite Reflectance (%)	CPI
24-3600-3700	Stanley	b	b	1.03	1.02
-4140-4320		b	56-60	0.86	0.90
40-6600-6700	Arkansas Novaculite	b	54-62	b	b
-7200-7300		b	b	0.96	0.89
-7600-7700		b	c	b	b
-7700-7800		b	b	0.99	b
31-9240-9295	Missouri Mountain	1.21	c	b	1.10
OGS GCN 21[d]		1.25	b	b	b
OGS GCN 30[d]	Polk Creek	1.21	c	b	1.04
OGS GCN 28[d]	Womble	1.02	c	b	b

[a] Estimated from color of spores in sample (see text).

[b] Not determined.

[c] No recognizable spores present in sample.

[d] Outcrop sample.

EOM/TOC and HC/TOC contents (table 11) also yields information concerning the thermal maturity of these samples.

H/C values for the kerogen concentrates (table 12) range from 1.25 to 1.02. Therefore, we can conclude from the atomic H/C ratio that the four samples analyzed are within the oil-generation window, and are thermally mature but not postmature (Tissot and Welte, 1978).

The second maturity parameter employed was an estimate of the fixed-carbon percentage in a kerogen, based on the color of spores in the rock (Gutjahr, 1966). Wilson (1971) showed that the level of fixed carbon (determined by proximate analysis) of coals is manifested in the color of spore and pollen in organic matter of associated noncoaly sediments. The color of these palynomorphs is known to change with increased temperature, as shown by Staplin (1969) and Sengupta and Muir (1977). Thus, one may estimate the fixed-carbon content of a kerogen from the color of its spores and pollen. This palynological technique therefore yields a more precise numerical figure for maturity than does, for example, the thermal alteration index for kerogen color, proposed by Staplin (1969). My two samples of kerogen concentrate containing recognizable spores exhibit fixed-carbon values of 54–62 percent (using standard colors recommended by Wilson, 1971), from trilete spores that are orange to light brown in transmitted light. According to Dow (1977), kerogen with such fixed-carbon levels is approximately in the middle of the oil-generation window.

Data from four samples in the present study yield average vitrinite-reflectance (VR) values of 0.86–1.03 percent. As shown in figures 46 and 47 for Stanley Group and Arkansas Novaculite samples, respectively, the spread in values is large, perhaps reflecting the flysch-type deposition prevalent in the Ouachita Trough in Mississippian and Devonian time. From these data, the samples appear to be in the middle to lower part of the oil window (Dow, 1977).

The samples analyzed for VR values were not from great depths (Stanley average depth: 3,940 feet; Arkansas Novaculite average depth: 7,500 feet). Depths at which R_o values of 1.0 are attained in other basins are generally much greater, ranging from 9,500 to 13,000 feet in various North American basins (Dow, 1977; Hunt, 1979). Hunt (1979, p. 344–345) suggested an average depth of 11,000 feet for the vitrinite reflectance to reach 1.0 percent, given an average geothermal gradient of 1.5°F/100 feet (2.7°C/100 m). Therefore, assuming an average geothermal gradient (as well as an average paleogradient), one can suggest that a minimum of 4,000 to 7,000 feet of overburden has been removed by erosion at the sites of these two wells (T. 2 S., R. 15 E.; T. 1N., R. 14 E.).

The three maturation parameters discussed so far have involved only the kerogen component of sedimentary organic matter. However, if one presupposes that the organic matter in a sample is

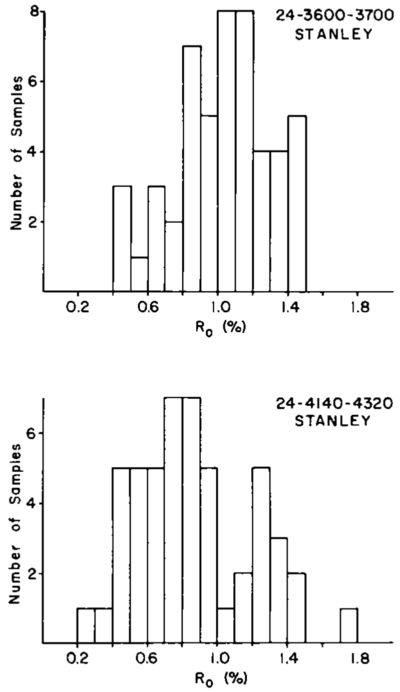

Figure 46. Vitrinite-reflectance histograms for Stanley Group samples. Each histogram represents distribution of 50 random vitrinite particles. All reflectance data were derived by conventional immersion oils.

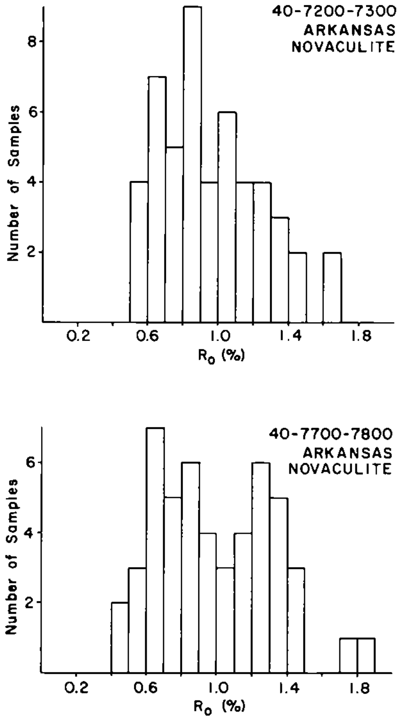

Figure 47. Vitrinite-reflectance histograms for Arkansas Novaculite samples. See figure 46 for further information.

indigenous, then EOM can also be used to evaluate maturation. One parameter of the EOM, the carbon-preference index (CPI) of the n-alkanes, is commonly used in such determinations (Heroux and others, 1979). In general, the CPI must attain values of about 1.13 to 0.92 before a type-I or type-II kerogen can be considered thermally mature (Bray and Evans, 1961). As shown in table 11, most CPI values in the present study are less than 1.13.

The EOM terpane data for each of the samples analyzed by GCMS are also of value as a maturity indicator for the organic matter in these rocks. Seifert and others (1980) noted that the two C_{22} epimers of the homohopanes (peaks 6a and 6b in the terpane figures of this report) occur in an "equilibrium" mixture in fossil-fuel samples of approximately 60/40 (S/R), with the early-eluting epimer being predominant. Conversely, living organisms contain predominantly the second-eluting epimer (R). Therefore, a change with maturation suggests that the ratio of the first- to the second-eluting epimer of the homohopanes will increase from an initial value that is very small to a thermodynamically equilibrated mixture of the two. Thus, mature (as opposed to immature) petroleum source rocks can be expected to contain such an equilibrium mixture (Seifert and others, 1980). The terpane distributions (figs. 39–44) for the Ouachita rocks all have a ratio of about 60/40 for the epimers in question, indicating again that these rocks are thermally mature.

Summary and Conclusions

Formations of Mississippian through Ordovician age in the Oklahoma Ouachita Mountains are clearly potential source rocks, and are mature enough to have generated liquid hydrocarbons. Total organic carbon of most samples exceeds 0.5 percent, and extract yields suggest that the EOM content is high enough for all formations to have source potential. This is particularly true for samples of the Stanley Group and the Womble Formation. Finally, the hydrocarbon content of many samples is high; Philippi's (1957) classification of source-rock hydrocarbon content indicates that the Stanley Group, Polk Creek Shale, and Womble Formation are "good" source rocks. By this classification, the Womble Formation is consistently the best source rock examined.

The type of organic matter in this mid-Paleozoic section indicates that a mixture of marine and nonmarine organic matters is present in the Ouachita facies. This mixture is consistent with the known depositional environment of these rocks (Morris, 1974). In the present study, carbon-isotope ratios of the total organic carbon in the samples fall between ratios expected for marine and nonmarine rocks. Further, the sterane distributions show approximately equal amounts of C_{27}

and C_{29} steranes, indicating marine and nonmarine conditions, respectively.

Thermal-maturation data indicate that all formations and groups are mature enough to have generated oil. The H/C atomic ratios and the coloration of spores of the kerogen indicate that the material is in the middle of the oil window. Vitrinite-reflectance data from these samples are indicative of the middle or bottom half of the oil window (as described by Dow, 1977). These observations are confirmed also by the equilibrium ratio of the homohopane C22 epimers in all potential source samples, which suggests that the samples are mature enough to have generated oil.

In summary, the Womble Formation appears to be the best source rock in the Ouachita facies in Oklahoma, as suggested by several criteria. In addition, the Polk Creek Shale must be considered a source, owing to the high HC/rock ratio noted in one of its samples (table 11). Finally, the Stanley Group shales represent a potential source on the basis of extract yield, although the type of organic matter suggests that this material should be considered a gas source.

CHEMICAL CORRELATION BETWEEN OIL AND SOLID BITUMEN

This study indicates that both differences and similarities exist between oils and solid bitumens in the Ouachitas. Atomic H/C ratios versus atomic O/C ratios for oils and bitumens are plotted in figure 48. These data show that no obvious relationship exists among the solid bitumens; each is clearly depleted in hydrogen and enriched in oxygen, in comparison with the oils. Differences in concentrations of vanadium and nickel also are obvious, as shown in figure 49. However, even though these metals are concentrated in the bitumens, by an average factor of 41, the vanadium/nickel ratios for both oils and bitumens range only from 0.5 to 3.5 in all but one of the samples. Thus, the extreme concentration of metals in an oil-to-bitumen conversion, if such a conversion occurred, did not affect the V/Ni ratio as severely.

The relationship between sulfur- and carbon-isotope ratios for the oils and bitumens is shown in figure 50, for three oils and five bitumens. Unlike the elemental data, the small range of carbon-isotope values for both materials (−30.2 to −28.9 o/oo) indicates a good correlation (Nissenbaum and Goldberg, 1980). A similar conclusion can be drawn from the sulfur-isotope data in figure 50; the oils range from +14.3 to +18.9 o/oo, and the bitumens range from +15.5 to +20.3 o/oo. The range overlap here is +15.5 to +18.9 o/oo, which represents 74 percent and 71 percent, respectively, of the total range for oils and solid bitumens analyzed. This large overlap in the range of sulfur-isotope ratios again indicates a cogenetic relationship between oil and solid bitumen. Because these materials are unusually depleted in light sulfur (Thode and others, 1958), such a correlation is unlikely to be fortuitous.

In addition to correlation of oil and bitumen on the basis of bulk chemical parameters, two types of pyrolysis were used to characterize the grahamites and impsonite (high temperature–short term and low temperature–long term). High-

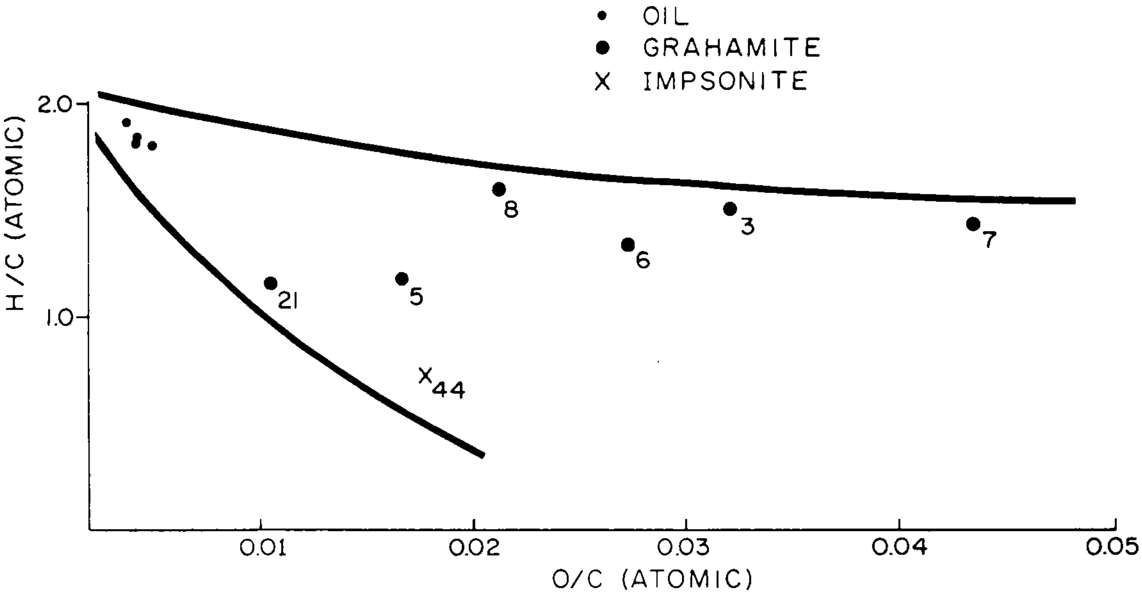

Figure 48. Atomic H/C versus atomic O/C ratios for crude oils and solid bitumens. Lines of enclosure are for display purposes only and have no chemical significance.

temperature pyrolyses of grahamite, impsonite, and gilsonite created alpha-olefins as well as n-alkanes. Figure 19 presents the quasi–n-alkane distributions (that is, the sums of n-paraffins and alpha-olefins) for each of these materials, and figure 9 presents the n-alkane distributions for the four Ouachita oils. As seen from these figures, grahamite samples yield pyrolyzate distributions that are very similar to those of the crude oils. In addition, except for an anomalous peak at C_{20}, the impsonite sample also is very similar to the oils. However, a gilsonite pyrolyzate exhibits a distribution that is significantly different from that of the Ouachita oils, having a maximum at C_{24}. The carbon-preference indices (CPIs) shown in figures 9 and 19 also suggest similarities between pyrolyzates and oils. The CPI range for crude oils (1.01–1.08) is within the CPI range for the grahamites and impsonite (0.96–1.17). The gilsonite, however, has a CPI value that is lower than both of these ranges (0.89). These data suggest that the oils and bitumens can be correlated on the basis of grahamite and impsonite quasi–n-alkane distributions.

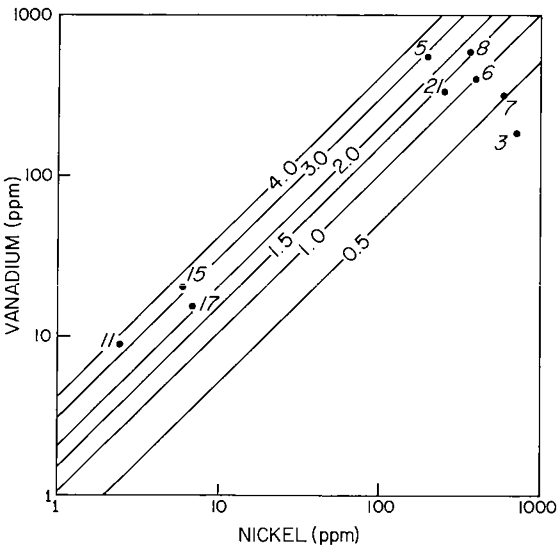

Figure 49. Content of vanadium versus nickel for crude oils and solid bitumens. Diagonal lines represent constant V/Ni ratios. Reproduced by permission of American Association of Petroleum Geologists.

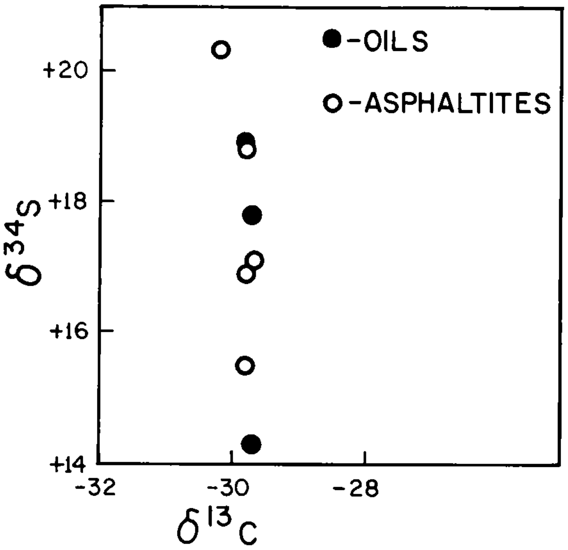

Figure 50. Sulfur-isotope ratios versus carbon-isotope ratios for oils and solid bitumens. Carbon isotopes are relative to PDB standard, and sulfur isotopes are relative to Canon Diablo troilite standard. This plot is not meant to indicate a functional relationship between carbon- and sulfur-isotope ratios.

Low-temperature–closed-tube grahamite and impsonite pyrolyzates also show a positive correlation with the Ouachita oils examined, on the basis of sterane and terpane distributions. Figure 21 shows the sterane (m/e 217) distributions for the four grahamites and one impsonite examined, along with the sterane pattern for oil 11. Similarities and differences are evident. Peak 2 represents 50–75 percent of peak 1 (by height) in both the oil and the pyrolyzates, and other diasterane ratios (for example, those peaks between peaks 2 and 3) are very similar throughout the samples. However, prominent differences in the regular steranes exist between oils and pyrolyzates. For example, peaks 3–9, all consisting at least partially of regular steranes (see table 4), diminish greatly in the following order: oil 11, and pyrolyzates 7, 5, 6, 3, and 44 (the reasons proposed for such a change will be discussed later). Similarities in ratios of regular steranes persist from oil to bitumen. For example, the ratio of peaks 7:8:9 appears constant for all pyrolyzates, and is similar in oil 11, with peak 8 predominating in all cases.

Despite the differences discussed above, the distribution of steranes (both regular and rearranged) by carbon number (fig. 51) suggests that these materials have a common source. In all samples examined, C_{28} steranes make up less than 20 percent of all steranes present. Although the ratio of C_{29}/C_{27} (or approximately the ratio of terrigenous–marine influence) varies somewhat, this ratio for pyrolyzates of samples 6, 3, and 44 is similar to that found in the crude oil. From similarities in the distribution of sterane carbon numbers, and several other similarities discussed earlier, one can conclude that the oils, grahamites, and impsonite are cogenetic.

Similarity is also evident in the terpane distributions of oil 11 and the pyrolyzates (fig. 22). The ratio of peaks 4 and 5 (C_{29} and C_{30} hopanes; see table 5) is approximately 1:1 in both the oil and the

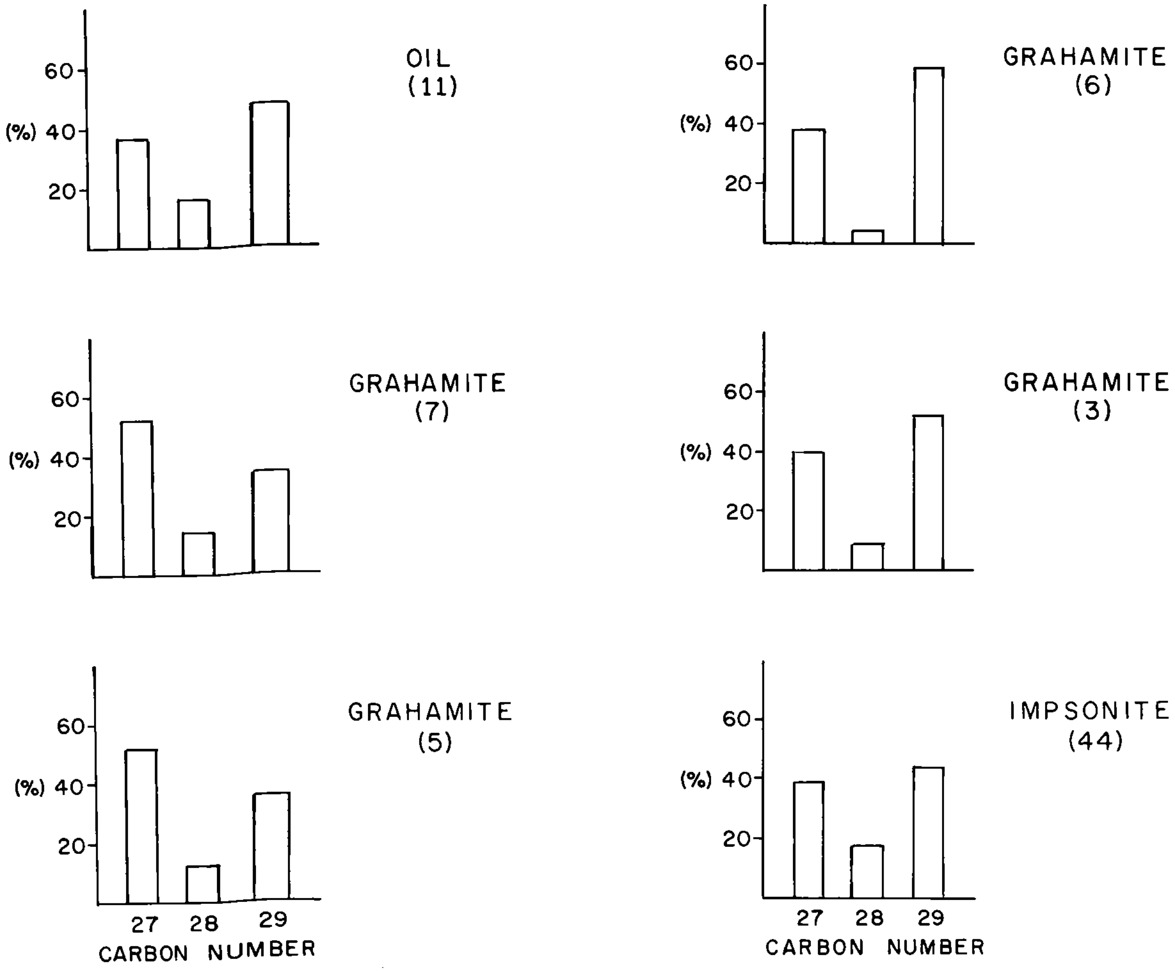

Figure 51. Histograms of steranes by carbon number in oil 11 and solid-bitumen pyrolyzates. Obtained as described in figure 11.

pyrolyzates, and the ratio of peaks 6a and 6b (C_{31} homohopanes) is about 60:40 in all cases. Differences in the distributions of the two materials include the stronger presence of moretanes [17b(H),21a(H)] and the very low concentration of peaks 1a–1f (with the possible exception of peak 1e) in the pyrolyzates. The C_{27} trisnorhopane (peak 2, fig. 22) is more prominent in the pyrolyzates than in the oils. By comparison, the C_{28} bisnorhopane (peak 3, fig. 22) is more prominent in the oil. The anomalously strong presence of peak 1e (probably a coeluting tricyclic terpane and a monoaromatic compound, as discussed earlier) in the pyrolyzates is unexplained, although this same peak is very strong in the terpane patterns of the source rocks examined (see figs. 39–44). The unidentified peak B, eluting just after peak 1e in all of the crude oils, also is present in each of the solid-bitumen pyrolyzates examined, although in small amounts. Its presence, as well as its similar concentration in the C_{29}, C_{30}, and C_{31} hopanes in pyrolyzates and oils, again suggests that the oils, grahamites, and impsonite result either from a common source or from sources having very similar types of organic matter.

ORIGIN OF SOLID BITUMEN

Solid bitumen has been ascribed to two modes of formation that differ widely in the evolutionary scheme of bituminous materials. Some workers (Brooks, 1936) consider solid bitumen to be a primary product, or "protopetroleum," whereas others (Taff, 1909) favor a secondary origin (degraded petroleum). If the Ouachita Mountains solid bitumen is secondary, the question arises as to the mechanism of formation (that is, high-temperature or low-temperature alteration). Detailed discussion of these two origins is presented below, in an attempt to establish a reasonable explanation for grahamite and impsonite of the Ouachitas.

The concept of protopetroleum, involving the first-generation product of a very rich, relatively immature source rock, has existed in the literature in one form or another for more than 45 years (Brooks, 1936). Such a material would consist of high-molecular-weight compounds, rich in heteroatoms, and would have minor but measurable amounts of n-alkanes (Silverman, 1978). This material would therefore represent a source-rock primary product that has not attained the physical and chemical characteristics of conventional crude oil (Welte, 1965; Silverman, 1978). Alteration of such a primary material would ultimately yield a paraffinic crude oil (Barton, 1934). According to Silverman (1964), such a crude oil should be isotopically lighter than its precursor protopetroleum. Thus, the primary material should be recognizable by (1) high heteroatom content (O, N, S, V and Ni), (2) high molecular weight (very viscous or solid, high melting point), (3) isotopic enrichment in heavy carbon relative to its associated petroleum, and (4) minor quantities of n-paraffins.

Data in table 7 suggest that criteria 1 and 2 are satisfied by the Ouachita solid bitumens, indicating that the material has some characteristics of a protopetroleum. Criteria 3 and 4, however, are not satisfied by either the grahamite or the impsonite. Silverman (1964), in a discussion of changes in carbon-isotope ratios with maturation of oil, indicated that thermal maturation of an immature oil (for example, protopetroleum) will yield "lower molecular weight daughter molecules" enriched in ^{12}C. Thus, a protopetroleum associated with a liquid oil would be isotopically heavier than the oil. Comparison of data in tables 2 and 7 shows no significant difference in the carbon-isotope ratios of the oil and solid bitumen, indicating a lack of isotopic fractionation in the creation of oil from solid bitumen.

Criterion 4 also is not satisfied by either grahamite or impsonite. Gas chromatograms of the dichloromethene extracts of two solid bitumens (fig. 15) show a total absence of n-paraffins. Silverman (1978, p. 23–24) noted that depletion in n-paraffins "cannot be misconstrued as an indication of immaturity because, although the total saturate hydrocarbon content of immature petroleum is low, n-paraffins constitute a major portion of the saturate fraction" (emphasis added). Thus, the absence of n-alkanes indicates that the Ouachita solid bitumens are not immature oils, or protopetroleums. Therefore, they are secondary products, resulting from extensive alteration of liquid oil.

Having established the above relationship, the question of high-temperature versus low-temperature crude-oil alteration remains. The similarities in isotopic characteristics of oils and bitumens can be utilized to help resolve this question. Rogers and others (1974), in comparing crude oils with solid reservoir bitumens, attributed increased carbon-isotope ratios of reservoir bitumens to differing degrees of thermal alteration, suggesting that high-temperature alteration of an oil can result in enrichment of ^{13}C in the bitumen by as much as 2 o/oo. Thermal destruction of Ouachita oils should yield a residual material (that is, grahamite or impsonite) that is isotopically heavier. However, as seen from the data in tables 2 and 7, the carbon-isotope ratios (as well as those for sulfur) are very similar, indicating that these solid materials did not result from thermal degradation of crude oil. Therefore, we can conclude that the grahamite and impsonite are products of oil alteration, and the alteration itself was of relatively low temperature. The isotopic data thus suggest that grahamite and impsonite are not the end products of thermally altered petroleum. This conclusion is consistent with the maturity of potential source rocks in the region, as discussed earlier.

At least three independent lines of evidence support the conclusion that these solid bitumens did not result from thermal degradation of crude oil:

1. The presence of recognizable palynomorphs in rocks adjacent to solid bitumens precludes temperatures associated with metamorphic processes. Wilson (1971, p. 127) stated that "palynomorphs disappear in extremely low-grade metamorphism."

2. At several localities throughout the frontal Ouachitas, liquid oil is found within 1 mile of solid-bitumen deposits. In the Redden Field area (see fig. 1), oil deposits are found in conjunction with asphaltic sandstone. It would be highly unlikely that one portion of an oil accumulation could become thermally destroyed to form grahamite, while a nearby reservoir retained liquid oil.

3. Grahamite in one of the mines was reported to change in consistency with depth. Ham (1956, p. 2) noted, "The grahamite worked in the deepest mine reportedly was becoming softer with depth, thus indicating a downward gradation toward liquid asphalt and possibly liquid petroleum itself." Such a change over just a few hundred feet in depth, as well as the coexistence of liquid material and solid grahamite, suggests a lack of significant thermal alteration.

Assuming that the evidence presented thus far precludes (1) a primary origin and (2) a high-temperature genesis for solid bitumen, it is useful to consider data that support low-temperature processes. Two possibilities are considered here, namely, deasphalting and near-surface alteration (including biodegradation, water washing, and inorganic oxidation by dissolved molecular oxygen).

The deasphalting process has been discussed by several workers (for example, Rogers and others, 1974). They attribute natural deasphalting to the differences in solubility of crude-oil compounds in low-molecular-weight hydrocarbons. Specifically, passage of natural gas through an oil reservoir will lower the average molecular weight of the oil and selectively precipitate those compounds that are relatively insoluble in the lower-molecular weight oil (McKay and others, 1978, p. 141). This effectively concentrates asphaltenelike materials in the residue, which, presumably, would be chemically similar to the grahamites and impsonite described from the Ouachita Mountain region of Oklahoma.

Geologic considerations appear to minimize the possibility of significant deasphalting in the Ouachita Mountain area. The following relations were considered: (1) deasphalting is most efficient in conventional reservoirs; however, the grahamite and impsonite in the Ouachitas commonly occur in large veins and show no evidence of continual precipitation (that is, no layering is evident in the veins); (2) the phenomenon of grahamite becoming less viscous with depth (Ham, 1956) is inconsistent with a deasphalting origin; one would expect the deasphalting process to precipitate asphaltenes upward from the bottom, because natural gas is presumably migrating upward from depth; (3) calculations indicate that large quantities of natural gas must be present for deasphalting to occur. If we assume that the 90,000 tons of solid bitumen recovered thus far in the Ouachitas (Fay, 1976) represents all the resin and asphaltene material precipitated from a crude oil by deasphalting, and that the oil originally contained 18.5 percent resins and asphaltenes (a worldwide average, from Tissot and Welte, 1978, p. 339), we can calculate the volume of methane required to precipitate the resins and asphaltenes from the oil, at standard temperature and pressure (25°C, 1 atm). Assuming a methane:oil stripping ratio of 50:1, found commonly in laboratory deasphalting procedures (Rubinstein and others, 1979), calculations suggest that more than 1 trillion cubic feet of gas is necessary. Although recent reworking of oil wells has resulted in the production of gas in the frontal and central Ouachitas, the areal extent of this gas is unknown. However, natural gas may have migrated from the thermally metamorphosed core of the Ouachitas (fig. 1) and could have contributed to natural deasphalting. Although gas could have escaped at the surface in the past, such huge quantities of flowing natural gas cannot presently be documented.

These observations support an origin for grahamite and impsonite that is attributable to near-surface alteration of crude oil. The chemical effects of near-surface alteration of crude oil, from the influx of meteoric water, have been studied in field and laboratory settings, and have been reviewed by Bailey and others (1973a, 1973b), Price (1980), and Curiale (1980). These investigations show that such alteration results from a combination of effects, including biodegradation, water washing, and devolatilization (that is, evaporation) of the initial material. In the following discussion, the chemical characteristics of the grahamites and impsonite will be examined, and an attempt will be made to show that biodegradation and devolatilization are the predominant causes for alteration of liquid oil to form solid bitumens in the Ouachita Mountains.

Several studies discussed the loss of n-alkanes and isoprenoids resulting from severe biodegradation of crude oil (Bailey and others, 1973a; Deroo and others, 1974). Laboratory simulations have documented the gradual loss of these components from oils subjected to metabolism by microbes (Jobson and others, 1972). The depletion of straight-chain alkanes is currently interpreted as resulting from severe biodegradation (Sassen, 1980). On this basis, the solid bitumens in the present study appear to represent severely biodegraded crude oil, as shown by the virtual lack of these alkanes in dichloromethane extracts of grahamite (fig. 15).

Bailey and others (1973a) showed that the asphaltene fraction of oils apparently is not metabolized during biodegradation, allowing one to recognize a biodegraded oil by its higher (relative) asphaltene content. In addition, biodegradation appears to result in the incorporation of nonasphaltenes into the asphaltene fraction, bringing about a further (absolute) increase in asphaltene content. For the four solid bitumens fractionated in the present study, the asphaltene concentrations are very high. If one classifies the dichloromethane-insoluble organic material of the solid bitumens as asphaltenes, and includes the asphaltene portion of the extract (tables 6, 7), the solid bitumens contain a total of 92.1 to 98.9 percent asphaltene. In view of the work by Bailey and others (1973a), these numbers support a biodegradation origin.

The elemental content of the grahamite and impsonite is also consistent with biodegradation. Rubinstein and others (1977) showed that simulated biodegradation of Prudhoe Bay and Bellshill Lake crude oils altered the H/C, O/C, N/C, and S/C atomic ratios significantly. Each of these oils was incubated for 168 hours with a mixed culture of bacteria, and each showed a decrease in the atomic H/C ratio (fig. 52), and an increase in the atomic O/C, N/C, and S/C ratios, following biodegradation. The same changes are noted in the present study, between oils and bitumens (tables 2, 7). Furthermore, a plot of H/C versus O/C atomic ratios for the oils used by Rubinstein and others (1977) shows a trend very similar to that

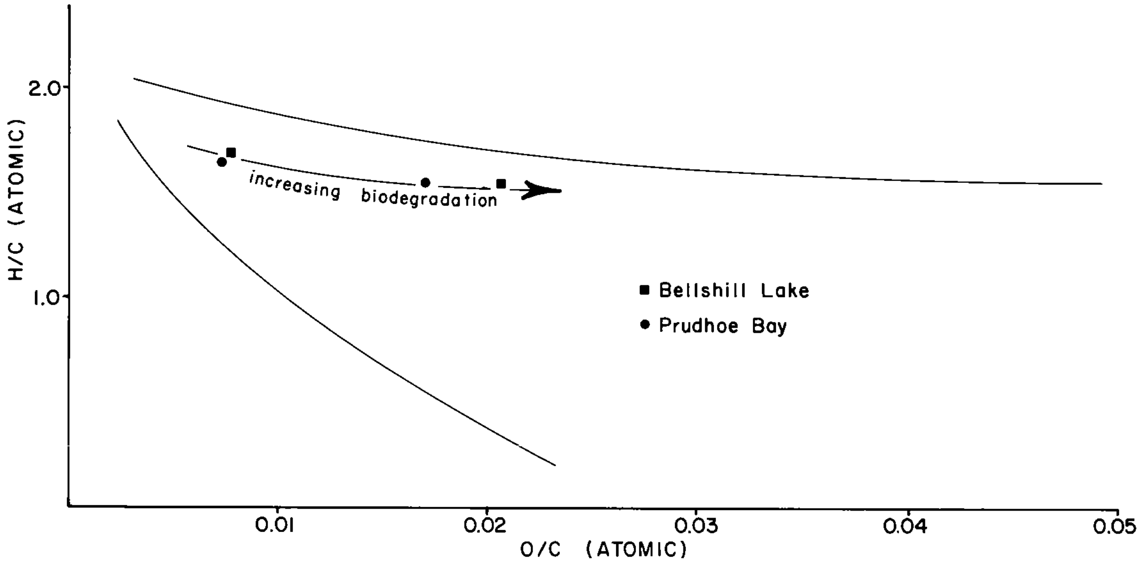

Figure 52. Atomic H/C versus atomic O/C ratios, showing crude-oil biodegradation path. Data from Rubinstein and others (1977). Low O/C values are for unaltered oil. Compare with figure 48.

observed for oils and bitumens of the Ouachitas. This is seen by comparing figures 48 and 52. It is apparent, however, that biodegradation of the Ouachita materials proceeded far beyond the 168-hour limit used by Rubinstein and others. These workers simulated naturally occurring asphaltic material through a series of biodegradation experiments. However, similar results were suggested by Amit and Bein (1979) in their study of real asphalts from the Dead Sea area. They reported atomic H/C ratios as low as 1.33 for Dead Sea asphalts, much lower than has been reported for any liquid crude oil.

The sulfur content of these solids also implies a biodegradation origin. Several workers (for example, Orr, 1978) have shown that sulfur is generally concentrated in the high-boiling fraction of oils, that is, in the asphaltenes. Therefore, because biodegradation effectively concentrates this fraction, the sulfur content is increased in a biodegraded oil. This relationship is observed in the oils, grahamites, and impsonite of the study area. Sulfur-isotope ratios, however, do not change significantly during biodegradation (Orr, 1978). This is observed in the present study as well: sulfur isotopes of the solid bitumen overlap those of the oils by 70 percent or more.

In view of the vertical carbon-isotope type curves derived for three of the Ouachita oils (fig. 6), additional isotopic support may exist for a biodegradation origin of the grahamites and impsonite. Microbial utilization (as well as water washing and devolatilization) of crude oil depletes particular types of compounds in an oil, namely, the n-alkanes, branched-chain alkanes, and some aromatic and naphthenic structures, among others. Thus, the carbon-isotope ratios of whole oil will be altered only if the metabolized compounds are isotopically different from the nonmetabolized compounds. However, as shown in table 3 and figure 6, the carbon-isotope ratios of various fractions of three of the Ouachita oils do not differ by more than 1.0 o/oo. For example, removal of all hydrocarbons from oil 11 would result in a residue with a carbon-isotope ratio very similar to that of the original whole oil. Comparison of carbon-isotope data for oils (table 2) and solid bitumens (table 7), therefore, indicates that the isotopic evidence is consistent with a biodegradation origin, that is, removal of alkanes and other substances. This interpretation is consistent with data reported by Orr (1978), who noted little difference in carbon-isotope ratios of biodegraded oils from the Midway Sunset Field (California).

Results of the vanadium and nickel determinations also are useful as indicators of biodegradation. Vanadium appears to be slightly concentrated in the nonasphaltene materials of the Ouachita oils examined. Thus, biodegradation and devolatilization, which concentrate the asphaltenes, should result in lower V/Ni ratios. This has apparently occurred, as shown in tables 2 and 7. The average V/Ni ratio for the three oils examined is 3.02 (standard deviation = 0.77), whereas that for the six grahamites is 1.22 (standard deviation = 0.87). Thus, the recording of decreasing V/Ni ratios may represent a novel way of monitoring the course of biodegradation and devolatilization of a crude oil.

Analysis of both high- and low-temperature pyrolyzates of grahamites and impsonite provide further evidence for the biodegradation of these materials. Results of high-temperature pyrolysis of grahamite and impsonite have been presented earlier. Quasi–n-alkane distributions are shown in figure 19. Comparison with the n-alkane distributions of the Ouachita oils (fig. 9) suggests many similarities, as discussed earlier. Although these experiments were conducted at high temperatures (570°C), pyrolysis products were removed drom the heat source immediately upon formation (Curiale, 1981). Therefore, the results may be compared to those reported by Rubinstein and others (1979) for low-temperature (300°C) closed-tube pyrolyzates of asphaltenes isolated from a biodegraded oil. These authors reported that the pentane-soluble fraction of the pyrolyzate bore "a striking resemblance to a typical unbiodegraded conventional crude oil, with a full complement of n-alkanes." Similar results in the present study imply that biodegradation produced the Ouachita material.

Recent work has shown that the distribution of terpanes and particularly steranes appears to be significantly altered in cases of severe biodegradation (Reed, 1977; Seifert and Moldowan, 1979). Seifert and Moldowan (1979) studied specific effects of biodegradation on the sterane and hopane content of crude oils. They found a progressive decrease in the ratio of regular to rearranged steranes, with regular steranes absent in heavily biodegraded oil. In addition, several changes were observed in sterane stereochemistry. They also found that excessive biodegradation alters the terpane distribution as well: although tricyclic terpanes appear to be preserved, regular hopanes apparently undergo ring-A/B demethylation, resulting in a hopane series in which m/e 177 is the base peak in the mass spectra.

Other studies suggest that internal alteration of the sterane distribution in biodegraded oils is minor or absent (Rubinstein and others, 1977; Wehner and Teschner, 1981). However, in the work of Rubinstein and others (1977), the oils in question were artificially biodegraded, for only 168 hours. It appears that either the biodegradation did not proceed far enough to alter the steranes, or the mixed culture used did not permit the alteration to occur.

Oils used in each of the preceding studies were conventional oils. The Ouachita bitumens, however, are solids containing predominantly asphaltene compounds. Consequently, low-temperature pyrolysis (Curiale, 1981) of these materials was necessary to liberate sufficient quantities of steranes and hopanes for GCMS analysis. Figure 21 shows the m/e–217–ion chromatograms for oil 11, four grahamite pyrolyzates, and an impsonite pyrolyzate. These suggest a progressive depletion of regular steranes (shaded), in the following order: oil 11, grahamites 7, 5, 6, and 3, and impsonite 44. However, recognizable regular steranes are present even in sample 44. In light of the studies discussed above, my results strongly suggest that the solid bitumens are biodegraded remnants of crude oil, yet the survival of regular steranes suggests limited biodegradation.

The m/e–191–ion chromatograms, which show the hopane distributions for these same samples, are shown in figure 22. The regular hopanes [17a(H),21b(H)] are present in both the oils and the pyrolyzates, although the "tricyclic terpanes" concentrations in the pyrolyzates are diminished greatly. Also, the relative sizes of peaks 1e and 2 are greatly increased in relation to the C_{29}, C_{30}, and C_{31} hopanes (peaks 4, 5, 6a, 6b), which in turn survive longer than the "tricyclic terpanes" 1a–1d and 1f. However, Reed (1977) and Seifert and Moldowan (1979) reported that tricyclic terpanes generally survive biodegradation. Therefore, until further data become available, a full interpretation of the terpane distribution will not be possible.

In summary, there appears to be considerable evidence for biodegradation as one of the dominant processes in the formation of the Ouachita solid bitumens. However, biodegradation was probably not the sole mechanism, because these substances are now solids. Crude oils are known which, in terms of sterane distributions, are biodegraded to a greater extent than these bitumen pyrolyzates and yet still remain liquids, even though viscous liquids (Reed, 1977). The proximity of these deposits to the Earth's surface suggests that water washing and devolatilization may have occurred simultaneously, until the bitumens became impermeable to meteoric water. At that point, biodegradation and the other actions of water washing would cease, while devolatilization would slowly continue (over a maximum time of 300 million years) until the material became solid. The implications of such a development are significant with respect to petroleum exploration in the Ouachitas. Solid bitumens in the Ouachita Mountains could currently be serving as a reservoir seal for liquid hydrocarbons below.

The "mature" nature of the terpane and n-alkane distributions in the solid-bitumen pyrolyzates indicates that the oils were mature before the solid material formed. This, however, does not preclude a continuation of the maturation process *after* the solids formed, perhaps analogous to the conversion of bituminous coal to anthracite by continued coalification. This appears to be the explanation for low H/C and high fixed-carbon values for sample 44, the impsonite from near the Oklahoma–Arkansas state line (see fig. 1). Perhaps initially produced grahamite was thermally altered here to an impsonite. This conclusion would be consistent with that of Jacob (1975, 1976) for the origin of impsonite. It is also consistent with the high fixed-carbon values for coals in the Arkansas Ouachitas (Hendricks, 1935).

CHEMICAL CORRELATION BETWEEN OILS AND ROCK EXTRACTS

Correlation between rock extracts and oils on the basis of molecular distributions of aliphatic hydrocarbons is the most common rock–oil correlation technique in use today. Such methods include correlation of n-alkane distributions (Williams, 1974), isoprenoid ratios (Welte and others, 1975b; Alexander and others, 1981) and sterane–hopane distributions (Seifert and others, 1980). Each of these parameters will be discussed in this section, for the oils and potential source rocks of the Ouachitas.

N-alkane distributions for oils and source-rock extracts are presented in figure 9 and figures 27–29, respectively. The distributions for oils show a smooth envelope, with decreasing n-alkane content as carbon number increases; exceptions include minor highs at n-heptadecane and n-nonadecane. The n-alkane distributions for the rock extracts show four samples with distributions similar to those of the oils. The samples are OGS GCN 30 (Polk Creek Shale), and the three deepest samples from well 28, all Womble Formation samples. Of these four, the Womble Formation samples from well 28 (fig. 29) correlate best with the crude oils. On the basis of n-alkane distributions, therefore, the oils examined in this study appear to be derived from Silurian–Ordovician rocks. Average pristane/phytane ratios for Stanley, Arkansas Novaculite, Missouri Mountain, Polk Creek, Bigfork, and Womble samples are, respectively, 1.17 (standard deviation = 0.27), 1.25 (s.d. = 0.32), 1.34 (s.d. = 0.37), 1.10 (s.d. = 0.11), 1.22 (s.d. = 0.10), and 1.49 (s.d. = 0.13). The four Ouachita oils examined average 1.42 (s.d. = 0.04). On this basis, the Womble Formation appears to be the most probable source rock for the oils studied. Specifically, extracts of the three deepest Womble Formation samples from well 28 have pristane/phytane ratios averaging 1.38 (s.d. = 0.05). However, the n-heptadecane/pristane and n-octadecane/phytane ratios are much higher for the Womble Formation than for the oils. If the Womble Formation is the only source of these oils, the n-alkanes appear to have been depleted during or after migration.

In addition to the n-alkane distributions and the isoprenoid ratios, the sterane–hopane distributions in the rock extracts also suggest a Silurian–Ordovician source. Comparison of mass chromatograms of Ouachita oils (fig. 10) with those obtained from Stanley, Missouri Mountain, Polk Creek, and Womble samples (figs. 33, 35, 36, and 38, respectively) shows fairly good agreement. The significance of the Stanley sample is questionable, however, because nonindigenous organic matter may be in this sample, as discussed earlier. The mass chromatograms in figures 10, 35, 36, and 38 are shown together in figure 53. The strong similarity in sterane distributions among all three rock extracts is striking. Therefore, this particular distribution cannot be used to reduce the potential source samples to fewer than the three

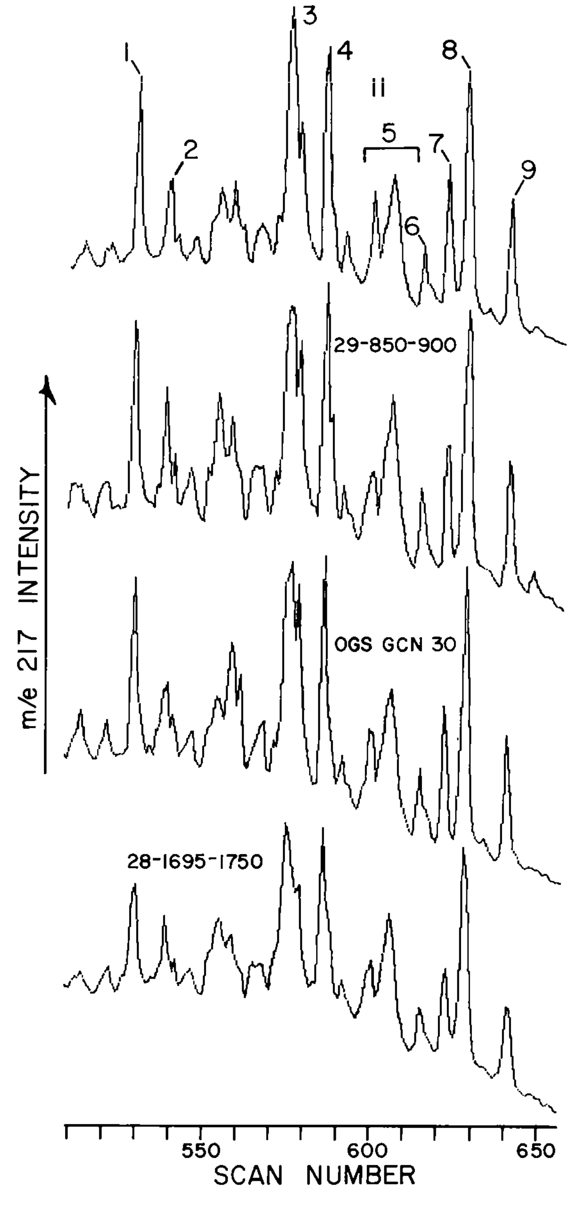

Figure 53. Mass chromatograms of m/e 217 for oil 11 and probable source rocks. See table 4 for peak identifications.

shown. Nevertheless, it should be noted that the best match to oil 11 in figure 53 is sample OGS GCN 30, a Polk Creek sample.

Each extract was also analyzed to determine the distribution of steranes by carbon number. Results of these analyses are shown in figure 45; the sterane carbon-number distributions for the oils are shown in figure 11. These figures show that, of the three samples exhibiting good sterane matches in figure 53, only OGS GCN 30 (Polk Creek) has a sterane carbon-number distribution similar to that of the crude oils. The other Polk Creek sample in figure 45 is also very similar. On this basis, the Polk Creek Shale appears to be a probable source for the Ouachita oils.

Figure 54, comparing terpane distributions for oil 11 and the three rock extracts discussed above, indicates that none of the extracts match well with the oils. Sample 29–850–900, the Missouri Mountain sample, can be assigned low priority as a source on the basis of terpane correlations, because it contains a compound eluting between peaks 1b and 1c that is only minor in the crude oil. All three extracts under discussion contain some amount of unidentified peak B (see fig. 13, and earlier discussions), found in the crude oils. This compound is much more concentrated in the Polk Creek extract than in the Missouri Mountain or Womble extracts. The m/e–177 chromatograms for oil 11 and OGS GCN 30 (fig. 55) indicate a high degree of similarity. Although the m/e–191 terpane chromatogram suggests some dissimilarities, the m/e–177 chromatogram indicates that the Polk Creek Shale is still a likely source, as was concluded also from the sterane data.

One of the unusual features of the terpane distributions shown in figure 54 (an in other m/e–191 mass chromatograms, for example, figs. 39–44) is the prominence of peaks 1e and 2 in relation to the C_{29} and C_{30} hopanes, peaks 4 and 5. Such a prominence is not seen in any of the crude oils, although it is obvious in the terpane distributions of the solid-bitumen closed-tube pyrolyzates (fig. 22). For example, with the single exception of the terpanes 1a–1d, the pyrolyzate of sample 7 (fig. 22) is almost identical with that of 29–850–900 (fig. 54). Similarly, the pyrolyzate of sample 3 (fig. 22) is almost identical with that of OGS GCN 30 (fig. 54). Some of these correlations are striking, although their meaning is not clear.

Sources of Ouachita Oils

The distribution of n-alkanes, isoprenoids, and steranes—hopanes indicates that the oils in the frontal and central Ouachitas could have originated in Silurian–Ordovician rocks of the Ouachita facies. Other data in this study support this conclusion as well. In particular, the sulfur-isotope ratios for crude oils and asphaltites of the Ouachitas appear to corroborate a Silurian–Ordovician source. These ratios range from +14.3 to +20.3 (tables 2, 7), which is relatively high for petroleum (Coleman, 1977). Thode and Monster (1964), and others, have suggested that sulfur in sedimentary organic matter (including petroleum) is significantly heavier than sulfur in contemporaneous evaporites; Orr (1978) suggested a

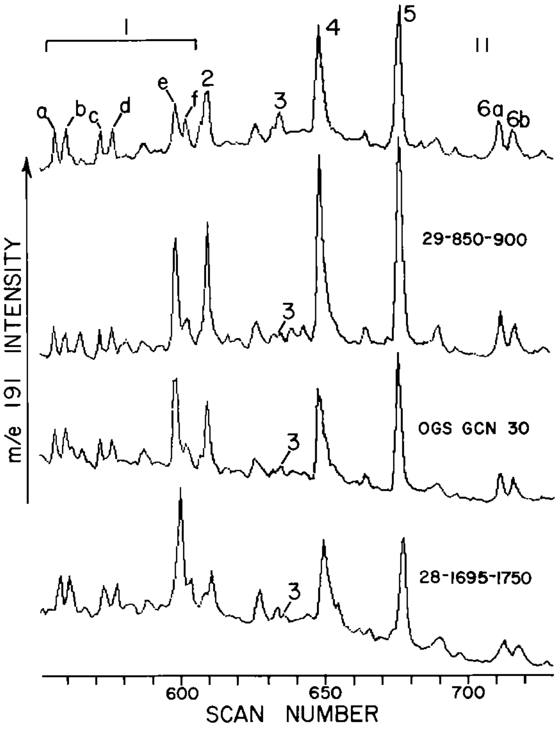

Figure 54. Mass chromatograms of m/e 191 for oil 11 and probable source rocks. See table 5 for peak identifications.

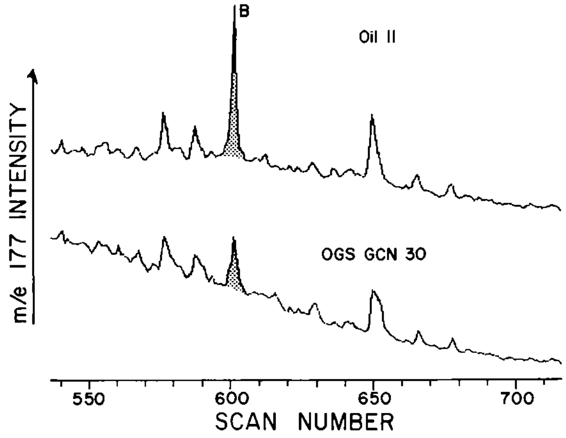

Figure 55. Mass chromatograms of m/e 177 for oil 11 and OGS GCN 30 (Polk Creek). Unidentified peak B is shaded.

difference of 15 ± 5 o/oo. In addition, other workers (for example, Claypool and others, 1980) have shown that the sulfur-isotope ratio of seawater sulfate varied through geologic time, and reached a maximum average value, in Ordovician and Cambrian time, of +26 to +31 o/oo. Therefore, one might expect the sulfur of an Ordovician oil to be unusually heavy. For example, a 15 o/oo fractionation for sedimentary organic matter would yield an oil with a sulfur-isotope ratio of +11 to +16 o/oo, which is approximately the range for the oils of the present study. However, the curves derived for changes in isotopic composition of seawater sulfate presuppose open-marine conditions (Orr, personal communication, 1980). Such conditions have not been fully documented for Polk Creek or Womble strata. Nevertheless, the "heavy" sulfur ratios for the oils of this study do appear to corroborate a Silurian–Ordovician source.

Additional corroborating evidence for such a conclusion is the stable-carbon–isotope ratios for the Ouachita oils. Although the "light" average ratio encountered (approximately −30 o/oo) suggests a nonmarine origin, such ratios are also common in oils from lower Paleozoic rocks. Silverman (*in* Welte, 1965, p. 2250) cited a study by Eckelmann and others (1962) in which almost all the oils identified as nonmarine, based on "light" carbon-isotope ratios, are produced from lower Paleozoic reservoirs. Clearly, oils from the lower Paleozoic cannot be correctly classified as nonmarine (Welte, 1965). The same situation holds in the present study. The geochemical evidence for source-rock–oil relationships in the Ouachita Mountains indicates a Silurian–Ordovician source for an oil whose carbon-isotope ratio averages −29.5 o/oo. This value is consistent with a lower Paleozoic source, according to the studies cited above.

Other evidence for a Silurian–Ordovician source comes from the V/Ni ratios of the EOM of the Missouri Mountain and Polk Creek samples. The average V/Ni ratios of these formations (table 10) are 2.9 and 3.7, respectively, and the average ratio of the three oils analyzed is 3.0 (table 2), suggesting that this ratio may provide a useful parameter for source-rock–oil correlation.

Of the three formations under consideration as sources (the Missouri Mountain, Polk Creek, and Womble), the Polk Creek Shale and Womble Formation appear to be the most probable sources. Thus, one might conclude that only the black shales of the mid–Upper Ordovician served as source rocks for the four oils examined in this study. However, because the Blaylock Sandstone is absent in most of the study area (fig. 2), the Missouri Mountain and Polk Creek Shales may be considered a single sequence of shales, spanning the Silurian–Ordovician boundary. Lithologic distinctions between these two formations are therefore somewhat arbitrary. In light of this, the Missouri Mountain–Polk Creek–Womble sequence appears to be the source for oils of the frontal and central Ouachita Mountains of Oklahoma.

Still another oil source may be considered, however, in view of the tectonic configuration of the Ouachita Mountains. Cretaceous rocks, which once overlapped the frontal and central Ouachitas (and, to the south, still do), might have generated these oils (P. A. Dickey, personal communication, 1981). This proposal would be supported by the shallow occurrence of the oils and solid bitumens; that is, migration would be downward in this case, rather than upward. However, numerous references are given on "scout tickets" to oil staining in wells at depths below 2,000 feet. Further, between the time the Cretaceous was eroded from the frontal belt (if, in fact, it fully overlapped the belt at any time) and the present, a (presumably) large amount of overburden has been removed, down through which a Cretaceous-source oil would have had to migrate to its present-day Stanley Group reservoirs. Nevertheless, despite such circumstantial reasoning, a Cretaceous source (or, in addition, a foreland Arbuckle facies source) may not be ruled out for Ouachita oil until these rocks are fully evaluated for their source potential and their similarity to these oils.

CONCLUSIONS

Several general conclusions can be drawn from the data in this study. First and foremost, it is clear that the sequence comprising the Stanley Group through Womble Formation of the Oklahoma Ouachita Mountains contains enough organic matter to have produced oil. It is also clear from thermal-maturity data that these rocks are within the oil window.

The oils in the study area are paraffinic and generally unaltered. Further, the four oils examined have a common source. The solid bitumens, grahamite and impsonite, also have a common source, and are products of near-surface, low-temperature alteration of oil. Specifically, the solid bitumens of the Ouachitas are products of limited biodegradation, water washing, and devolatilization. Previous assumptions that this material was essentially "dead oil," and the result of high-temperature alteration, are erroneous.

The most probable source rocks for these oils and solid bitumens are Missouri Mountain–Polk Creek–Womble strata, each possessing some characteristics of the oils. The absence of the Blaylock Sandstone in the study area requires lithologic (shaly) continuity between the Missouri Mountain Shale and the Polk Creek Shale, suggesting that both of these units were oil sources.

Several observations, when taken together, imply large-scale vertical migration. Among these are that (1) oils are confined largely to Pennsylvanian and Mississippian rocks; (2) solid bitumens are found in these same rocks, and also as far downsection as the Bigfork Chert; and (3) these materials most probably originated in Middle and Upper Ordovician rocks. I propose that such migration was facilitated by fractures, and by listric reverse faults that cut Ordovician source beds. Following oil generation and perhaps limited expulsion from these source beds, the faulting allowed oil to migrate upward. As oil approached the meteoric water zone, near-surface alteration began. Initially, biodegradation and water washing were predominant, until decreased permeability impeded water flow through the degraded oil. At that time, as long ago as 300 million years, biodegradation ceased, and devolatilization continued, and still continues at the present time.

The Oklahoma portion of the frontal and central Ouachita Mountains should definitely be considered a potential oil province, because one of the most important requirements for finding crude oil in a basin, namely, the presence of a good source sequence, is clearly satisfied. The high-temperature history frequently ascribed to the study area is unfounded. Further, the oil is low in sulfur and of high quality. These conclusions, and the relatively large untested areas, suggest that optimism concerning the Ouachita Mountains as an oil province is warranted.

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TABLE 13.—SAMPLE LOCATIONS AND TYPES OF OILS AND SOLID BITUMENS

Sample Number and Type	Field/Deposit	Location		Reservoir	Comments
		County	Township/Range		
3 Grahamite	Sardis (east) Deposit	Pushmataha	T2N-R18E Sec. 9	Stanley Group	---
5 Grahamite	Bigfork Veins	Pushmataha	T2N-R19E Sec. 1	Bigfork Chert	Sampled from veins and fractures in the Bigfork
6 Grahamite	Jumbo Deposit	Pushmataha	T1S-R15E Sec. 28	Stanley Group	---
7 Grahamite	Sardis (west) Deposit	Pushmataha	T2N-R18E Sec. 9	Stanley Group	---
8 Grahamite	Pumroy Deposit	Atoka	T1S-R13E Sec. 25	Stanley Group	---
11 Oil	South Bald Field	Atoka	T1N-R15E Sec. 5	Jackfork Group	Producing interval: 188-236 feet
15 Oil	Bald Field	Pittsburg	T2N-R15E Sec. 28	Stanley Group	Producing depth: 350 feet
17 Oil	Redden Field	Atoka	T1S-R14E Sec. 9	Stanley Group	Producing depth: 148 feet
21 Grahamite	South Bald Deposit	Atoka	T1N-R15E Sec. 4	Stanley Group	---
44 Impsonite	Page Deposit	Le Flore	T3N-R26E Sec. 23	Jackfork Group	Received from Mrs. Walker, Page, Oklahoma
45 Oil	North Daisy Field Now part of S. Bald	Atoka	T1N-R15E Sec. 8	Stanley Group	Received from Chevron USA, Inc. From Frank Sellmeyer #1 Loman well

TABLE 14.—SAMPLE LOCATIONS AND TYPES OF ROCK SAMPLES (SUBSURFACE CUTTINGS)

Sample Number	Location		Well	Stratigraphic Interval Sampled	Sampling Library
	County	Township/Range			
24	Atoka	T1N-R14E Sec. 26	US Mineral & Royalty, 1-26 Wyrick	Stanley (3850-4320 ft)	Shawnee, Oklahoma
25	Atoka	T1N-R14E Sec. 26	Max Pray Wyrick	Stanley (2980-4285 ft); Womble (9856-10600 ft)	Shawnee, Oklahoma
26	Atoka	T1N-R14E Sec. 26	Vaughn #1 Miller	Stanley (380-939 ft)	Ardmore, Oklahoma
27	Pushmataha	T2N-R20E Sec. 11	Sam Herrick #1	Womble (2705-2995 ft)	Ardmore, Oklahoma
28	Latimer	T3N-R20E Sec. 33	Helen Mattice #1	Polk Creek (700-800 ft); Womble (1640-1860 ft)	Ardmore, Oklahoma
29	Pushmataha	T2N-R19E Sec. 8	L. L. Kenman	Missouri Mt (800-900 ft)	Ardmore, Oklahoma
31	Pushmataha	T2S-R15E Sec. 9	Denton Perrin #1	Missouri Mt (9240-9465 ft); Polk Creek (9565-9765 ft)	Ardmore, Oklahoma
34	Atoka	T1S-R14E Sec. 14	B & C Mason #1	Stanley (383-384 ft; 1440-1465 ft)	Oklahoma Geological Survey, Norman, OK
35	Pittsburg	T2N-R15E Sec. 28	James-Able #4	Stanley (30-365 ft)	Oklahoma Geological Survey, Norman, OK
40	Pushmataha	T2S-R15E Sec. 9	Denton Perrin #1	Arkansas Novaculite (6500-9200 ft); Bigfork (9900-11100 ft)	Oklahoma Geological Survey, Norman, OK

TABLE 15.—SAMPLE LOCATIONS AND TYPES OF ROCK SAMPLES (OUTCROP)

Sample Number (OGS GCN)	County	Location	Stratigraphic Interval	Comments
17	Latimer	T3N-R21E Sec. 31 SE SE SE	Missouri Mountain (upper)	From Walnut Creek; 135 ft north of fence line
21	Latimer	T3N-R21E Sec. 31 SE SE SE	Missouri Mountain (middle)	From Walnut Creek; 435 ft north of fence line
22	Latimer	T3N-R20E Sec. 31 SE NE NW NE	Bigfork (upper)	From Cedar Creek
24	Pushmataha	T2N-R21E Sec. 6 NE NE NE	Arkansas Novaculite (lower)	From west bank of Walnut Creek
25	Latimer	T3N-R20E Sec. 30 SW SW NE	Stanley (lower)	From east side of Cedar Creek
28	Atoka	T2S-R11E Sec. 14 E ½	Womble	From south side of Highway 7
30	Latimer	T3N-R20E Sec. 28 N ½	Polk Creek	Potato Hills
31	Latimer	T3N-R19E Sec. 33 SW SW NE	Stanley (lower)	From east side of Highway 2
32	Pushmataha	T2N-R19E Sec. 2 SE SW NE	Bigfork (lower)	Black shale
35	Pushmataha	T2N-R20E Sec. 11 SE NE SE	Womble (upper)	---
36	Pushmataha	T2N-R20E Sec. 11 SE NE SE	Bigfork (lower)	---

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