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SOURCE ROCK GEOCHEMISTRY AND LIQUID AND SOLID PETROLEUM OCCURRENCES OF THE OUACHITA MOUNTAINS, OKLAHOMA

The University of Oklahoma PH.D. 1981

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THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

SOURCE ROCK GEOCHEMISTRY AND LIQUID AND SOLID PETROLEUM OCCURRENCES OF THE OUACHITA MOUNTAINS, OKLAHOMA

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

BY

JOSEPH ANTHONY CURIALE

Norman, Oklahoma

1981

SOURCE ROCK GEOCHEMISTRY AND LIQUID AND SOLID PETROLEUM

OCCURRENCES OF THE OUACHITA MOUNTAINS, OKLAHOMA

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ABSTRACT

Crude oils, solid bitumens and potential oil source rocks of the Frontal and Central Ouachita Mountains of southeastern Oklahoma are 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) are 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 are commonly sourced, as suggested by n-alkane, sterane and hopane distributions, stable isotope ratios, infrared spectra and vanadium/nickel ratios. A common source for the solid bitumens is also suggested by isotope ratios and pyrolyzate characteristics. An origin due to crude oil biodegradation is suggested for these solids, based on carbon isotope ratios, elemental analyses, and sterane distributions of the solid bitumen pyrolyzates.

Several stratigraphic intervals in the Ouachita Mountains possess adequate source potential for petroleum generation, based on contents of total organic carbon and extractable organic matter. Mississippian/Devonian rocks are probably gas-generative, while pre-Devonian rocks are oil-generative. The entire Paleozoic section examined is thermally mature enough to have generated oil, being located at about the middle of the oil window. In general, the best oil source potential is present in upper Ordovician (Polk Creek/Womble) rocks.

Oil-source rock correlation techniques indicate that oils examined from the Frontal and Central Ouachita Mountains have a Siluro-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 are proposed as migration conduits, connecting Siluro-Ordovician source rocks with 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.

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For my parents

SOURCE ROCK GEOCHEMISTRY AND LIQUID AND SOLID PETROLEUM OCCURRENCES OF THE OUACHITA MOUNTAINS, OKLAHOMA

INTRODUCTION

Purpose

The major objectives of this study are to: (a) characterize oils and solid bitumens (grahamites and impsonite) produced from rocks of the Ouachita Facies in southeastern Oklahoma; (b) evaluate the potential of Ouachita rocks as hydrocarbon source rocks; and (c) geochemically correlate 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 present.

This study is limited stratigraphically to rocks of the Ouachita Facies (see Appendix I for definitions) which consist entirely of Paleozoic sandstones, shales and cherts (see Figure 1 for the stratigraphic section in the Ouachitas). Specifically, only rocks from the Mississippian Stanley Group to the Ordovician Womble Shale (inclusive) and oils and solid bitumens produced from the Jackfork Group to the Bigfork Formation (inclusive) have been considered in this study. Consequently, generation of oil in Arbuckle Facies rocks (see Appendix I), and subsequent migration along faults into the

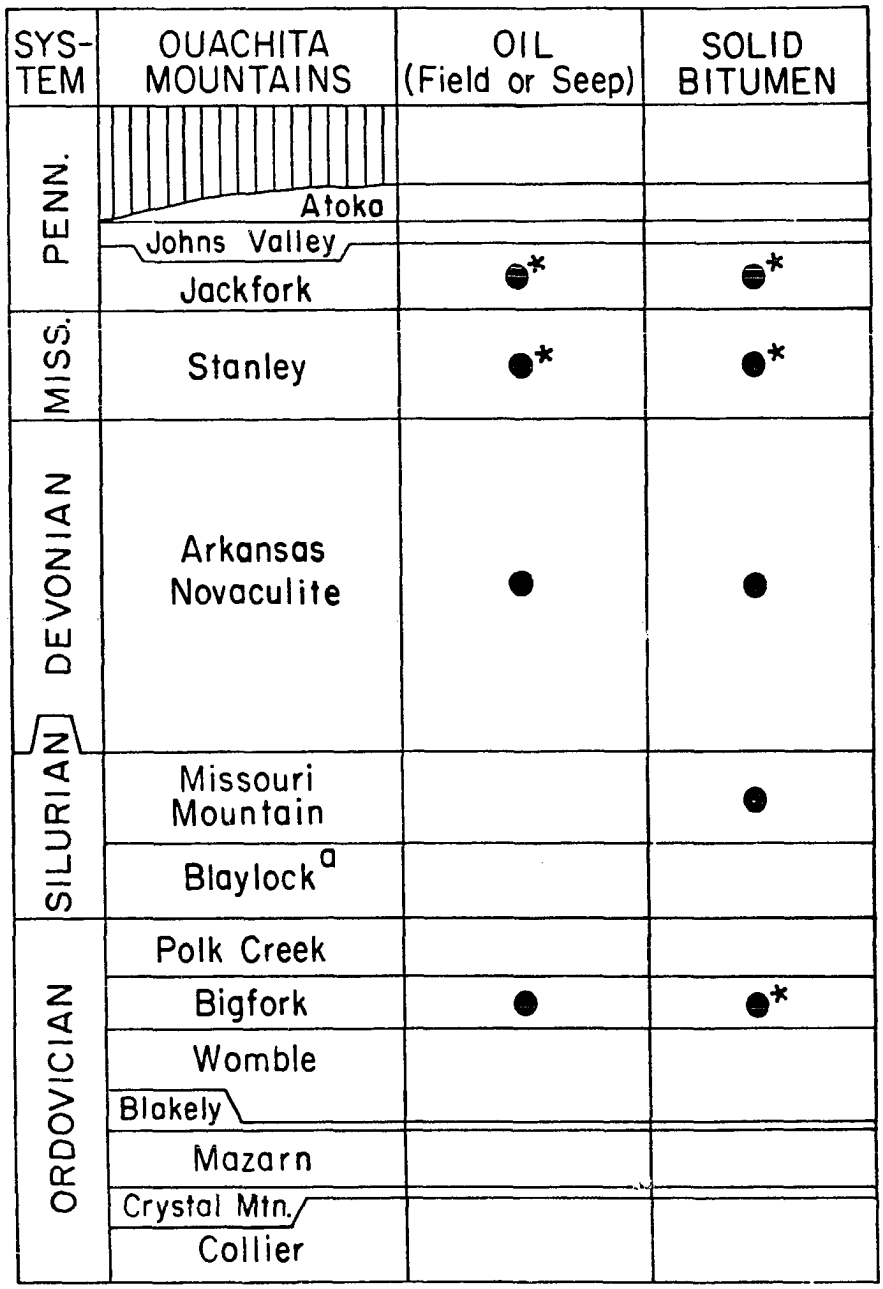


Figure 1. Stratigraphic Location of Oils and Solid Bitumens in the Ouachita Mountains. Asterisk (*) indicates location of samples analyzed in this study. Letter "a" signifies that the Blaylock Formation is locally missing in most of the study area.

Ouachita section, was not investigated, although this is possible. Further, this study is limited to the Frontal and Central Ouachita Mountains (Figure 2), as defined by Cline (1968).

Study Area

The oils, solid bitumens and rock samples investigated in this study were obtained from Atoka, Latimer, Le Flore, Pittsburg and Pushmataha Counties in southeastern Oklahoma (Figure 2). The entire study area covers approximately 1400 square miles and consists of 40 townships. Specific sample locations are listed in the tables of Appendix III.

Sampling constituted a major problem throughout the course of this study. Surface rock samples were avoided where possible, to reduce problems of contamination, weathering and loss of volatiles (Leythaeuser, 1973; Clayton and Swetland, 1978). Therefore, the majority of rock samples studied were composites of 50- to 100-foot cuttings intervals, although cuttings themselves are often contaminated by uphole caving. Unfortunately, no core material was available. All solid bitumens were collected from mine sites; oils were sampled from stock tanks or flow lines leading to stock tanks. Appendix II contains specific information on sample sites and methods of collection and preparation.

Four oils, seven solid bitumen samples and 127 rock samples were analyzed in this study. Oil and bitumen samples are designated by a single number, while subsurface rock samples are denoted by a single number (corresponding to a specific well), followed by the

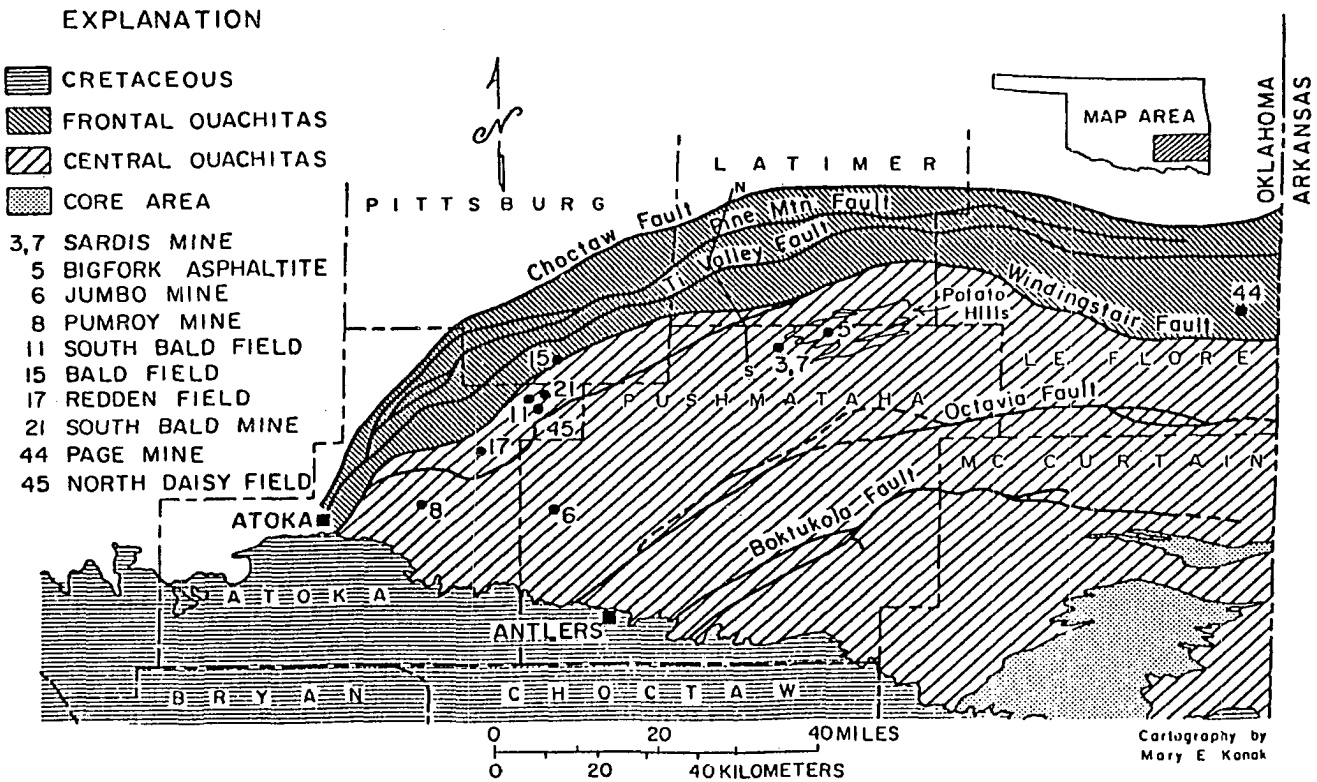


Figure 2. Map of Oklahoma Ouachita Mountain Region. Adapted from Cline and Shelburne (1959). North-south cross section is shown in Figure 6.

subsurface depth interval, in feet. Oils and solid bitumens will also be discussed in terms of field or mine name. Figure 2 relates sample number to field or mine, and presents geographic and physiographic location information for each of the samples.

Previous Investigations

Oil

Several references to the petroleum potential of the Ouachita Mountains have been made in the literature (Honess, 1927; Hendricks, 1951; Howell and Lyons, 1959; Chenoweth, 1959, 1960; Jordan, 1964; Schramm and Caplan, 1971; Fay, 1976; Morris, 1977; Morrison, 1980a, 1980b; and Fay, in preparation). However, major studies on the chemical characteristics of the crude oil and potential source rocks present in the Ouachitas are lacking in the public literature.

Honess (1927) initially dismissed the possibility of oil accumulations in the Ouachitas, considering the area to be too highly metamorphosed to warrant further consideration. Other workers however, have suggested that the Ouachitas may contain large amounts of oil and gas, either within the thrust plates (Chenoweth, 1960) or below them (Hendricks, 1951). Several lines of evidence that suggest the presence of oil and gas in the region were listed by Schramm and Caplan (1971). Their evidence included the presence of numerous liquid oil seeps and solid bitumens as well as gas shows and isolated producing oil wells. In addition, Morris (1977) notes that the region is thermally mature, stating that "Dark shales of many zones have been brought to stages of diagenesis adequate to generate oil and gas...."

The most recent publications concerning Ouachita oil potential in the general literature are those of Morrison (1980a, 1980b), which described the recent Isom Springs oil discovery. This field is located in Marshall County (T7S R5E), approximately 80 miles southwest of the center of the present study area. Morrison suggests that this discovery in Ouachita Facies rocks "...may have opened a new petroleum province that had been previously overlooked."

Specific discussions concerning the origin of the oil and solid bitumen of the Ouachita Mountains are also rare in the literature, particularly in the more recent literature. A paper by Miser and Purdue (1918), which adopted many ideas of Taff and Reed (1908), suggested a specific origin for the asphaltite and oil, particularly in Arkansas. Miser and Purdue (p. 280) proposed the following:

> The asphalt ... is doubtless a residue of crude petroleum, whose lighter and more volatile parts have escaped by evaporation. The petroleum yielding the asphalt in Arkansas is believed by the writers to have been derived from the Carboniferous rocks underlying the Trinity Formation, near the base of which the asphalt is found.... There is, however, no direct proof that some or all of the petroleum did not originate in the basal part of the Trinity formation, which contains some fossiliferous limestone.
>
> On the assumption that the petroleum yielding the asphalt herein described originated either in the Trinity or in the underlying rocks, the petroleum has probably migrated northward. There is, however, a possibility that it came upward from the Paleozoic strata immediately subjacent to the areas containing the asphalt deposits.

The possibility of a stratigraphically older source for the oil was also suggested by Honess (1927, p. 100):

> The asphalt and heavy residues of petroleum in the exposed Carboniferous rocks of the Ouachita Mountain area may also be thought of as having had a deeper seated origin,

> especially since there are so many fissure veins of a large size in the lowermost formation of the Carboniferous, i.e., in the Stanley shale, and since a certain amount of these materials, asphalt and oil, is actually found in Ordovician to Devonian rocks, namely the Talihina chert.

However, as a result of his feeling that "flints and slates" predominate below the Stanley Group in northern Pushmataha County and western Atoka County, Honess (1927, p. 101) concludes that pre-Carboniferous rocks could not be the source beds of the petroleum in the Frontal Ouachitas.

All later publications concerning the origin of the solid bitumens in the Ouachita Mountains (Ham, 1956; Goldstein and Flawn, 1961; Krivanek, 1962; Fay, in preparation) are essentially variations on the mechanisms proposed by Honess (1927) and Miser and Purdue (1918). Deitrich (1956) even specifically suggests an oil-derived origin for impsonite (generic definition, Figure 3), based on ash content and x-ray diffraction data. It is interesting to note however, that no adequate geochemical relationship has been established to support any of the claims made concerning the source of the oil or the solid bitumen. One of the purposes of this study is to present evidence for a genetic relationship between these two materials.

Despite the significant number of previous studies concerning the chemical properties of Ouachita Mountain bituminous materials, no mention exists in the literature of a possible primary origin for either the grahamite or impsonite. This is in contrast to the secondary origin discussed by Miser and Purdue (1918) and Honess (1927). In view of this lack of published information about a primary origin, the present work was initiated without preconceived notions on the

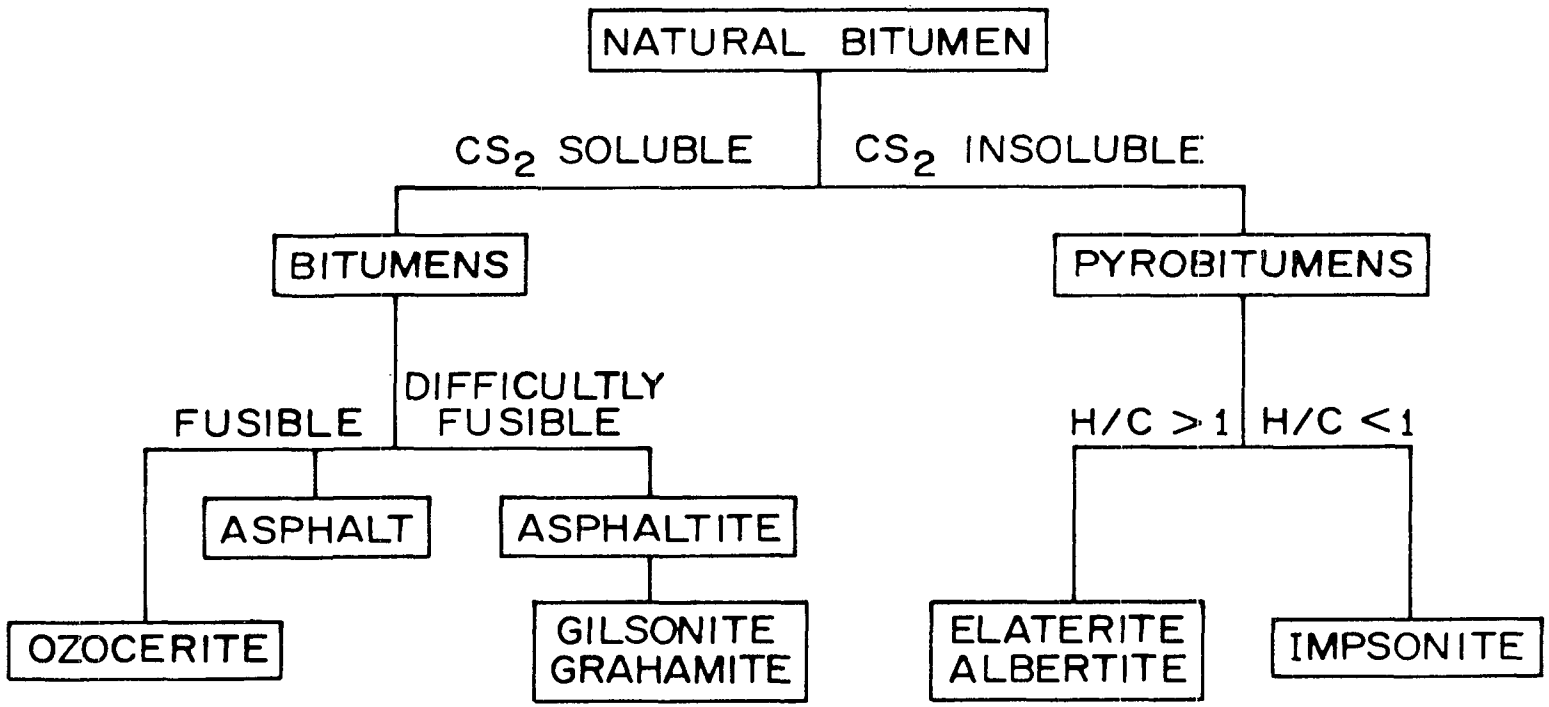


Figure 3. Classification Chart for Natural Bitumens. (Adapted from Hunt, 1979.)

primary or secondary origin of grahamite or impsonite. In view of this, it will be useful to briefly discuss the implications of each possibility.

The notion of the existence of a primary, first-generation product of a relatively immature source rock has existed in the literature for several years, often as an integral part of the low-temperature oil-generation concept (Brooks, 1934, 1936). The concept of "protopetroleum," a material expelled very early from a rich source rock, has been suggested as a theoretical starting material for the production of liquid crude oil. The reader is referred to Silverman (1964) for a review of these concepts. This early-formed material would presumably be high in molecular weight and heteroatom content, and would contain little or no paraffin-type constituents. At the present time, I am unaware of published information that conclusively demonstrates the existence of "protopetroleum" anywhere in the world.

The alternative explanation for the existence of grahamite and impsonite in the Ouachita Mountains involves degradation of once-liquid oil. This is the concept originally proposed by Taff and Reed (1908) for Ouachita Mountain grahamite, and by White (1899) for grahamite from West Virginia. Such a mechanism however, does not permit a definite conclusion as to origin, since there are several pathways for the degradation of oil (Bailey, et al., 1973b). If the asphaltite is of secondary origin, it is critically important to determine whether such material resulted from a high-temperature or a low-temperature alteration of oil. If the former is the case, this gives some indication of the thermal maturity of the frontal and central Ouachitas. If

the latter is true, then near-surface alteration effects have been predominant.

Results of this study indicate that a chemical distinction between a primary and secondary origin of grahamite and impsonite can be made. Further, isotopic data can be utilized to distinguish between the two secondary origins (high versus low temperature alteration) discussed above. Conclusions from this work that have a bearing on the solid bitumen origin problem will be presented in detail in a later section.

Solid Bitumen

The chemical properties of Ouachita asphaltite and pyrobitumen (grahamite and impsonite, respectively; see Figure 3) have been discussed in the geochemical and geological literature (Taff, 1909; Aurin, 1919; Miser and Purdue, 1918; Honess, 1927; Shelley, 1929; and Ham, 1956), but most such studies were made prior to the advent of modern analytical techniques. Excellent summaries of these studies, and a review of past asphaltite mining activities, are provided by Fay (1976) and Fay (in preparation).

Taff (1909) published an early work concerning the physical and chemical properties of Ouachita solid bitumen. He summarized knowledge to date, and became the first to suggest varying levels of metamorphism as an explanation for the difference in chemical properties of grahamite and impsonite. Forty-seven years later, Ham (1956) published the next study on the chemical properties of Ouachita solid bitumen. In addition to documenting the major grahamite localities

of the Oklahoma Ouachitas, Ham presented chemical information, including vanadium-in-ash content, of the impsonite mined at Page, Oklahoma (Figure 2). Whereas this work expanded on that of Taff (1909) and others, the analytical techniques utilized were largely the same, as were the conclusions drawn from the data. Comparison of these past chemical analyses with the results of the present study will be discussed in detail in a later section.

Review of the Geology of the Ouachita Mountains

Lithostratigraphy

Sediments are known to have been deposited in the Ouachita trough from the pre-Cambrian or Cambrian until at least the middle to upper Pennsylvanian. Most geologists who have worked in the area consider the section to be time-continuous, although there is evidence to suggest an unconformable contact between the Stanley Group and the Arkansas Novaculite Formation (Kramer, 1933; Morrison, 1980a). However, for the purposes of this report, the Oklahoma Ouachita Mountain section will be regarded as having no major unconformities (Figure 1).

The presence of proximal and distal turbidites, as well as generally disturbed bedding throughout the Carboniferous in the Ouachitas, has led investigators to propose a flysch-type depositional environment for the Mississippian and Pennsylvanian sediments of the Ouachita trough (Cline, 1966). In view of the presence of disturbed bedding in the pre-Carboniferous section, Morris (1974) maintains that pre-Stanley sediments also indicate flysch-deposition. Most workers however, have described the pre-Mississippian rocks of the Ouachitas

as products of deposition in a "starved trough" (Goldstein, 1961; Cline, 1966; Morris, 1974). This condition ended in Stanley time, as the trough deepened, and thick accumulations of the Stanley-Jackfork-Johns Valley-Atoka sequence were deposited (see Table 1 for formation thicknesses).

The general lithostratigraphy of the Ouachita section has been discussed thoroughly (Ham, 1959; Cline and Shelburne, 1959; Cline, 1960; Hill, 1966; Morris, 1974; Briggs and Roeder, 1975). The treatment here will constitute a brief review of the lithostratigraphy and environment of deposition for each formation. The interested reader is referred to the papers above for more detailed discussions. Note that, owing to widespread exposures throughout the Ouachita Mountains, the Carboniferous section has been the most frequently studied. Consequently, the present discussion will be somewhat more detailed for rocks of Stanley age and younger.

Cambro-Ordovician Rocks. Although the presence of pre-Cambrian rocks in the area has been suggested by at least one worker (Wroblewski, 1972), the earliest unit described in the Ouachitas is the Cambrian Lukfata Formation (Pitt, 1955). However, Repetski and Ethington (1977), on the basis of faunal evidence, have shown the Lukfata to actually be early or middle Ordovician. The Collier Formation of the early Ordovician therefore, is the earliest commonly recognized formation in the Ouachita section. This formation is predominantly a shale interbedded with steel-gray limestones. The Collier represents abyssal sedimentation (Morris, 1974) and contains distal turbidites. Morris places deposition of the Collier above the

Table 1

Stratigraphic Interval Thicknesses, Ouachita Mountains

Age	Stratigraphic Interval	Thickness (Feet)	
		Morris (1974)	Honess (1927)
Pennsylvanian	Atoka Formation	27,500	--
	Johns Valley Formation	1500	--
	Jackfork Group	6000	--
Mississippian	Stanley Group	8500	--
Devonian	Arkansas Novaculite Formation	950	600
Silurian	Missouri Mountain Formation	250	60-100
	Blaylock Formation	1500	0-1500[a]
Ordovician	Polk Creek Formation	175	100-200
	Bigfork Formation	800	800
	Womble Formation	3500	1000
	Blakely Formation	400	--
	Mazarn Formation	3000	1000
	Crystal Mountain Formation	850	500+
	Collier Formation	1000+	200+
Cambrian	Lukfata Formation	---	--

[a] From Miser (1918).

carbonate compensation depth. The thin Crystal Mountain Formation, a structureless quartz arenite, overlies the Collier. This sandstone is thought to result from submarine slides (Morris, 1974), although provenance is not clearly established. The Mazarn Formation (Figure 1) is a dark gray graptolite-bearing shale, and is interbedded with quartzose or carbonate distal turbidites. The Blakely Formation overlies the Mazarn Formation, and is lithologically similar to the Crystal Mountain Formation. The Blakely Formation is overlain by the Womble Formation, which consists of very thick (see Table 1) black graptolitic shale. The Womble Formation is locally interbedded with distal turbidites (Goldstein, 1959).

The interbedded sandstone-shale units typical of early Ordovician rocks are interrupted after deposition of the Womble Formation. This formation is overlain by the Bigfork Formation, which consists of interbedded cherts, shales, and limestones. The Bigfork Formation is considered by Morris (1974) to represent turbidite and pelagic conditions. The youngest Ordovician unit represented in the Oklahoma portion of the Ouachita Mountains is the Polk Creek Formation. This unit also contains graptolites and is locally rich in organic matter.

Silurian Rocks. The Blaylock and Missouri Mountain Formations constitute the Silurian rocks of the Ouachitas, the former being a flysch deposit of poorly sorted sands and shales, and the latter a platy shale interbedded with quartz arenite. The Blaylock Formation is considered by Morris (1974) to represent the first non-cratonic sequence deposited in the Ouachitas. The suggestion (Morris, 1974,

p. 132) that the Blaylock Formation has a non-cratonic source is consistent with its limited areal extent. Goldstein (1961, p. 28) notes that this formation is "...missing in the northern and northwestern parts of the Ouachita Mountains...," and thus is not present in the study area. The absence of the Blaylock Formation is somewhat confirmed in this study, as there was no evidence of this unit in any of the wells examined. This observation is extremely important in terms of potential source rocks in the Frontal and Central Ouachita Mountains of Oklahoma, because it suggests predominantly shale deposition from the Arkansas Novaculite-Missouri Mountain contact to the Polk Creek-Bigfork contact (Figure 1). Thus, in terms of source potential, the Missouri Mountain and Polk Creek Formations may be considered as upper and lower limits, respectively, of a potential source sequence. This concept is pursued in greater detail in the section on source rock potential.

Devonian Rocks. The Devonian system in the Oklahoma Ouachitas consists entirely of the Arkansas Novaculite Formation. Conodonts of the Lower Mississippian have been described from the upper part of the Novaculite (Hass, 1956). Morrison (1980a) suggests a practical segregation of the Arkansas Novaculite into five members, as follows: (a) an upper massive brown and white chert; (b) a blocky maroon shale; (c) a green and brown, very siliceous novaculite-shale; (d) a laminated zone of alternating beds of chert and green shale laminae; and (e) the so-called Pine Top Chert Formation. Morrison notes that true thickness of these units is difficult to determine because of steeply dipping beds and other structural complexities in the Ouachita Mountains. As

shown in Table 1, there are serious discrepancies as to true formation thicknesses of units in the Ouachita section.

Mississippian Rocks. The Mississippian Stanley Group is by far the most studied unit in the Ouachita Mountains. Consequently, much more detailed information is available about the lithology and depositional environment of the Stanley than of the pre-Carboniferous units. The Stanley Group consists of the Tenmile Creek, Moyers and Chickasaw Creek Formation. These units are comprised of alternating sandstones and shales. The thinning of the Stanley Group from south to north has led some workers (Goldstein, 1961; Morrison, 1980b) to conclude that the contact between this unit and the Arkansas Novaculite is an unconformity. Some evidence for such an unconformity is present in the literature (Morrison, 1980a). Cline and Shelburne (1959) note however, that this thinning can simply be regarded as a depositional feature.

The oldest formation of the Stanley Group is the Tenmile Creek Formation. This unit comprises approximately eighty percent of the Stanley Group and consists of a series of "...laminated shales and platy siltstones interbedded with thin sandstones..." (Cline and Shelburne, 1959, p. 181). The shales are dark gray and weather to olive green, while the sands are dark gray and weather to a greenish-buff color. The sands are poorly sorted and become the dominant lithology higher in the section. The Hatton volcanic tuff occurs approximately 270 feet above the base of the Stanley, and varies in thickness from 90 to 228 feet. Overlying the Tenmile Creek is the Moyers Formation which consists of approximately 1000 feet of

alternating massive sandstones and thin-bedded dark gray to greenish-gray shales. The Moyers is overlain by the Chickasaw Creek Formation, a distinctive thin-bedded series of siliceous shales and cherts.

Pennsylvanian Rocks. Overlying the Stanley Group sands and shales is the Jackfork Group. The Jackfork consists predominantly of very fine-grained, quartz-rich turbidite sandstones which are interbedded with gray to black shales. The Jackfork Group contains five formations, the (basal) Wildhorse Mountain, Prairie Mountain, Markham Mill, Wesley and (upper) Game Refuge. The Johns Valley Formation overlies the Jackfork Group and consists predominantly of shale. The lower portion of the Johns Valley consists of dark gray to black shales which grade upward into gray shale. The shale contains interspersed sandstone beds and lenses.

Probably the most prominently studied features of the Johns Valley are the boulder beds and exotics found within the formation. Studies indicate that these were derived from Arbuckle and Ouachita Facies and the area affected by the Ozark uplift. The most common type of boulders are those deposited from the Ordovician of the Arbuckle Facies to the northwest. Detailed reviews of the theories of origin for these boulders are presented by Tomlinson (1959) and Cline and Shelburne (1959), and will not be discussed further here. The Johns Valley Formation grades into the Atoka Formation above, which is subdivided into an upper shale and lower sand, and transitional facies. The shale is gray to black and carbonaceous, while the sand is predominantly a sub-graywacke. The alternating sand-shale sequences of the Atoka are considered to be classic flysch deposits (Stark, 1966).

There are no known units that conformably overlie the Atoka Formation in the Ouachita Mountains of Oklahoma. Specifically, no material resembling the Desmoinesian Series of the Arkoma Basin has ever been found (Laudon, 1961). Thus the suggestion is made that the uplift of the Ouachita Mountains occurred during the Desmoinesian, and supplied the basin to the north with sediments.

Biostratigraphy

Biostratigraphic techniques have been used in the Ouachita Mountains for both age determination and correlation purposes. Figure 4 is a compilation by Morris (1974), and shows the relation between Ouachita rocks and those of the Arbuckle Mountains in south-central Oklahoma. Correlation is difficult throughout most of the Ouachitas because of scant fossil evidence in the Carboniferous. However, Decker (1959) correlated Cambrian, Ordovician and Silurian formations of the Arbuckle and Ouachita Mountains on the basis of graptolites. He interprets the upper beds of the Cambrian Lukfata Formation as being the stratigraphic equivalent of the Reagan Formation. Decker also considers the Missouri Mountain Formation to be the equivalent of the Henryhouse Formation. The correlation chart compiled by Decker is reproduced in Figure 5.

Little published information is available concerning the palynology of Ouachita Facies rocks. One exception is a paper by Morrison (1980a), who notes that abundant spores (of undetermined age) are present in the Upper Chert of the Arkansas Novaculite Formation. In summarizing correlation efforts to date however, Morrison (1980a,

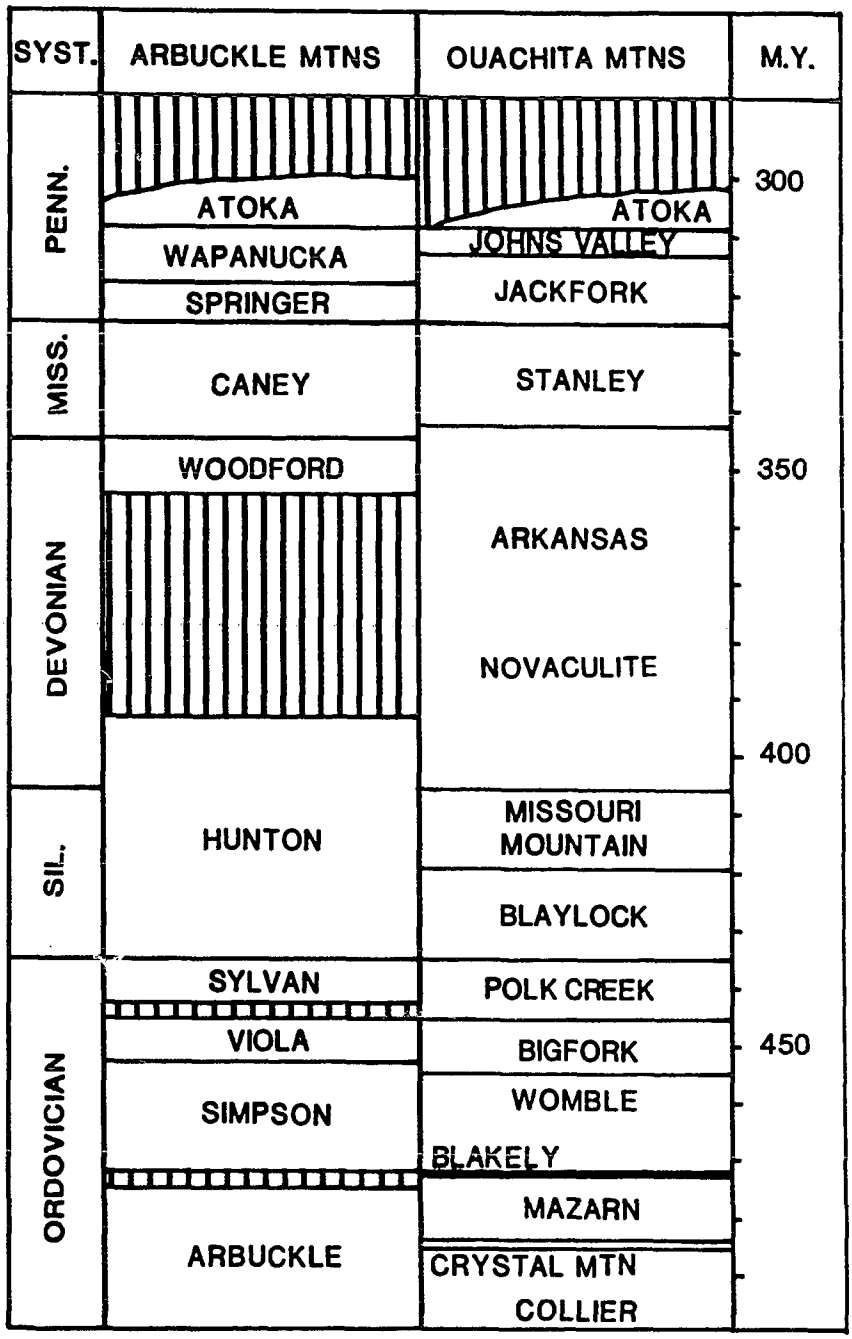


Figure 4. Stratigraphic Correlation Chart for the Arbuckle and Ouachita Mountains. (From Morris, 1974.)

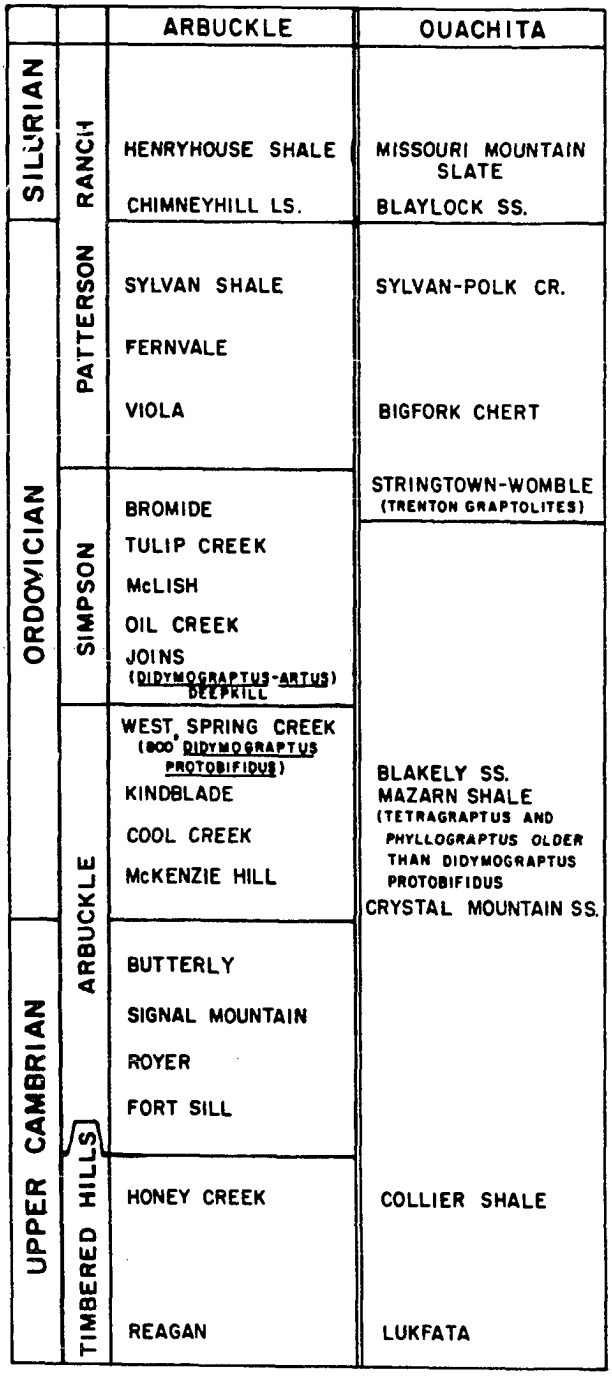


Figure 5. Graptolite Correlation Chart of Arbuckle and Ouachita Mountains. (From Decker, 1959.)

p. 24) also states:

> The literature relating the facies equivalents and ages... is rather confusing. Also comparing columnar charts of several major oil companies indicates that some serious paleontological and perhaps palynological work remains to be done.

Structural Geology

As described by Cline (1968), the Ouachita Mountains are generally subdivided into Frontal, Central and Core regions. According to his scheme, the Frontal Ouachitas (Figure 2) are bounded on the north by the Choctaw Fault and on the south by the Windingstair Fault. The Core Area of the Oklahoma Ouachitas occurs in the far southeast corner of the province, while the region in between the Frontal and Core Areas is known as the Central Ouachitas.

Listric thrust faults predominate in the Ouachita Mountains (Figure 6). The formation in which these faults sole is commonly the Womble, as indicated by the frequent occurrence of that formation along the hanging wall of the thrusts (Hopkins, 1968; Wickham, 1978). The interpretation shown in Figure 6 shows that the high angle, near-vertical faults at the surface become more horizontal with depth. In the study area, these faults sole at the level of Ordovician rocks (Berry and Trumbly, 1968). As a result of this faulting, broad synclines and anticlines are characteristic of the Frontal and Central Ouachitas. In addition, isoclinal folds and recumbent anticlines are evident in the area and are prominent features in Ordovician rocks (Wickham, 1978). In addition to drag-created synclines, another consequence of the prevalent listric faulting in the Ouachitas is repetition

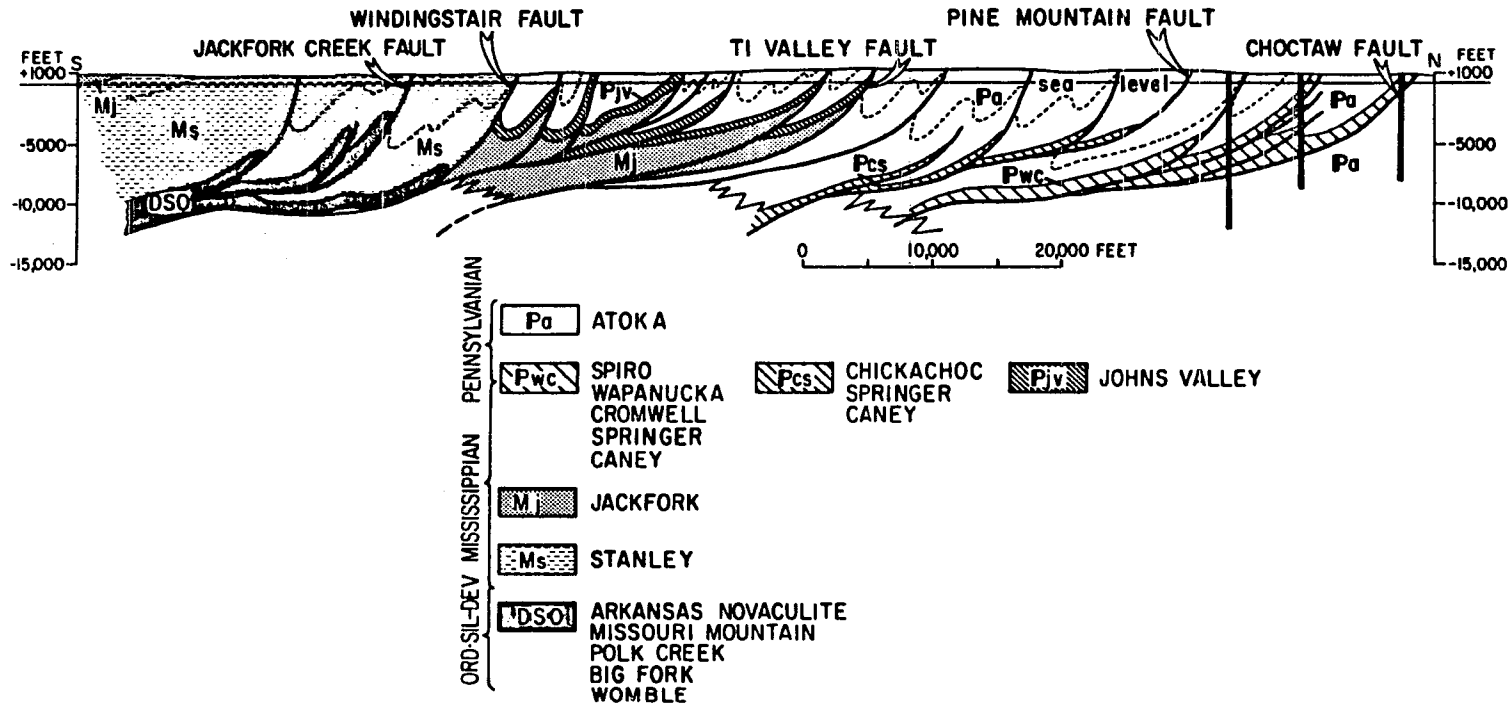


Figure 6. North-south cross section of the Oklahoma Ouachita Mountains. Adapted from Berry and Trumbly, 1968. No vertical exaggeration.

of the sedimentary sequence. This characteristic is often encountered in overthrust regions.

The Frontal Ouachitas include the region between the Choctaw Fault on the north and the Windingstair Fault on the south (Cline, 1968; Figure 2). The three major thrust faults (Figure 2) strike northeast-southwest in the study area, and are all considered to be listric reverse faults, although the amount of displacement is uncertain. Cline (1968) cites workers whose estimates for displacement along the Choctaw Fault vary from 15,000 feet to approximately eight miles. The fault movement deduced from stratigraphic displacement by Hendricks (1959) for the Choctaw, Ti Valley and Windingstair Faults are, respectively, 0.5, 20 and 2 miles. Accurate palinspastic reconstructions of the region must rely on detailed seismic data, which is unavailable in the public literature.

Hendricks (1959) makes the interesting observation that beds north of the Choctaw are steeply dipping to the north, whereas beds south of the fault dip steeply to the south. These features appear to be indicative of a large faulted anticline. The structural features of the Ti Valley and Windingstair Faults are very similar to those of the Choctaw Fault.

South of the Windingstair Fault is the Central Ouachita area, consisting of synclinal topographic highs and anticlinal valleys, the former made of Jackfork and Atoka sands and the latter being mostly Stanley shales. These synclines reasonably result from drag along high-angle faults. A typical example of this is the Lynn Mountain Syncline. This syncline is bordered on the south by the Boktukola Fault, which

cuts the surface at a high angle, and probably becomes horizontal in the subsurface (Viele, 1973). Valleys between the synclinal highs in most cases are severely deformed and partially eroded anticlines. These features are typified by McGee Valley, which is located immediately south of the Windingstair Fault.

The southernmost of the major Ouachita structural provinces is the Choctaw uplift, also referred to as the Benton-Broken Bow uplift (Flawn, et al., 1961), or simply as the Core Area (Pitt, 1959; Figure 2). Wickham (1978, p. 47) describes this area as one of "... extremely deformed slates, cherts and sandstones with a well-developed rock cleavage." Hopkins (1968) noted that the Womble Formation appears to be the major plane of detachment for faults in this area. A minor controversy has existed for several years concerning the nature of the structural complexities in the Core Area. The debate centers on whether the Core Area represents a fenster, or is simply a large eroded anticlinorium. Although the resolution of this problem is not germane to the present study, the discussions presented by Pitt (1959) and Tomlinson (1959) seem reasonable. These workers believe the feature in question is not a fenster, but is in fact a large anticlinorial structure, albeit extensively eroded.

Plate Tectonics

Figure 7a shows the locations of the major elements in the Ouachita Foldbelt. In the east, the Ouachita Mountains extend into Arkansas and are probably connected to the extreme southern Appalachians in the deep subsurface, beneath an overlap of Cretaceous Coastal Plain

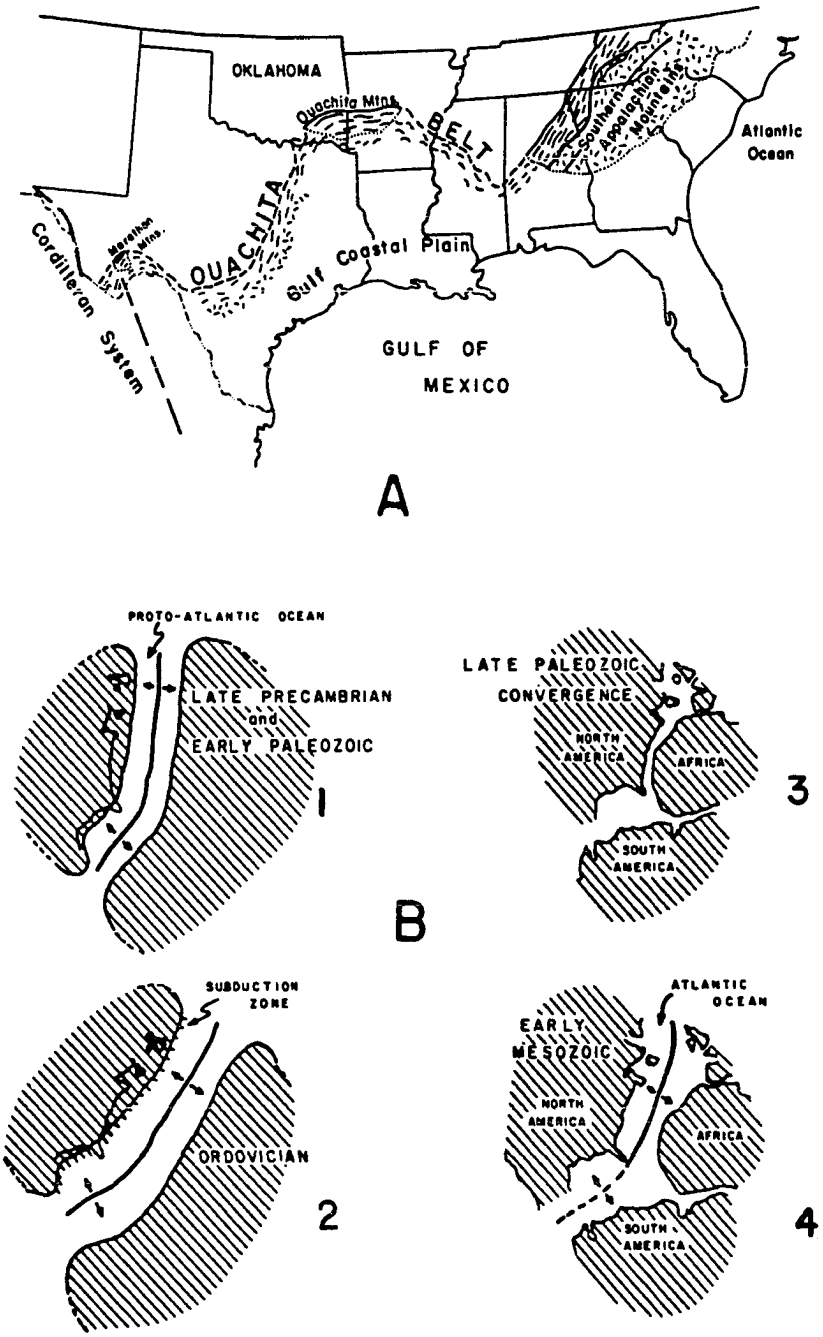


Figure 7. Tectonic Map of the Ouachita Foldbelt, including Paleozoic plate positions. (A) From Cebull and Shurbet, 1980. (B) Modified after Keller and Cebull, 1973: 1. Opening of the proto-Atlantic Ocean; 2. Formation of a subduction zone along North American margin; 3. Complete convergence at the end of the Paleozoic; 4. Opening of the present-day Atlantic Ocean.

rocks (Viele, 1973). Despite the large areal extent of the foldbelt, it achieves surface expression in only a few localities, with the Ouachita Mountain Region of Oklahoma and Arkansas being one of them. As a result, it is these surface features that have been investigated for clues as to the tectonic origin of the foldbelt.

Before discussing the tectonic causes of the present physiography of the Ouachita Mountains, it is helpful to outline the overall plate tectonic history of the foldbelt. The following discussion is adapted largely from Keller and Cebull (1973) and Thompson (1976).

Late Pre-Cambrian rifting between the North American land mass on the north and an undetermined land mass on the south, created a subsiding continental margin on the southern edge of the North American continent (Figure 7b). After rifting for several million years, a subduction zone formed parallel to the edge of the North American craton. The extensive chert beds in mid-Ordovician strata (Keller and Cebull, 1973) have been attributed to volcanic contribution of large volumes of silica (Goldstein and Hendricks, 1953). Thus the time of formation of the subduction zone is considered to be Ordovician. However, the direction of dip of the subducting plate is debatable. Following mature development of the subduction zone and accompanied by further chert formation during the Devonian, convergence continued unabated until continent-continent or continent-island arc collision occurred in the late Pennsylvanian. This resulted in the formation of the listric faults and the other complex structural features noted today in the Ouachita Mountains.

Following formation of the suture zone, Cebull and Shurbet

(1980) suggest that the opening of the Gulf of Mexico occurred in a region which is in geographic proximity to previous closure of a suture zone. Formation of a subsiding Atlantic-type continental margin south of the present-day Ouachita Mountains was then accompanied by eventual deposition of originally Cretaceous, and then later Cenozoic sediments (Figure 7b). The region affected is recognized today as the Gulf Coast Plain of the southern United States.

Tectonic interpretations of the Ouachita Foldbelt generally can be divided into two categories, those that regard the North American plate as the active plate (Burgess, 1976; Keller and Cebull, 1973) and those that regard it as the passive margin (Wickham, et al., 1976). Because of the lack of volcanics on the North American plate, which would be present were it an active margin, I concur with Wickham (1978). Most of the evidence to date implies a continent-continent or continent-island arc collision origin for the Ouachita Foldbelt.

The tectonic history of the Ouachita Foldbelt, particularly the establishment of southern North America as a passive margin, has significant implications for the structural framework of the Ouachita Mountains of Oklahoma and Arkansas. As discussed previously, the frontal and central Ouachitas are comprised of numerous thrust sheets which are delineated by listric faults that become bedding plane faults in the deep subsurface. Two major questions arise regarding these faults. Why are these faults listric in nature? What is the total amount of shortening across the Ouachitas?

The faulting in the frontal Ouachitas is predominantly reverse listric (Figure 6). Utilizing the concepts of plate tectonics,

one can infer that the extremely complex geology of the Frontal Area is the result of this region being deformed due to a collision with a northward-moving plate in the south. Thus, the physical configuration of the faulting in the Frontal Area can be attributed to forceful emplacement of a sedimentary wedge against an unyielding abutment, which would force the sedimentary sequence upward. The idea is described by Hopkins (1968, p. 105), albeit in a non-plate tectonic format:

> The Choctaw and associated faults are probably localized here because forces directed northwestward in the sedimentary cover were deflected upward by the relatively unyielding sloping basement surface.

In like fashion, the Boktukola and Octavia Faults to the south could reasonably have been caused by original minor basement (i.e., continental slope) topographic irregularities, which diverted the sediment package in a vertical direction (Hopkins, 1968). This general idea is depicted in Appendix VI (Figure 72).

The total shortening, or the extent of overthrusting, in the Ouachita Mountains has been a subject of debate (Hendricks, 1959; Hopkins, 1968). Hendricks (1959) estimated the minimum displacement for each of the faults in the Frontal Area (exclusive of the Boktukola and Octavia Faults) and suggested a total movement on the order of 50 miles. This value is consistent with a tectonic shortening in the Ouachita Foldbelt of approximately fifty percent, a value common for overthrust belts in general (Royse, et al., 1975). Tomlinson (1959) however, in an excellent discussion of the extent of tectonic shortening in the Ouachitas, notes that the dips of most of the faults at

the surface are from 60-80 degrees, with little or no direct evidence for soling at depth. Arbenz (1968), utilizing well information on the Sinclair Reneau #1 gas well in the Potato Hills, suggested that this well penetrated a major thrust fault at approximately 6000 feet subsurface. Arbenz postulated this fault to be the Windingstair Fault. Very high dip on the Windingstair Fault plane, where it cuts the surface approximately five miles northwest of the Reneau well, implies that this fault must sole prior to being penetrated by the subject well. This interpretation agrees in principle with cross sections published by Berry and Trumbly (1968) and Hopkins (1968), which indicate extensive soling of surface high-angle faults throughout the Frontal and Central Areas (Figure 6). In summary, both the cause of the high-angle listric faults, and the amount of total shortening they indicate are still a matter of debate. It is hoped that detailed seismic interpretation will help resolve these problems.

Correct interpretation of the subsurface structure of the Ouachita Mountains of Oklahoma is critical to one of the conclusions resulting from the present study. In particular, in invoking fault zone migration of liquid hydrocarbons, as is done in a later section, it is necessary that (a) the fault acts as a conduit rather than a barrier to migrating petroleum; (b) the fault in question cuts both the prospective source and the known reservoir at the time of migration; and (c) the fault be continuous from depth to the surface. Examination of recent seismic evidence and the results of the present study indicate that each of these three criteria is satisfied by the Windingstair Fault as well as other major listric faults in the Ouachitas.

Interpretations of the deep subsurface geology of the Ouachita Mountains in Oklahoma have been published as cross-sections by Hendricks (1947), Hopkins (1968) and Berry and Trumbly (1968). These cross-sections are constructed primarily on the basis of seismic information collected by the petroleum industry and are similar to the interpretation shown in Figure 6. These interpretations, as noted above, appear to satisfy conclusions of migration as outlined in a later section of this study. In addition, recently acquired proprietary seismic data is in general agreement with previously published interpretations. Thus later conclusions, based on fault zones acting as conduits for migration of oil, will refer to listric faults that have been confirmed as sole faults in the subsurface by both published and unpublished data.

Historical View of Solid Bitumens and Oil Potential of the Oklahoma Ouachitas

Following discovery of surface and near-surface deposits of asphaltite in the Oklahoma portion of the Ouachita Mountains in 1890, approximately 90,000 tons of this material was produced (Fay, 1976). Almost all of this was from the Jumbo, Sardis and Pumroy deposits of the study area (Figure 2). Although oil production from the study area has not been substantial, there are enough fields to demonstrate the presence of liquid petroleum. For example, from 1955 to 1975, six small oil fields (Bald, South Bald, West Daisy, Minnett, Potapo Creek and Redden) produced a total of 6000 barrels of oil. These fields are all in the study area and all produced from depths less than 1000 feet.

Since 1975, leasing has proceeded rapidly, although no major oil discovery has yet been made within the study area. However, Minnett Field in Atoka County has recently been reworked and is currently producing, as is Bald Field in Pittsburg County. In addition, a recent discovery in Marshall County, 80 miles southwest of the study area, has been made (Morrison, 1980a), and numerous wells are presently producing. In view of the present activity in the Ouachita Mountains, it is useful to review the geologic literature which deals with the potential of the area as an oil province.

Comments in the early literature concerning the oil potential of the Ouachita Mountains of Oklahoma were generally unfavorable. Early thinking concerning oil and gas exploration in the Oklahoma Ouachitas was summarized by Honess (1927, p. 31) as follows:

> ...While the Ouachita Mountains west and north of Kiamichi River cannot be condemned as an oil producing country, because of the theory of overthrust, neither can this region be highly recommended, or even recommended at all, to anyone who has not large sums of money to squander....Finally, as a warning to the inexperienced, and as giving the writer's own personal opinion, it seems that the Ouachita Mountains is one of the last places in the United States where one may expect to find petroleum in commercial quantities. As a last resource, sometime in the future, when gasoline is selling for 50 cents a gallon it might be worth while to study the Ouachita Mountains. Meantime there are too many other places and better places in which to drill prospect holes.

Honess (1927, p. 32) concluded his report on the oil and gas potential of Atoka, Pushmataha, McCurtain, Bryan and Choctaw Counties with the following statement: "Indeed there is no place anywhere in the five counties of southeast Oklahoma that can be recommended with any assurance that oil may be found in commercial quantities." The reasons for

such pessimism have more recently been reviewed by Chenoweth (1959, 1960) and Strothman (1981), and are listed below and discussed in turn.

1. Lack of porosity
2. Presence of high carbon ratios
3. Lack of source beds for oil
4. Presence of extensive thrust faulting
5. Silicification of pre-Atoka rocks
6. Presence of metamorphic rocks
7. Classification of Ouachita solid bitumen as thermally-destroyed "dead oil"

According to Chenoweth (1960), each of these so-called problems either represent over-generalizations from a relatively small number of samples, or present no real obstacle to further exploration. The data of the present study support many of Chenoweth's opinions in this regard.

The assumption that potential reservoir rocks lack porosity is based on examination of a few samples, and extrapolated to cover the entire Ouachita region. Chenoweth (1960, p. 95) notes that: "Sandstones of the outer belt of the mountains are no more tightly cemented than they are in many of the producing areas of south-central Oklahoma." Likewise, pessimistic conclusions resulting from carbon ratio determinations (see Appendix I) in the region also represent an unjustified extrapolation. Hendricks (1935) has measured fixed carbon values of coals to the east in the Arkansas Ouachitas. In addition, Wilson (1961, 1971), by measurement of fixed carbon in adjacent coals, has estimated levels of miospore carbonization in shales of the Arkoma

Basin to the north. These values range as high as 88% fixed carbon, well beyond the oil generation window. However, a lack of measurements within the Oklahoma Ouachitas suggests that extrapolation of the results of the cited studies to the present study area is inappropriate. This is shown conclusively by thermal maturity data of the present study, to be presented in a later section.

It has been suggested that there is a lack of source rock material in the Oklahoma Ouachitas. Empirically, this can be questioned because of the presence of oil fields (albeit small pools) in the region (although it is always possible that these pools can be explained by long-distance migration from an Arbuckle Facies source). Further, the present study provides evidence that source beds are in fact present, and that these beds are still within the oil window in many areas.

The presence of both extensive thrust faulting and highly silicified rocks in the region does not preclude significant oil accumulations, as is exhibited by production from overthrust belts and siliceous reservoirs throughout the world.

Two final factors concerning oil potential in the Ouachita Mountains deserve extended discussion, because they both have been considered in a negative sense and represent major obstacles to further exploration. These are the occurrence of metamorphosed rocks, and the classification of solid bitumen as thermally-destroyed "dead oil." These topics represent a "cause and effect" phenomenon and will be discussed together.

Taff (1909, p. 297) was the first to suggest a relation between solid bitumen and the metamorphism in the Ouachitas:

> The bitumen deposits are known to vary in composition in three localities and probably vary from one to another of all localities so far discovered. This variation is evidently due to differences in the degree of metamorphism, the progressive change brought about by the loss of the more volatile hydrocarbon. It is apparently not due to the age of the rocks in which these deposits occur.... The deposits containing the highest percentage of fixed carbon occur where they are either associated with sandstone or occur in closely folded and extensively fractured strata. In such relations the more volatile substances of the bitumen veins would escape with greater facility than where the material is in contact with shales and in association with less intense disturbance of the strata.

The idea of extensive metamorphism in the Ouachitas was also discussed by Honess (1923, cited by Chenoweth, 1960), who referred to the rocks of the Ouachita Facies as "...profoundly metamorphosed...." However, it has since been shown that only those rocks in the Core Area of the Ouachita Mountains of Oklahoma and Arkansas exhibit even low-grade metamorphism (Honess, 1923; Pitt, 1955).

These concepts were developed further in a model proposed by Rich (1927). He suggested that mountain-making crustal movements could result in "distillation" of petroleum from underlying thrust sheets. This zone of distillation, presumably the Ouachita Mountains in this case, would be the result of intense metamorphism, with either no oil accumulations, or small amounts of high-grade oil accompanied by gas. Surrounding this zone are second and third zones of <u>in situ</u> accumulation and secondary migration, respectively. Rich (1927) recognizes the rich oil accumulations of southern Oklahoma as zones 2 and 3, while zone 1, the zone of distillation, would represent the Ouachita

Mountains.

Although most of these ideas are now over fifty years old, some are still held by operators who have considered exploration programs in the area (Curiale and Harrison, in press). In particular, the presence of solid bitumens, still regarded as thermally-destroyed "dead oil" by many of the operators, has discouraged further investigation in the Ouachitas. In contrast to these concepts, there is considerable evidence that oil exists in economically significant amounts within the Ouachita Mountains, including the following: (a) The presence of solid bitumens and oil confirms the existence of source rocks either within or below the Ouachita thrust sheets; (b) Softening of the grahamite with depth indicates "...a downward gradation toward liquid asphalt and possibly to liquid petroleum itself" (Ham, 1956, p. 2); (c) A recent discovery in the far western edge of the Ouachita Mountains indicates that economically significant amounts of oil are present at least in part of the region (Morrison, 1980a); and (d) Reworking of a well on the Jumbo anticline, T2S, R15E, has resulted in a producing gas well (Morrison, 1980a). In addition, results from the present study indicate: (a) a cogenetic relationship between the oil and solid bitumen; (b) the presence of source rocks that correlate well to both oil and solid bitumen; and (c) that the study area is still thermally within the "liquid window." It is hoped, therefore, that this paper will help eliminate some of the previously mentioned obstacles to oil exploration in the region.

OIL AND SOLID BITUMEN CHARACTERIZATION

Previous Investigations

Physical and chemical analyses of crude oil and solid bitumens have been made for over 100 years. The initial purpose of these investigations was to classify these materials, although as analyses became more sophisticated, attempts to chemically correlate oils became increasingly common. Several comprehensive reviews of the physical and chemical properties of oil and solid bitumens have been published. The reader is referred to Smith (1968), Tissot and Welte (1978, Part IV) and Hunt (1979, Part I) for a summary of crude oil characterization and classification studies. Abraham (1945) presents a detailed discussion of the chemical and physical properties of asphaltic materials. Each of the techniques utilized in this paper is discussed in the above publications. Comparison of the results of this study with those of previous studies will be discussed later, where appropriate.

Although the literature on characterization and classification of crude oil is too voluminous to review separately, it will be useful to discuss in some detail previous studies concerning grahamite and impsonite, the two bituminous materials occurring in the Oklahoma Ouachitas. Preliminary to such a discussion however, it is necessary to present a brief history of classification schemes for asphaltic materials.

The earliest comprehensive classification scheme for bituminous substances was presented by Abraham (1945, pp. 66-67). He divided these materials into bitumens and pyrobitumens on the basis of their relative solubility in carbon disulfide. Bitumens are further divided into petroleums, native mineral waxes, native asphalts and asphaltites, while pyrobitumens are either asphaltic pyrobitumens or non-asphaltic pyrobitumens. These subdivisions are determined mainly by variation in physical properties such as color, hardness, luster, etc. Thus it should be stressed that these definitions are generic in nature, and have no genetic connotation.

Because these materials cannot be precisely defined in a chemical sense, the Abraham classification scheme is generally still utilized today, although usually in a modified form (Hunt, et al., 1954; Bell and Hunt, 1963; Rogers, et al., 1974; Wen, et al., 1978; see Figure 3). Such a generic classification scheme is sometimes useful in distinguishing one material from another, however in many cases physical properties intermediate between two types of materials have been noted. Such cases are discussed in detail by Abraham (1945). Since the present study concerns the genesis of specific asphaltic materials, a generic classification scheme will not suffice, and the discussion will concentrate on genetic relationships. Thus the terms grahamite and impsonite will be used only for historical convenience (Figure 3), because they have already been ingrained in the literature of the Ouachita Mountains.

Genetic classification schemes for solid bitumens have been proposed and are currently in use in Europe (Jacob, 1973, 1976). These

studies postulate a genetic relationship between grahamite and impsonite, in that the latter represents a metamorphosed product of the former. This idea was originally suggested by Abraham (1945, p. 279, 289). Evidence supporting this concept will be discussed in another section.

Grahamite occurs in several countries around the world, including Argentina, Cuba, Mexico, Peru, Trinidad, Turkey and the United States (Abraham, 1945; Lebkuchner, et al., 1972). Physical and chemical properties of grahamite, including Ouachita Mountain materials, are discussed in detail by Abraham (1945), Ham (1956) and Fay (1976; Fay, in preparation). Grahamite is classified as an asphaltite (Figure 3) having a specific gravity of 1.15-1.20 (at 77°F) and a fixed carbon content of 30-55%, on a mineral-free basis. Table 2 lists the results of chemical and physical analyses of grahamite worldwide, as compiled by several authors. The reader should take note of the variability in the elemental analyses, particularly that of sulfur, even from the same mine (e.g., Jumbo Mine, Oklahoma). Although ash content data are unavailable for these samples, the sulfur variability is still significant when normalized to carbon content. Results of the present study further suggest such non-homogeneity, based on elemental data.

Impsonite is considered to be the metamorphic equivalent of grahamite (Abraham, 1945, p. 298; Jacob, 1976), and is found in several countries, including Argentina, Australia, Brazil, Peru, Turkey and the United States (Abraham, 1945; Lebkuchner, et al., 1972). Typical analyses from the literature are listed in Table 3.

Table 2

Properties of Grahamite at Selected Localities, Worldwide

Locality and Reference	Fixed Carbon (%)	Solubility in CS_2 (%)	Specific Gravity	Elemental Analysis (Weight %)				
				C	H	O	N	S
West Virginia, USA Ritchie County (Abraham, 1945)	42.15-42.48	97.61	1.18-1.185	86.56	8.68	--	--	1.79
Texas, USA Fayette County (Abraham, 1945)	37.7	--	--	76.2	6.6	--	0.4	7.4
Texas, USA Webb County (Abraham, 1945)	52.8	--	--	78.6	7.5	--	1.2	5.4
Oklahoma, USA Location unknown (Wen, et al., 1978)	--	--	--	86.6	8.7	0.7	2.2	1.8
Oklahoma, USA Jumbo Mine (Abraham, 1945)	48.5-53.0	90.5-96.2	--	83.90	7.14	--	--	1.04-2.24
Oklahoma, USA Jumbo Mine (Taff, 1899)	--	--	1.175	86.57	7.26	2.00	1.68	1.38
Oklahoma, USA Sardis Mine (Abraham, 1945)	52.76-55.00	99.5+	1.18-1.20	--	--	--	--	--
Trinidad Vistabella (Abraham, 1945)	31.5-35.0	91.7-96.0	1.17-1.18	84.0	5.7	--	2.2	3.0-3.8

Table 3

Properties of Impsonite at Selected Localities, Worldwide

Locality and Reference	Fixed Carbon (%)	Solubility in CS_2 (%)	Specific Gravity	Sulfur (Wt.%)
Oklahoma, USA Page Mine (Abraham, 1945)	75.0-81.6	4-6	1.235	1.69
Oklahoma, USA Page Mine (King, et al., 1963)	-	3.2	1.27	1.1
Arkansas, USA Fourche Mt. Mine (Abraham, 1945)	80.0	Trace	1.25	-
Peru Canta & Yauli (Abraham, 1945)	72.2-88.2	-	1.25	-
Turkey (Southeastern) (Lebkuchner, et al., 1972)	-	4.9	-	-

Comparison of grahamite data from Oklahoma in Table 2 with impsonite data from Oklahoma and Arkansas in Table 3 indicates a lower solubility in methylene chloride for impsonite, as well as higher specific gravity and fixed carbon contents. These data are consistent with Jacob's (1976) description of impsonite as being metamorphosed grahamite. The data also correlate with changes in independent thermal maturity parameters for a west-to-east transect in southeastern Oklahoma, which indicate increasing thermal maturity to the east (Figure 2).

The following section concerns physical and chemical characteristics of oils and bitumens found in the study area. The purpose of this section is to present conclusions concerning oil-oil and bitumen-bitumen correlations, based on the chemical characteristics of each oil and bitumen sample. Such conclusions will be used to determine if the crude oils are commonly sourced, and if the solid bitumens have a common source.

Oil Characterization

Physical Characteristics

The four oils analyzed in this study were sampled at the fields indicated on Figure 2. These fields, South Bald, Bald, Redden and North Daisy, are located in the Frontal and Central Ouachitas and produce from the Jackfork and Stanley Groups (Figure 1; see also Appendix III, Table 16). Specific gravities and API gravities are listed in Table 4. These values are for untopped oils, at 60°F. Color determination (Table 4) is by comparison to the GSA Rock-Color Chart, distributed by the Geological Society of America. Loss on topping

Table 4

Ouachita Oils -- Physical Properties

Oil	Specific Gravity (60°F)	API (60°F)	Color[a]	Topping Loss[c] (%)
11 (South Bald)	0.8541	34.2	N 1 (Black)	15.7
15 (Bald)	0.8655	32.0	N 1 (Black)	14.5
17 (Redden)	0.8664	31.8	N 1 (Black)	9.3
45 (North Daisy)	(0.8106)[b]	(43.1)[b]	N 1 (Black)	19.1

[a] GSA Rock Color Chart

[b] Measured as weight per unit volume; i.e., a hydrometer was not used.

[c] Precision is better than $\pm$ 0.1%.

(definition, Appendix I) is also indicated in Table 4, although most of the chemical analyses discussed below were conducted on untopped oils.

Most of the API gravities in Table 4 are significantly lower than those noted by Fay (1976) for these oils, probably due to the earlier determinations being made at a much higher oil temperature. Nevertheless, although shallow oils are generally lower in API gravity than their deeper counterparts (Price, 1980), the API gravities listed in Table 4 are still relatively high for oils produced from as shallow as 148 feet subsurface (Oil 17, Redden Field; see the tables in Appendix III for other subsurface depths of production).

Chemical Characteristics

Conventional chemical techniques were used to analyze the four crude oils of this study. These analyses are listed below, in the order in which they will be discussed. The numerical data are presented in Tables 5 and 6.

Fractionation Data

Elemental Analyses and Ratios

Metal Analyses and Ratios

Isotopic Analyses

N-Alkane and Isoprenoid Isoalkane Analyses

Infrared Spectra

Sterane and Terpane Analyses

Fractionations. Each of the four untopped crude oils was fractionated into paraffinic hydrocarbons, aromatic hydrocarbons,

Table 5

Ouachita Oils -- Whole Oil Data

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 = $\pm$ 15 %.

[c] Relative to PDB standard.

[d] Relative to troilite standard.

Table 6

Ouachita Oils -- Fraction Data

OIL	Saturate Hydrocarbons							Arom HC		NSO		Asphaltenes				
	%[a]	13_C[b] (ppt)	pr/ph	n-C_{17}/pr	n-C_{18}/ph	CPI[c]	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):

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

[d] Precision = $\pm$ 20 %.

nitrogen-, sulfur-, and oxygen-containing compounds (NSOs) and asphaltenes. Results are presented in tabular form in Table 6 and graphically in Figure 8. On this basis, these oils can be classified as normal undegraded crude oils, according to Tissot and Welte (1978, p. 338).

Elemental Analyses and Ratios. Table 5 lists results of elemental analyses for the oils, in raw weight percentage and also normalized to carbon content, on an atomic ratio basis. Few examples of whole oil carbon and hydrogen elemental data are available in the literature (Colombo and Sironi, 1961; Rubinstein, et al., 1977). Colombo and Sironi (1961) presented data for the "oily components" of some crude oils. Oily components were analytically defined as the non-(resin + asphaltene + carbene) fraction of the oil. H/C atomic ratios of the oily components of ten low sulfur oils from the Po Valley and Northern Apennine area of Italy (consisting of over 95% oily components) range from 1.57 to 1.84. Note that these oils, although from depths as shallow as 650 feet, are "...remarkably light and not very altered: this is indicative of good trap efficiencies and consequently of only weak contacts with alteration agents" (Colombo and Sironi, 1961, p. 37). Also of interest is the presence of asphalt in outcrops located north (100 miles) and south (200 miles) of the zone of oil production, whose "oily components" atomic H/C ratios are equal to or lower than those of the oils. A similar relationship is found in this study for solid bitumens associated with Ouachita oils.

Tissot and Welte (1978, pp. 356-363) have summarized analyses for nitrogen and sulfur that suggest that the oils analyzed for the

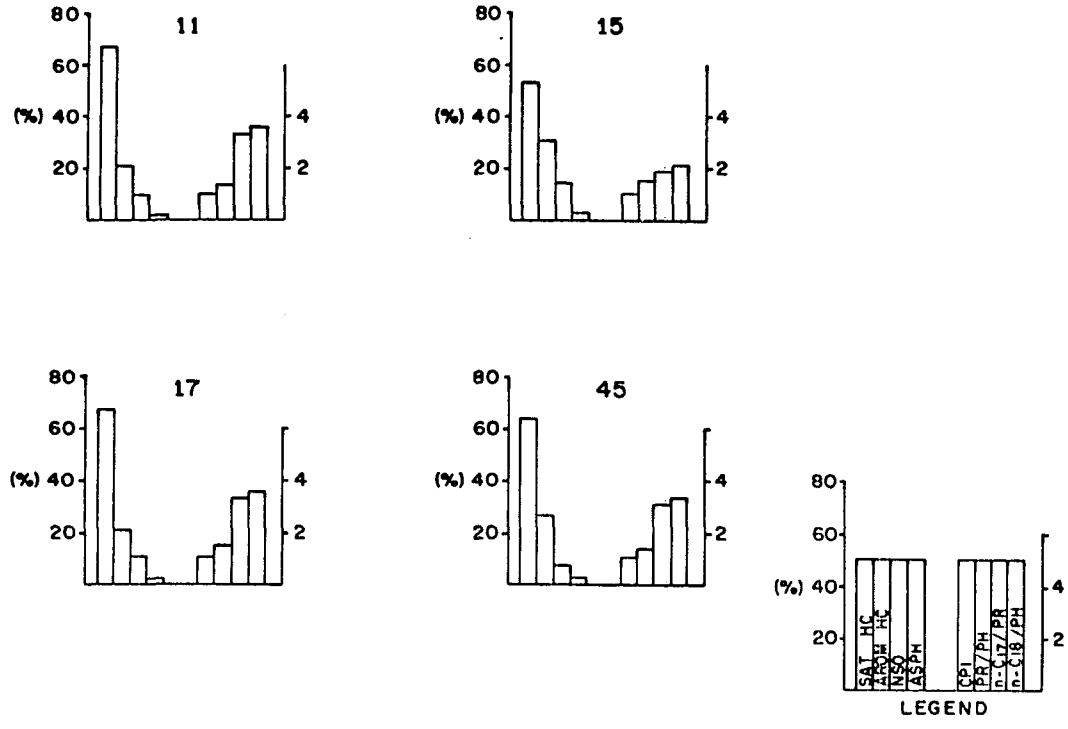


Figure 8. Graphic Display of Oil Fractions and N-Alkane/Isoprenoid Ratios. PR = Pristane; PH = Phytane. Others defined in text.

present study are average with respect to concentration of these elements. The nitrogen concentrations of the four oils listed in Table 5 agree with the 0.10% (by weight) nitrogen value reported by Costantinides and Arich (1967) for an average mid-Continent oil. Nitrogen concentrations for these oils would be considered fairly normal when compared with values cited by Tissot and Welte (1978), being less than 0.25% in all cases. This result is similar to the 0.17% average found by Vinogradov and Galimov (1970) for 24 oils of the Soviet Union. However, 2465 oil analyses plotted by Smith (1968) indicate a mean nitrogen content of about 0.06% nitrogen, indicating that Ouachita oils may be somewhat above average in nitrogen content. In view of this, note a comment by Strothman (1981) to the effect that the Vierson-Cochran well originally flowed a mixture consisting of 40% nitrogen gas. This well, located in Section 25, T5S R23E, is just east of the Core Area of the Oklahoma Ouachita Mountains. Unfortunately, no data suggesting an origin for this nitrogen is available.

The sulfur content of the oils is considered normal, being within the lower mode of a bimodal distribution of 9315 oil analyses published by Tissot and Welte (1978, p. 356). On this basis the Ouachita oils are classified as low-sulfur crudes.

Limited elemental oxygen data of crude oils are available for comparison with those of the present study. Ball, et al. (1959) analyzed Ponca City, Oklahoma, and Wilmington, California, crudes for total oxygen. The determinations were 0.06% and 0.44%, respectively. The latter value is within the range of oxygen values reported in Table 5. However, Rubinstein, et al. (1977) reported oxygen analyses

for Prudhoe Bay and Bellshill Lake oils of 0.82% and 0.87%, respectively. These values are much higher than those of the present study. Clearly, the oxygen content of crude oils varies considerably.

Metal Analyses and Ratios. Three of the whole (unfractionated) oils of this study were also analyzed for trace metal content, specifically the metals vanadium and nickel. Individual asphaltene fractions were also analyzed for these metals. Vanadium and nickel contents for the whole oils are in the ranges 8.8-20.2 ppm and 2.5-7.0 ppm, respectively, while the V/Ni ratio ranges from 2.15 to 3.59. Asphaltenes have vanadium and nickel contents of 112.1-149.9 ppm and 63.3-123.0 ppm, respectively, with a V/Ni ratio from 1.22-2.34. Results are listed in Tables 5 and 6.

The whole oil metal analyses show that the concentrations of vanadium and nickel fall within the typical crude oil ranges noted by Jones (1977) for these metals. 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-reservoired 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, it appears that the Ouachita oils are distinct among Oklahoma crudes.

I am not aware of any published analyses of metal content of the asphaltene fraction of conventionally-produced oil. However,

Branthaver and Dorrence (1978) have studied the asphaltene content of tar sands at Battle Creek, Wyoming, and found vanadium and nickel concentrations of 382 ppm and 164 ppm, respectively. In addition, Yen, et al. (1978) have analyzed shale oil asphaltenes from three samples of the Green River Formation for vanadium and nickel. These materials had average vanadium and nickel concentrations of 5.7 and 60.7 ppm, respectively.

It has been suggested that the bulk of the trace metals in crude oil, especially vanadium and nickel, reside in the heavy fractions of crude oil (Shirey, 1931; Bonham, 1956; Branthaver and Dorrence, 1978; Tissot and Welte, 1978). Other suggestions have been advanced relating porphyrin content and the nickel and vanadium content of an oil (Treibs, 1934; Dunning, 1963). Collectively, these suggestions imply that porphyrins themselves are associated with the resin and asphaltene fractions of crude oil. However, data from the present study do not support some of these findings.

The metal concentrations in the asphaltene fraction and the percentage asphaltene in the whole oil (Table 6) show that a large percentage of the nickel and vanadium in the oils is not contained in the asphaltene fraction in two of the three oils examined. The asphaltene fraction of oils from 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 present (Tables 5 and 6). These data indicate that vanadium and nickel are, in most cases, not concentrated in the asphaltene fraction of Ouachita oils and suggests that they exist in forms other that porphyrin complexes, as shown by Speight (1980, p. 76). A more important ramification of this data however,

concerns changes in V/Ni ratios with degradation. Because the V/Ni ratio is higher for the nonasphaltene compounds in these oils, the removal of these compounds, i.e., biodegradation and devolatilization, will reduce the V/Ni ratio of the residual material.

Isotopic Analyses. 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, NSO compound and asphaltene fractions were analyzed for their carbon isotope ratios. Data are reported in Tables 5 and 6. The notation used is as follows:

$$\delta^{13}C\ (^{o}/oo) = 1000\ X\ \left(\frac{(^{13}C/^{12}C)_{sample}}{(^{13}C/^{12}C)_{reference}} - 1\right)$$

$$\delta^{34}S\ (^{o}/oo) = 1000\ x\ \left(\frac{(^{34}S/^{32}S)_{sample}}{(^{34}S/^{32}S)_{reference}} - 1\right)$$

Reference isotope ratios for carbon and sulfur were the usual Peedee Formation belemnite (PDB) calcium carbonate standard for carbon, and Canon Diablo troilite for sulfur (working standards are listed in Appendix II). Values are cited as parts per thousand (ppt, or $^{o}/oo$).

The carbon isotope ratios for the four (whole) oils are very similar. These values are within the range reported by Craig (1953), Silverman and Epstein (1958), Eckelmann, et al. (1962), Silverman (1967) and Fuex (1977) for crude oils and bituminous materials. The ratio for these oils falls midway between oils of non-marine (-34 to -30 $^{o}/oo$) and oils of 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 non-marine origin to crude oils based solely on carbon isotope ratio. Studies have shown that oils sourced from, and kerogens isolated from, Cambro-Ordovician rocks show very light (often less than -30 °/oo) carbon ratios (Welte, 1965; Welte, et al., 1975a).

Based on numerical criteria cited above, this organic matter would be classified as non-marine in origin, even though a terrigenous source would presumably have been impossible in the early Paleozoic. Consequently, it is not possible to determine the marine or non-marine origin of the Ouachita oils until a source for these oils is established. As will be discussed in greater detail in the section on source rock-oil correlation, the light carbon isotope ratio for these oils is most probably due to a lower Paleozoic (marine) source, rather than a terrigenous source.

Several authors have reported sulfur isotope ratios for crude oils (Thode, et al., 1958; Thode and Monster, 1964; Monster, 1972; Mauger, et al., 1973; Orr, 1974). Thode, et al. (1958) reported a range of sulfur values of approximately +45 °/oo for petroleum, indicating that the range of values for the three oils of the present study is about 10% of the total range of all oils. The values for the present study, +14.3 to +18.9 °/oo, are relatively heavy for crude oils, being close to the value for present-day seawater sulfate of +20 °/oo. In general, the only oils exhibiting values in this range are from Devonian reservoirs in Canada and from the Uinta Basin, USA. Thode, et al. (1958) reported values of +10.8 to +15.5 °/oo for oils in the Alberta Basin. Sulfur isotope ratios of -2.0 to +28.2 °/oo were found for oils from Uinta Basin (Mauger, et al., 1973).

In addition to whole oil analysis, carbon isotope ratios were also determined for each of the fractions of the four oils (Table 6). These data are presented graphically as "isotope type-curves" in Figure 9 (Stahl, 1978). Most noteworthy about these data is the general lack of a trend of more negative isotopic ratios as fraction polarity decreases, as is 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, as discussed by Stahl (1980). Stahl suggests that this phenomenon is due to secondary formation of asphaltenes in the oil at the expense of the saturate hydrocarbon fraction. Although the steep slope of the isotope type-curve for the oils of the present study suggests that biodegradation is involved, chromatographic analysis of the paraffinic fraction shows that the microbial attack on these oils has been minimal.

A recent study of oils of the Bighorn Basin by Chung, et al. (in preparation) has also 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 non-biodegraded oils. Furthermore, one of the oils studied by Monster exhibited

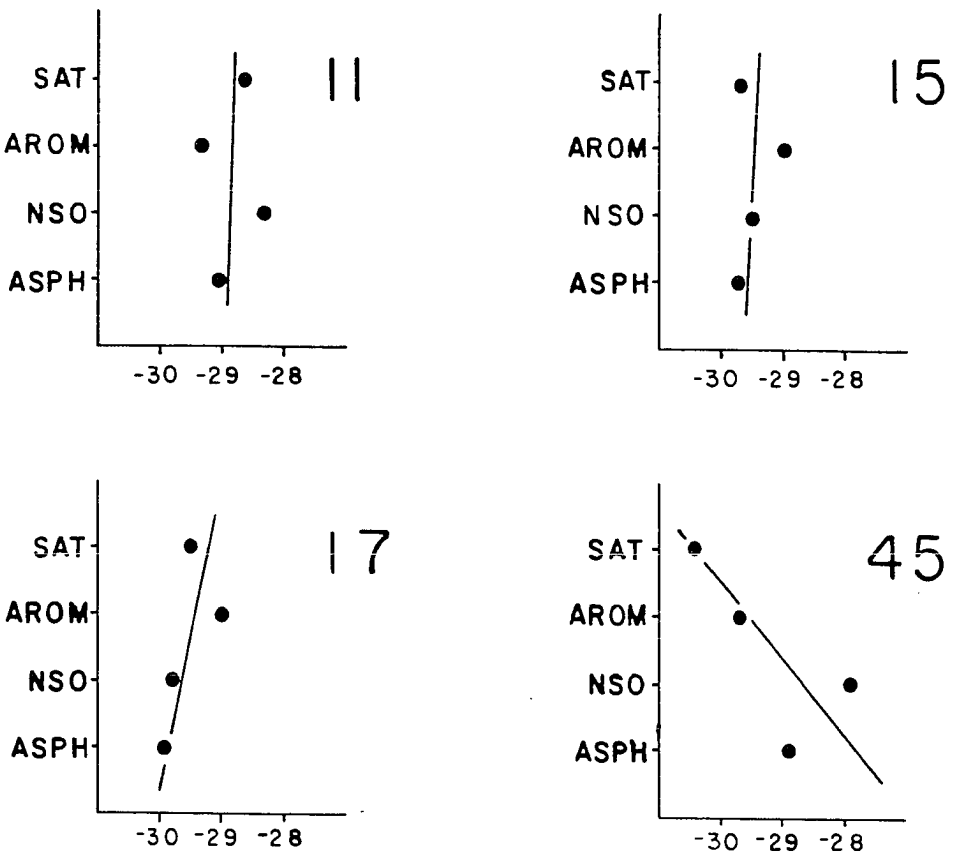


Figure 9. Isotope Type-Curves for Ouachita Oils. SAT = Saturate (i.e., Paraffinic) Hydrocarbons; AROM = Aromatic Hydrocarbons; NSO = Nitrogen-, Sulfur-, and Oxygen-Containing Compounds; ASPH = Asphaltenes. All carbon isotope values in this figure and all other figures are relative to the PDB standard.

an aromatic fraction lighter than the saturate fraction, as observed for oil 11 of the present study. These findings suggest that the interpretation of isotope type-curves is still very speculative and should be approached with caution. It is possible that the use of such curves may be invalid for Paleozoic oils.

Of the carbon isotope ratios of the four fractions examined in this study, the asphaltene ratios are consistently very close to the ratios of the whole oils (Tables 5 and 6). Similar effects were reported by Jha, et al. (1979) for the Athabasca tar sand bitumen. These authors noted that the isotope value of bitumen from the tar sand is very similar to that of asphaltene fractions of the bitumen. Origin of the bitumen in these sands is still in question, although biodegradation has been suggested (Deroo, et al., 1974).

N-Alkane and Isoprenoid Isoalkane Analyses. 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, and the saturate hydrocarbon fraction was analyzed by gas chromatography in order to determine whether n-alkanes were co-eluting with compounds of the aromatic, NSO or asphaltene fractions in whole oil chromatograms. The n-alkanes were not co-eluting with compounds from these fractions, and data reported on n-alkanes and isoprenoid isoalkane are from whole-oil gas chromatograms.

Table 19 of Appendix IV presents the crude oil FID-response-percentage data for the n-alkanes having 15 through 33 carbon atoms, and the isoprenoid isoalkanes possessing 15, 16, 18, 19 and 20 carbon

atoms. Figure 10 presents the chromatograms for each of the oils, while Figures 11 and 12 graphically depict the n-alkane and isoprenoid isoalkane distributions for the oils. Since 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 10.

The ratios of pristane/phytane (PR/PH), n-heptadecane/pristane ($n\text{-}C_{17}$/PR), and n-octadecane/phytane ($n\text{-}C_{18}$/PH) for each of the oils are listed in Table 6. The initial isoprenoid isoalkane composition of an oil can differ due to both maturity and organic matter source environment (Robinson, et al., 1965; Tissot, et al., 1971). Thus, correct interpretation of the above ratios will yield abundant information about the origin of an unaltered oil. Tissot and Welte (1978) note that production of pristane and phytane can result from deposition in reducing as well as oxidizing environments. Further, the phytane content of an oil will tend to decrease with time and depth due to thermal cracking, producing increased amounts of the lower molecular weight isoprenoids (Robinson, et al., 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 of the present study, in anticipation of its usefulness as a correlation parameter (Welte, et al., 1975b). In the case of the oils listed in Table 6, the ratio of pristane/phytane ranges from 1.38 to 1.46. These values are relatively low, and suggest an oil produced from a clastic marine rock sequence (Brooks, et al., 1969; Powell and McKirdy, 1975). In contrast,

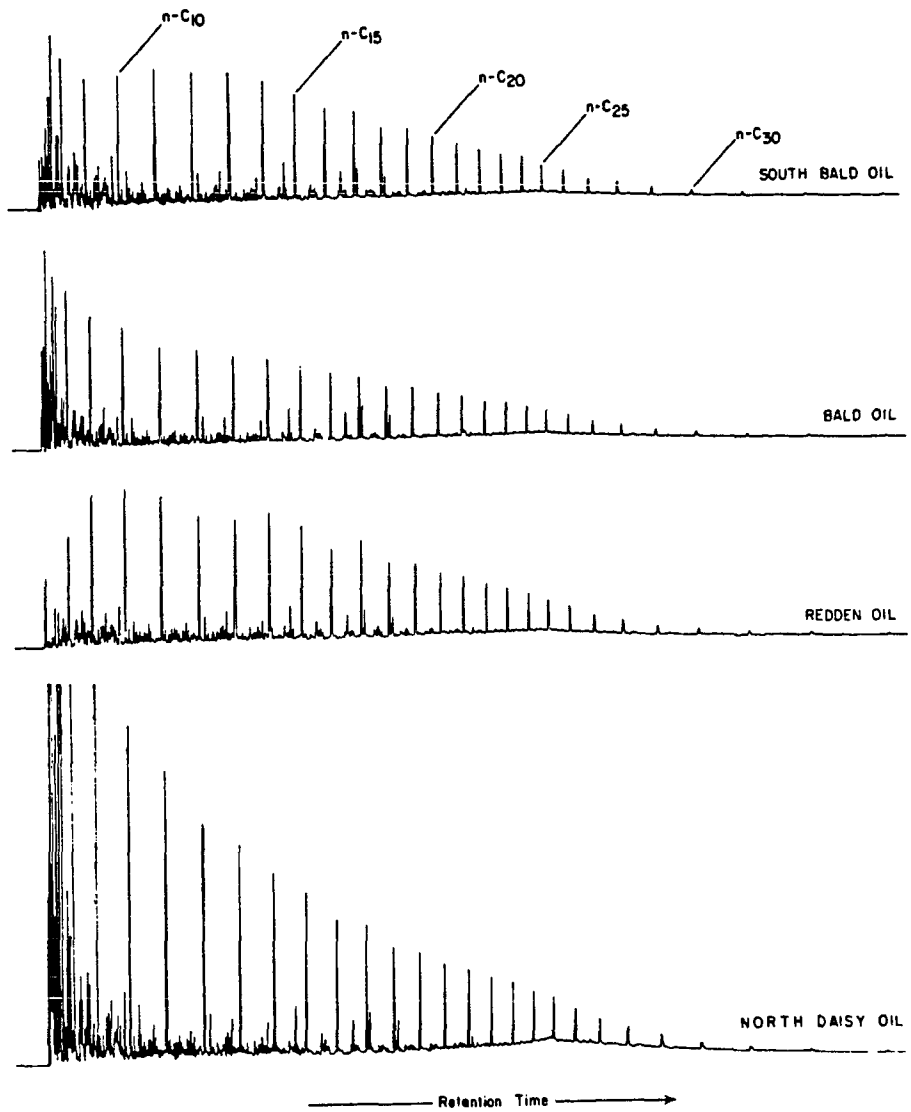


Figure 10. Gas Chromatograms of Ouachita Oils. Chromatograph conditions (see also Appendix II): 75°C (held 2 minutes); 10°C/minute ramp; 275°C (held 20 minutes). Injection temperature: 270°C; FID temperature: 300°C. Capillary head pressure: 20 psi.

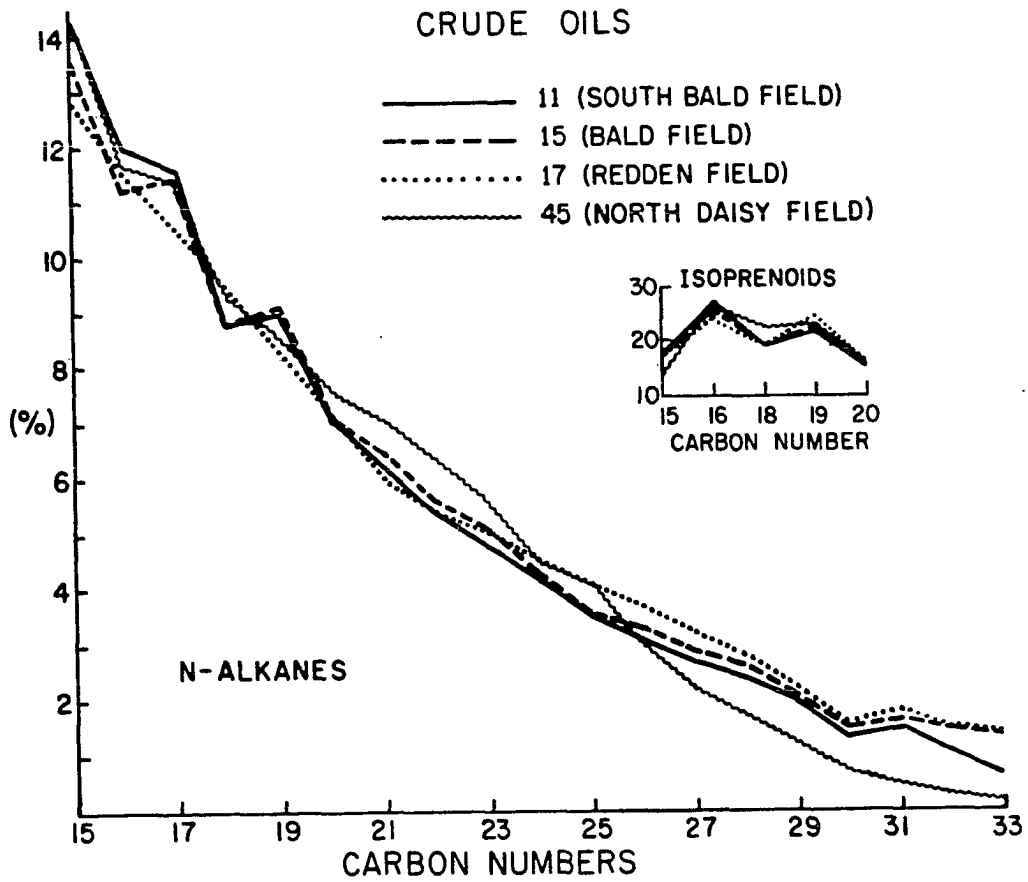


Figure 11. N-Alkane and Isoprenoid Isoalkane Distributions of Ouachita Oils. Depression of the high carbon numbers in curve for oil 45 is attributed to use of peak height measurements rather than automatic area integration (see Table 19, Appendix V).

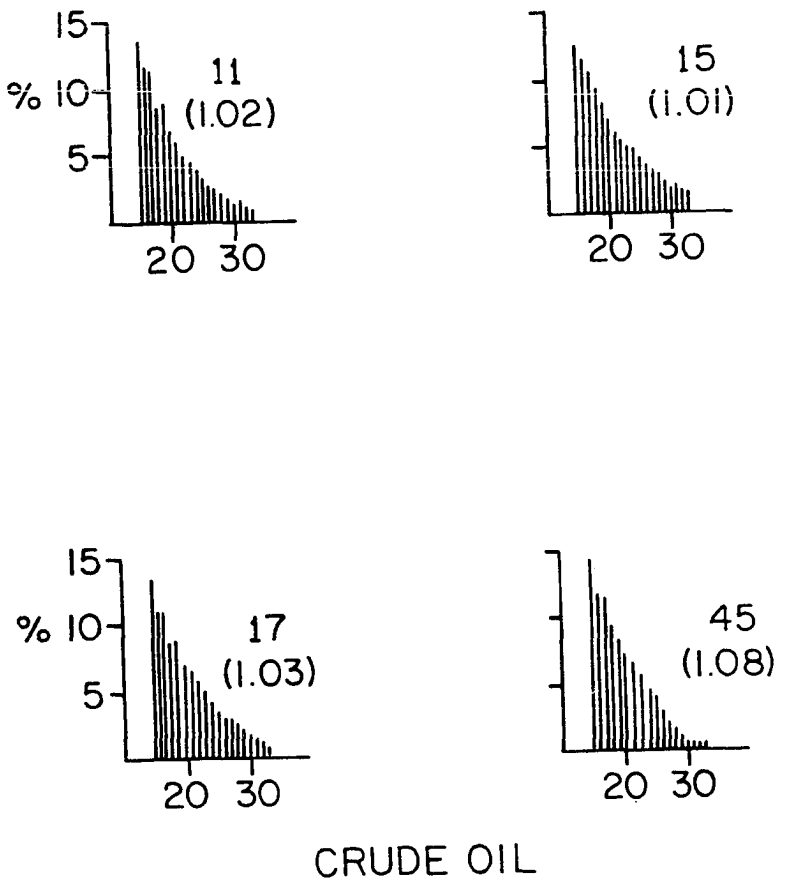


Figure 12. Histograms showing the N-Alkane Distributions of Ouachita Oils. Carbon preference indices, as defined in Table 6, are shown in parentheses.

some of the highest ratios measured to date are in high-volatile bituminous coals, having values from 7 to 10 (Tissot and Welte, 1978, p. 387).

Pristane/phytane ratios were utilized by Powell and McKirdy (1975) in a study of the composition of oils from Australia and New Guinea. These authors suggest that a greater marine source dominance produced a lower ratio in the resultant oils. Seven of the oils they analyzed were described as having an "unequivocal" marine source; all had a pristane/phytane ratio less than 3, as do the four oils of the present study. Of these seven oils, all were of naphthenic-to-aromatic type except one. This sample was a paraffinic Ordovician-reservoired oil of unusually low pristane/phytane ratio. Although use of this ratio as evidence for defining an oil as marine or non-marine in origin is still speculative, the data would certainly support a predominantly marine source in this case (Brooks, et al., 1969). However, the oils of the present study are undoubtably Paleozoic in origin, and thus would have had sufficient time for maturity-induced variation of the pristane/phytane ratio to occur.

In addition to the pristane/phytane ratio, the ratios of n-heptadecane/pristane and n-octadecane/phytane are also listed in Table 6, for each of the oils of this study. Interpretation of these ratios is also subject to debate. A decrease in both ratios would suggest biodegradation of a mature oil, since microbial attack will preferentially remove the n-alkanes (Deroo, et al., 1974). However, Lijmbach (1975) suggests that, for an undegraded oil, the ratio of n-heptadecane/pristane is indicative of the environment of deposition,

in that a high ratio (greater than or equal to 2.0) implies an aquatic origin, rather than a peaty or coastal environment. Data in Table 6 indicate that the oils of the present study exhibit such a high ratio.

A high ratio of n-heptadecane/pristane may also provide information about the ultimate source organism of these hydrocarbons. Han and Calvin (1969), in an excellent paper on the distribution of hydrocarbons in algae and bacteria, report that normal heptadecane ($n\text{-}C_{17}$) is the dominant compound in hydrocarbons present in photosynthetic microorganisms. For example, $n\text{-}C_{17}$ constituted an average of 85% of the major hydrocarbon present in four species of blue-green algae. This predominance is missing in most non-photosynthetic bacteria. In addition, Han and Calvin (1969) report that isoprenoid isoalkane, are common metabolic products of photosynthetic bacteria, yet are absent in blue-green and green algae. These findings suggest the possibility of a source environment control on the n-heptadecane/pristane ratio of a crude oil.

Although n-heptadecane ($n\text{-}C_{17}$) levels are fairly high in three of the oils analyzed in this study, one should be cautious in interpreting this data, because secondary sample contamination could also cause this phenomenon. For example, Nooner, et al. (1972) have demonstrated that recent algae are capable of synthesizing n-heptadecane. Later Debyser (1975) noted anomalously high concentrations of this n-alkane in recent sediments. In view of the earlier discoveries by Nooner, et al. (1972), Debyser attributed the presence of this hydrocarbon to contamination. In reference to the data of the present study however, this writer feels that the high concentration of $n\text{-}C_{17}$

in three of the oils (Figure 11) requires an explanation other than simple contamination, because n-nonadecane (n-C_{19}) shows a slight predominance as well.

It can be seen from Figure 11 that three of the oils show a minor predominance at both n-C_{17} and n-C_{19}, while the fourth (a sample from Bald Field) does not. Assuming this predominance is not due to contamination, biochemical input appears to influence the concentration of these two hydrocarbons. This many occur by deposition of organic matter rich in n-C_{17} and n-C_{19}, or by decarboxylation of C_{18} and C_{20} fatty acids. There is not enough evidence to make in interpretation as to which mechanism is most likely. However, one or the other of these n-alkanes is relatively high in concentration in certain species of blue-green algae and one species of non-photosynthetic bacteria examined by Han and Calvin (1969). These are two of the most primitive life-forms known.

A relative predominance of n-C_{17} and n-C_{19} was noted by Williams (1974) in oils of Williston Basin. Three oil types were distinguished, partially on the basis of n-alkane distribution of the C_{15+} saturate hydrocarbon fraction. One of these oil types, subsequently matched to a lower Ordovician source rock, showed (1) a pronounced dominance of n-C_{17} and n-C_{19} in the saturate hydrocarbon fraction, and (2) a gradual decrease in n-alkane content in the C_{20+} fraction. These features are similar to three oils in the present study, although the n-C_{17} and n-C_{19} dominance is not as strong for the Ouachita oils. Analyses reported by Martin, et al. (1963) suggest the possibility that such predominances are a result of simple life forms

existing at this time. Again however, no direct evidence exists to support this suggestion.

In addition to ratio data for the saturate hydrocarbons in Table 6, carbon preference indices (CPIs) for each of the oils are also listed. These CPIs are calculated for the interval C_{22} to C_{30}, rather than the original interval suggested by Bray and Evans (1961) of C_{24} to C_{34}, or a second interval from C_{24} to C_{32}, as used by Hunt (1973). Further, calculations used throughout this study are based on FID response, rather than mole percentages for each alkane.

Inspection of the CPI data in Table 6 shows that the Ouachita oils lack a significant odd-even predominance. If there was an initially high terrigenous component in the organic content of the source rock, one would expect (Tissot and Welte, 1978) a dominance of odd-carbon number n-alkanes in an immature oil sourced from this rock. A lack of such a dominance could indicate that these oils were expelled from a fully mature rock. Alternatively, if the organic matter of the source rock was originally predominantly marine in origin, such an initial dominance would not be expected. Therefore the carbon preference index, in the range C_{22} to C_{30} would be close to 1.0 regardless of the maturity of the oil, and the CPI would have no meaning for characterization purposes. The second case is a definite possibility in the event these oils were sourced from early Paleozoic rocks (Hunt, 1979, p. 310).

A better definition of the Ouachita oils as marine or non-marine is provided by Philippi (1974), who used the n-alkane ratio

$(C_{21} + C_{22})/(C_{28} + C_{29})$ as a source indicator. Analysis of many oils worldwide indicated that a value for this ratio of 0.6 to 1.2 suggests a terrigenous source for the organic matter which produced the oil, while a ratio of 1.5 to 5.0 suggests a marine source. Using the data listed in Table 19 (Appendix V), 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.

Infrared Spectra. Two of the four chemical fractions of each of the four crude oils were analyzed by infrared spectrometry (4000 cm^{-1} to 600 cm^{-1}). Due to the similarity of infrared spectra of paraffins, the paraffinic fraction was not analyzed. Nor was the NSO fraction, because so little is know of its chemical structure. The infrared (IR) spectra of the aromatic and asphaltene fractions of the oils are shown in Figures 13 and 14, respectively. Both figures list suggested band assignments from Yen, et al. (1978), and Silverstein, et al. (1974).

Very little information about infrared spectrometry of whole oils or their chemical class fractions exists in the literature. Most of the IR data available concerns spectra of specific distillation fractions. The information that does exist concerning chemical fractions pertains largely to the asphaltene fraction of crude oil (Witherspoon and Winniford, 1967) and shale oil (Yen, et al., 1978; Kemp-Jones, et al., 1978). The purpose of obtaining IR spectra for these fractions in this study is to establish their usefulness as an oil-oil correlation tool. This application will be discussed in more detail later.

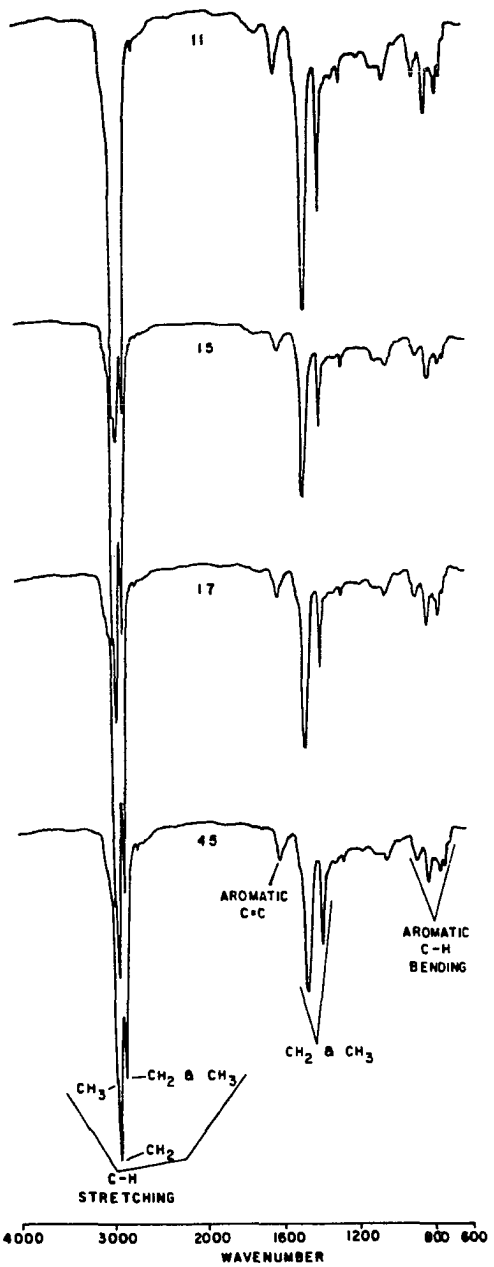


Figure 13. Infrared Spectra of Aromatic Fractions of Ouachita Oils. Abscissa scale changes at 2000 cm^{-1}.

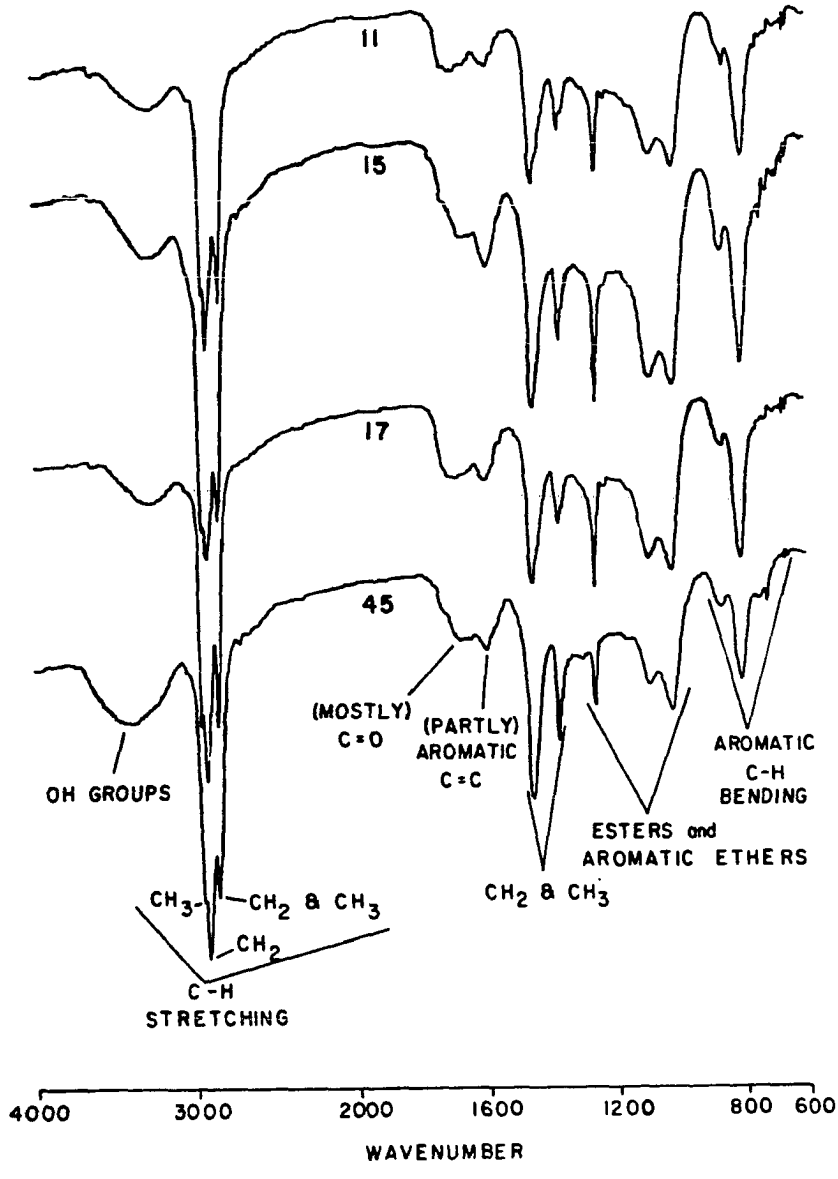


Figure 14. Infrared Spectra of Asphaltene Fractions of Ouachita Oils. Abscissa scale changes at 2000 cm^{-1}.

Sterane and Terpane Analysis. In addition to the previously discussed analyses, each of the four oils was analyzed qualitatively for steranes and terpanes. Prior to discussing the details of these distributions, a brief review of molecular structure and biochemical genesis of each of these compound types will be presented.

Steranes are tetracyclic saturated hydrocarbons, containing three six-membered rings and one five-membered ring (Figure 15). Steranes of 27, 28 and 29 carbon atoms have molecular formulae of $C_{27}H_{48}$, $C_{28}H_{50}$ and $C_{29}H_{52}$, respectively. Steroid nomenclature is based on assignment of a number to each carbon atom, and a capital letter to each ring, as shown in Figure 15. Carbon atoms 18 and 19 are methyl groups ($-CH_3$) located at carbon atoms 10 and 13, respectively. In addition, a hydrogen atom or a methyl group attached to a ring juncture is designated alpha (a) if it extends behind the plane of the paper, or beta (b) if it is above the plane of the paper. An alpha bond is designated by a dashed line, while a beta bond is designated by a solid line. A wavy line implies no assignment. Adjacent rings are designated cis to each other if the two substituent groups (H or CH_3) at their juncture are both alpha or both beta. If they are alpha/beta or beta/alpha, the ring juncture is trans. For example, the A/B rings of regular steranes are cis if the hydrogen at position 5 is beta, since all regular steranes discussed here possess beta "stereochemistry" for the methyl group at position 10 (see Figure 15). Finally, attachment of substituent groups at positions 20 (H) and 24 (H, CH_3 or C_2H_5) are configurationally-defined as R or S according to sequence rules that are beyond the scope of this paper. For more

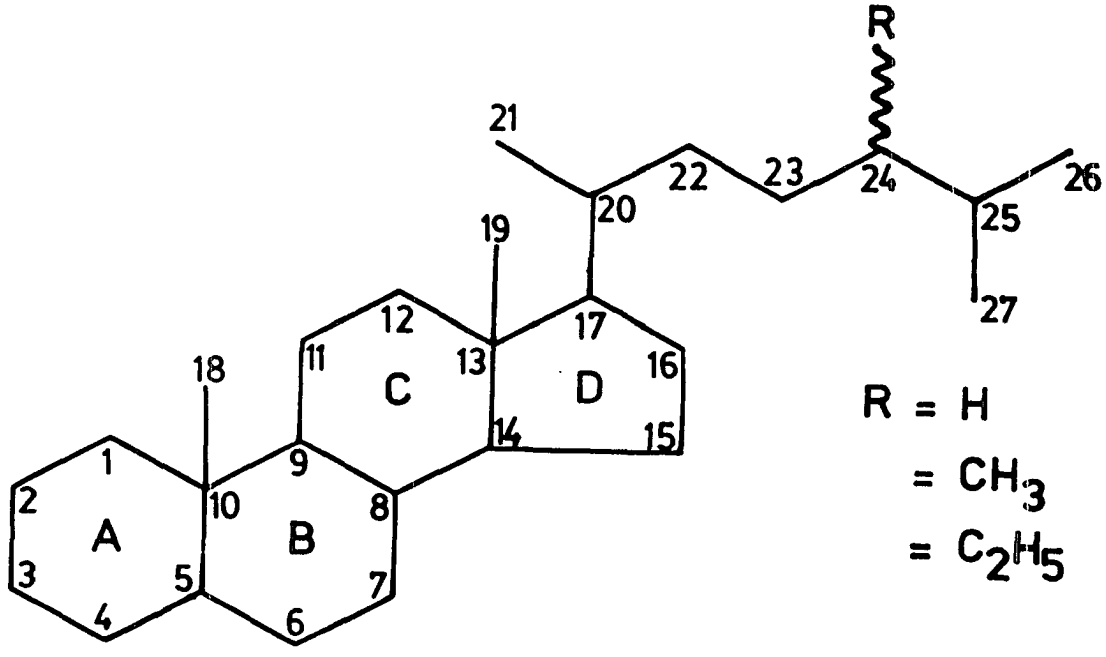


Figure 15. Molecular Structure of a Regular Sterane. Stereochemistry at all chiral centers is not shown. (From Seifert and Moldowan, 1979.)

details concerning steroid nomenclature, see Definitive Rules for Nomenclature of Steroids (1971), issued by the International Union of Pure and Applied Chemistry (IUPAC) Commission on the Nomenclature of Organic Chemistry, and the IUPAC-International Union of Biochemistry Commission on Biochemical Nomenclature.

Steranes are present in geologic materials in both regular and rearranged forms (Ensminger, et al., 1978; Seifert and Moldowan, 1979). The stereochemical assignment and methyl-group location differences in these two forms are depicted in Figure 15 (Regular) and in Figure 16 (Rearranged), and consist of a change from 8b, 9a, 10b in regular steranes, to 8a, 9b, 10a in rearranged steranes. Ensminger, et al. (1978) originally proposed classification of the rearranged steranes (or diasteranes) by defining the sterochemistry at the 13 and 17 positions. This convention is followed here: the diasteranes discussed in this study are 5b, 8a, 9b, 10a, 14b. Conversely, all regular steranes discussed are 8b, 9a, 10b, 13b. All discussion will be in terms of peak numbers, as shown in figures to be introduced later.

Because of significant structural similarities, steranes are assumed to be degradation products of sterols of living organisms (Whitehead, 1973a; Mulheirn and Ryback, 1975; Seifert, 1977), and are referred to as biomarkers or geochemical fossils. Their presence in many oils offers strong evidence of the biogenic nature of this material. Also, the presence of steroids in pre-Cambrian rocks suggests that complex processes of sterol biosynthesis were operative in life forms as long ago as 2.7 billion years (Burlingame, et al., 1965).

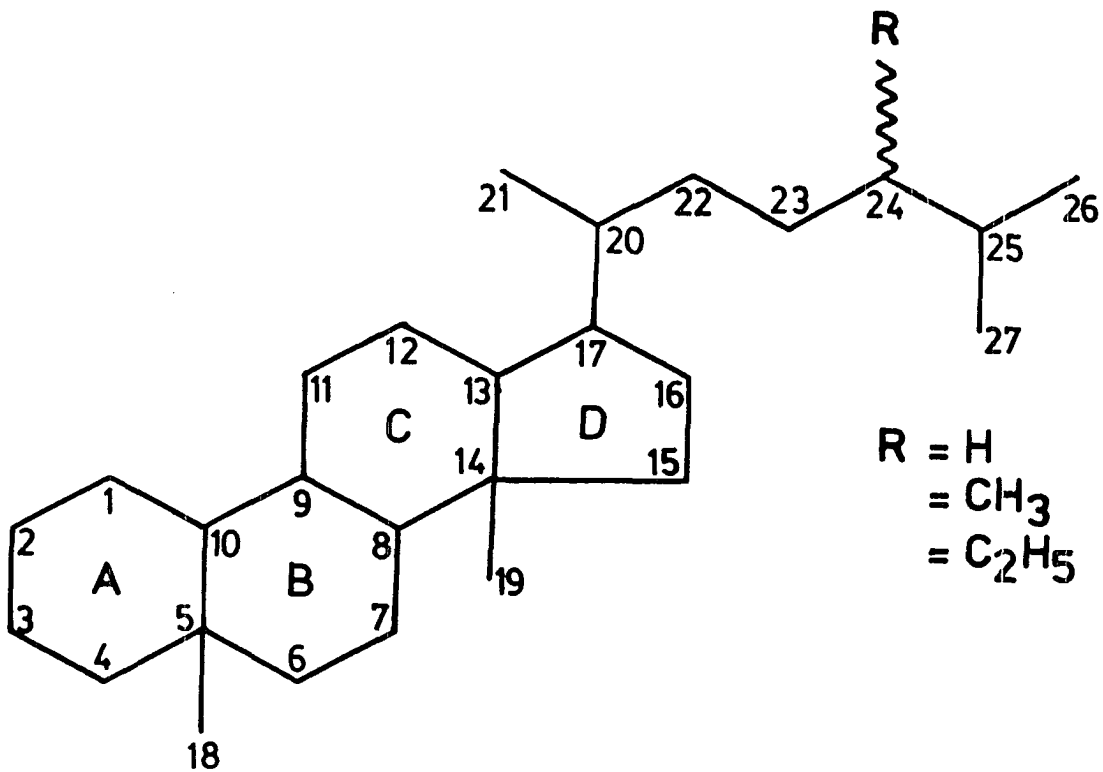


Figure 16. Molecular Structure of a Rearranged Sterane. Stereochemistry at all chiral centers is not shown. (From Seifert and Moldowan, 1979, and Ensminger, et al., 1978.)

In addition to steranes, terpanes are examined in the present study. These compounds, in the case of the present study, are tricyclic or pentacyclic saturated hydrocarbons. Although tricyclic terpanes are probably present in oils and source extracts of this study, pentacyclic triterpanes, and in particular hopanes, predominate. Thus only the nomenclature of hopanoids is reviewed here.

Figure 17 shows the carbon atom numbering and ring lettering appropriate for the common hopanes, including those discussed in this paper. The ab designations are identical to those of steranes. The stereochemistry of the H atom at positions 17 and 21 is used to define groups of triterpenoids having this structural framework. The 17b(H), 21b(H) is considered to be the "true" hopane series, because it is found in living organisms; the moretane series is 17b(H), 21a(H), while 17a(H), 21b(H) is another hopane series. The latter is common to crude oils, but has not been described from living organisms (Van Dorsselaer, et al., 1974). The 17a(H), 21b(H) series is the only one discussed here.

Hopanes signify loss or gain of a carbon atom (usually a methyl group) by a change in the name. The loss of one, two or three methyl groups from the hopane structure (Figure 17) results in a name change to nor-, bisnor-, and trisnorhopane, respectively. The gain of a methyl group (at the C_{30} position) is designated a homohopane. For example, 17a(H), 18a(H), 21b(H)-28, 30-Bisnorhopane is a 17a(H), 21b(H) hopane that has lost methyl groups 28 and 30, and replaced the loss of C_{28} at the 18 position, originally alpha to the rings, with a hydrogen atom that is also alpha to the rings.

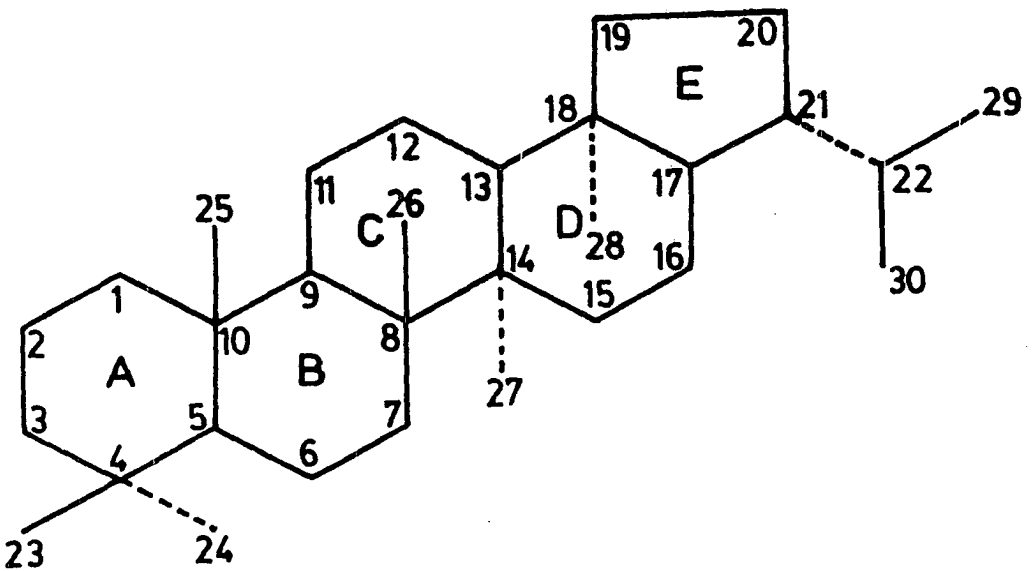


Figure 17. Molecular Structure of Hopane. Stereochemistry of hydrogen atoms at chiral centers is not shown.

The biochemical origin of the 17a(H), 21b(H) hopane series is less clear than in the case of the steranes, although they are presumed to derive from the 17b(H), 21b(H) series (Van Dorsselaer, et al., 1977; Ekweozor, et al., 1979b). Pentacyclic terpenoids in general were originally considered to result from contributions to the sediments of higher plant organic matter, although later evidence indicates a procaryotic origin. Hopanes have been found in measurable quantities in bacteria and blue-green algae (Ensminger, et al., 1973). More recently, Ourisson, et al. (1979) demonstrated that hopanoids are indeed widely distributed among procaryotes. These authors further suggest that hopanes themselves are more primitive, in an evolutionary sense, than steranes, although both are presumed to be biosynthesized from squalene, a C_{30} unsaturated acyclic precursor. Ourisson, et al. (1979) infer the probability of hopane biosynthesis prior to the evolution of photosynthetic organisms. Nevertheless, a general consensus as to biochemical origin of 17a(H), 21b(H) sedimentary hopanes is currently unavailable.

Before concluding this brief review of steranes and hopanes, it is necessary to discuss the nature of the instrumentation used in the isolation and determination of these compounds, namely the computer-assisted gas chromatograph-mass spectrometer (GCMS). The GCMS is fundamentally a gas chromatograph which has, as a detector, a mass spectrometer which is capable of scanning the mass range from one to several hundred atomic mass units (amu) very rapidly. Thus, a complete mass spectra can be obtained every 0.1 to 1.0 seconds, for example. Obviously a gas chromatograph run which lasts for several minutes will

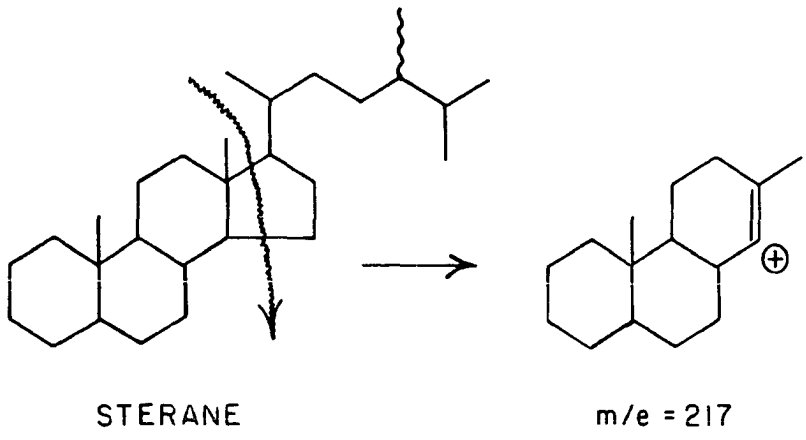
generate a huge amount of data. The most convenient and practical way to handle such data is by a computer. Although mass spectra are typically generated for a large amu range, organic geochemists usually concentrate on one or more ions of interest, either by monitoring these specific ions at a slower rate (multiple- or single-ion-detection) or by monitoring them during or after a conventional scan of the mass spectrometer. The former method is more sensitive to particular ions, while the latter allows simultaneous generation of mass spectra during a run. The latter method, that is, complete scanning by the mass spectrometer and then reconstruction of ion (or mass) chromatograms (also known as fragmentograms), is used throughout this study.

On entrance into the mass spectrometer, the compound eluting from the gas chromatograph column at that point is fragmented by electron impact (70 eV). Each class of compounds, in addition to its molecular "fragment" (i.e., parent ion), has several fragments of different masses (actually mass/charge, or m/e) that are characteristic of that class of compounds. Owing to the reproducibility of the fragmentation pattern, each compound has a unique mass spectrum. Therefore, if a fragment that is a major fragment of that compound class (e.g., the fragment of highest intensity, or the base peak) is monitored over time, a mass chromatogram, or ion chromatogram, is obtained for that particular mass (m/e). This mass chromatogram is then useful in monitoring the elution pattern of a single compound class. For example, if fragment m/e = x is characteristic of all compounds of type y, and if x is not contained as a major fragment in any non-y compounds in the mixture, then a mass chromatogram at m/e = x

will provide a distribution of y compounds present in the sample. Figure 18 shows the major fragments of steranes and hopanes.

The present study involves the distributions of steranes having 27, 28 and 29 carbon atoms, with molecular masses of 372, 386 and 400, respectively; and hopanes having 27, 28, 29, 30 and 31 carbon atoms, with molecular masses of 370, 384, 398, 412 and 426, respectively. Major m/e fragments of the steranes and hopanes are, respectively, 149, 217, 218, and 177, 191. Thus a general distribution for these compound types can be obtained by monitoring the mass chromatograms of these ions, along with the corresponding molecular ions. In this manner, the molecular distributions of the steranes and hopanes were determined for all crude oils, solid bitumen pyrolyzates and selected rock extracts of the present study.

Crude oils 11, 15, 17 and 45 were analyzed for sterane distribution by monitoring selected fragment ions and the three possible molecular ions. This process was greatly enhanced by the use of the MAP techniques possible with the INCOS data software package (Gallegos, 1977, in Seifert and Moldowan, 1978). With this technique, it is possible to monitor several ions at once, and display them in a format which preserves the relative intensities of the individual fragments. The advantages of the MAP technique are clearly expressed in Figure 19. Here the mass chromatograms for m/e 217 and 259 are shown in true intensity relationship to each other. For example, the intensity of the 259 fragment for peak 1 is in fact about 50% of the 217 intensity for that peak. Without MAP, each mass chromatogram would be normalized to its largest peak, obscuring the true intensity ratios.



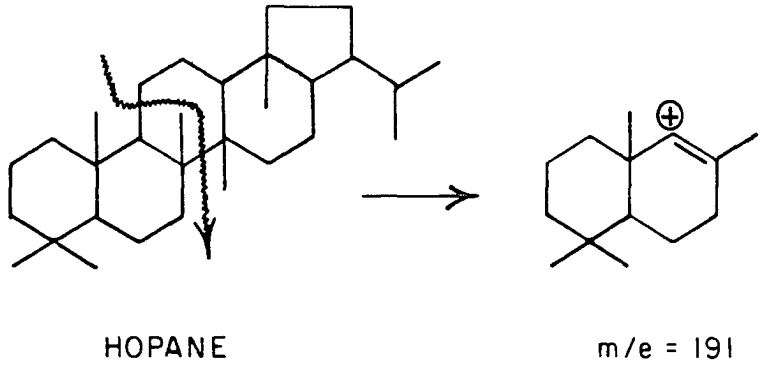


Figure 18. Major Fragmentation Pattern for Steranes and Hopanes. Wavy line with arrow indicates the major point of fragmentation for each molecule.

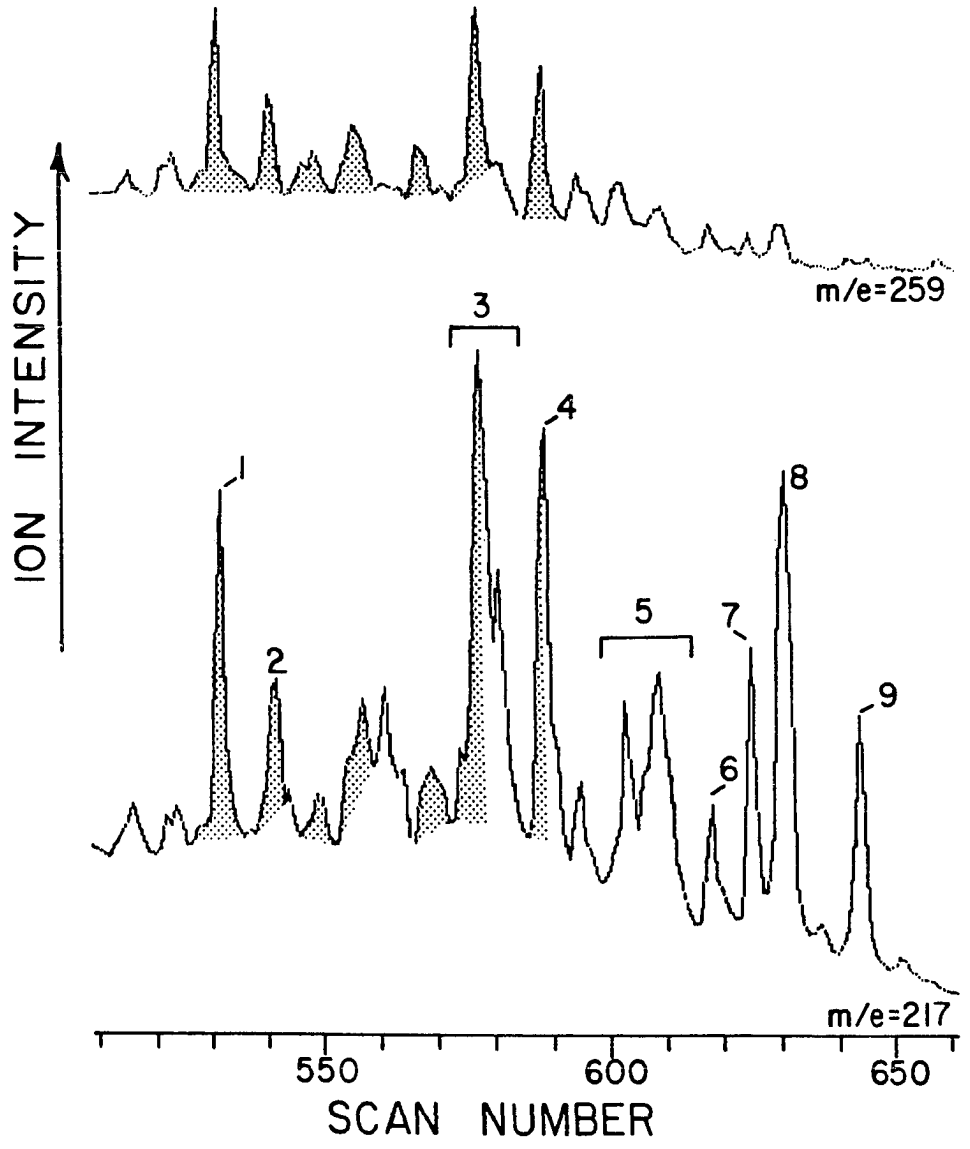


Figure 19. MAP of m/e 217 and 259 for oil 11. Rearranged (Dia-) Steranes are shaded, but shading is not meant to suggest elution order or the amount of each compound present. Peak numbers correspond to assignments in Table 7. See text for interpretation.

Tentative identifications were made on the basis of the MAP technique, mass spectra, relative elution order, and comparison with published data (Gallegos, 1971; Ensminger, et al., 1978; Seifert and Moldowan, 1978, 1979; Seifert, et al., 1980). Distinction between diasteranes and regular steranes (Ensminger, et al., 1978) was based on examination of the m/e 232 and 259 mass chromatograms, displayed in MAP format with the m/e 149, 151, 217 and 218 ions (Seifert and Moldowan, 1978). Figure 19 distinguishes rearranged (shaded) from regular major steranes by MAP. Elution order on the bonded DB-5 (SE 54 equivalent) column used (see Appendix II) is very similar to that observed on Dexsil phases used by Seifert and Moldowan (1979). As in the studies of these authors, co-elution of different stereoisomers occurred, particularly in the region of overlap due to late-eluting diasteranes and early-eluting regular steranes; this overlap is greater for DB-5 than for Dexsil. In most cases, it was impossible to determine the relative amounts of two or more steranes eluting in a single peak.

Mass chromatograms for the m/e 217 ion for each of the four oils examined are presented in Figure 20. Each peak or group of co-eluting peaks is labelled by number. Table 7 lists tentative identifications of each of the numbers. In some cases definite assignments of compounds are possible (e.g., peaks 1, 2, 7, 9 of Figure 20 and Table 7). However, in general, co-elution is the rule, and precise assignment is not possible. Consequently, compound names in Table 7 represent those compounds which may be present under a given peak, as determined by study of the mass spectra obtained across the peak.

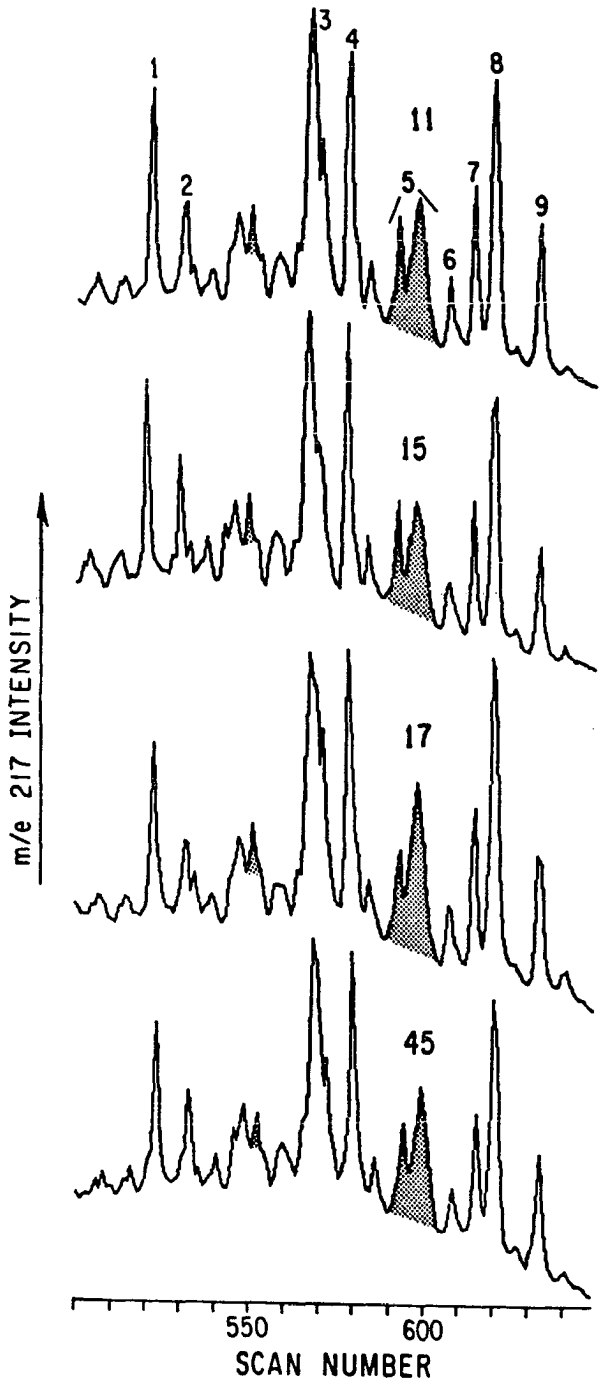


Figure 20. m/e 217 Ion Chromatograms of Ouachita oils. Differences between oils are shaded. Peak numbers correspond to assignments in Table 7.

Table 7

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 (Ergostane)
	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 19 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 co-eluting steranes are listed.

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

In addition to general sterane m/e 217 mass chromatogram patterns, the m/e 372, 386 and 400 molecular ion mass chromatograms were integrated over the sterane elution region, and normalized. Results are presented graphically in Figure 21 and indicate that most of the steranes present are ethylcholestanes, while methylcholestanes (C_{28}) are a minor component of the mixture. The close structural similarities between steranes and sterols, suggesting the 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) suggest that sterol distributions in recent sediments can serve as "ecological indicators," i.e., compounds typical of specific depositional environments. On this basis, the present data have interesting implications. If the sterane distributions in the Paleozoic oils analyzed in this study were actually sterol distributions in recent sediments, one would conclude that they were part of a near-shore depositional environment. In order 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 does not alter the 27, 28 and 29 distribution of steroids in the system.

Owing to strong structural similarities among this group, it is difficult to believe that migrational changes in gross distribution of the number of carbon atoms of these steranes is possible. Indeed, Seifert and Moldowan (1978), in an attempt to establish oil-oil correlation parameters, note that, while the ratio of 5a-C_{28}/ 5a-C_{29} is a good correlation parameter for source input, the ratio

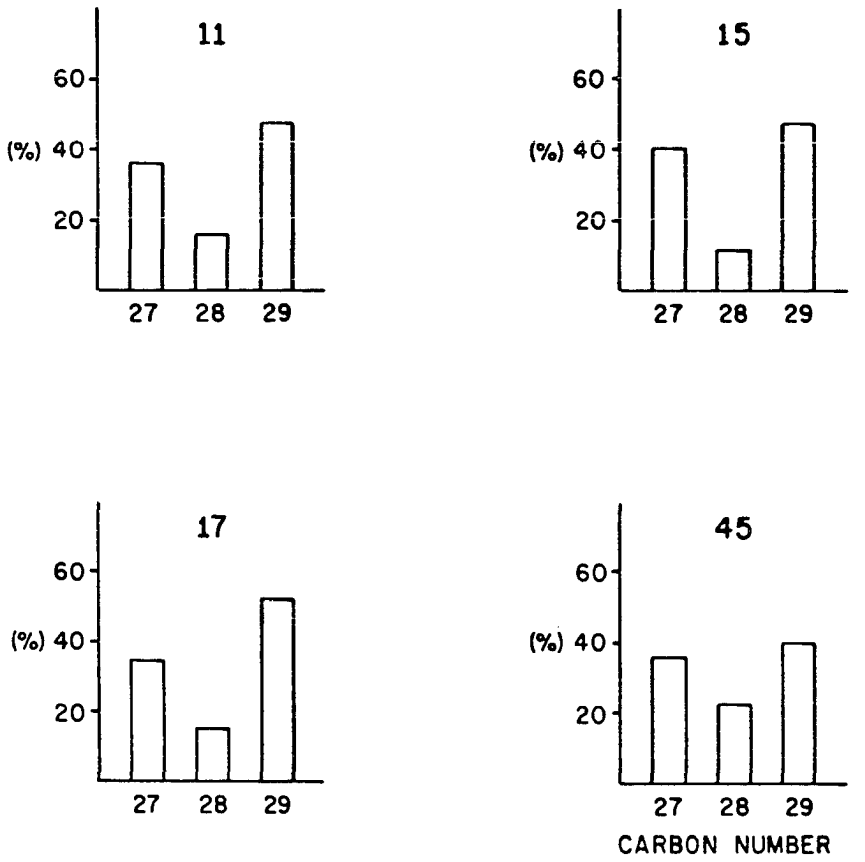


Figure 21. Distribution of C_{27}, C_{28} and C_{29} Steranes in Oils. Obtained by integration of the m/e 372, 386 and 400 mass chromatograms over the elution range of the common steranes (both rearranged and regular).

suggests no correlation at all based on migration or reservoir maturation. Seifert and Moldowan's (1978) ratio of rearranged steranes to regular steranes does change with migration. However, it is very possible that this ratio can change and yet the total C_{27}, C_{28} and C_{29} distribution remain unaffected. Thus it is possible that the distribution of steranes by carbon number in an oil represents a technique for predicting the environment of deposition of the oil's ultimate source rock. Finally, note that whole oil isotopic data is ambiguous as to non-marine (-34 to -30 $^{o}/_{oo}$) or marine (-30 to -21 $^{o}/_{oo}$) origin of these oils, and thus indicates a near-shore environment of deposition as well (Table 5).

Terpane analyses of oils 11, 15, 17 and 45 were carried out by monitoring m/e 191 (major fragment) and m/e 370, 384, 398, 412 and 426 (molecular ions). Identifications were based largely on mass spectra published by Hills and Whitehead (1966), Whitehead (1973b), Kimble, et al. (1974a), Seifert, et al. (1978), and Ekweozor, et al. (1979a), and on elution order (Seifert and Moldowan, 1978, 1979). Although elution order for Dexsil and DB-5 phases are similar, retention indices were again significantly different. Co-elution was less of a problem with the terpanes, and thus assignments are more certain for the terpanes than for the steranes.

Figure 22 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 8 gives suggested peak assignments, by numbers corresponding to those in Figure 22.

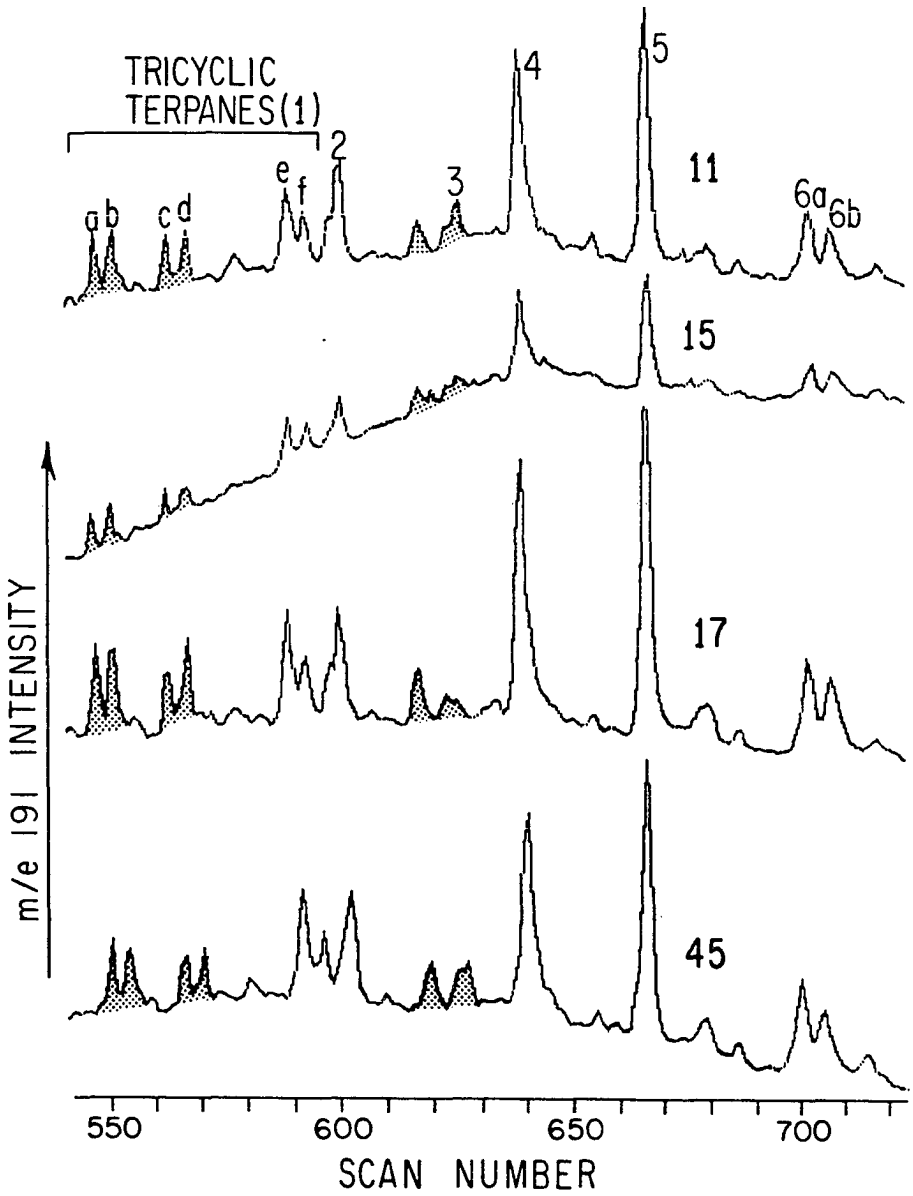


Figure 22. m/e 191 Ion Chromatograms of Ouachita Oils. Differences between oils are shaded. Peak numbers correspond to assignments in Table 8. Shaded peak eluting just before peak 3 has not been identified; the mass spectral scan for this peak is obscured by peak 7 of the steranes (see Figure 20), which is in much higher abundance.

Table 8

Terpane Assignments

Number[a]	Assignment
1a-1f	Tricyclic Terpanes[b]
2	(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 is limited for these compounds.

[c] Possibly Triterpane H of Hills and Whitehead (1970); also,see Pym, et al., (1975).

[d] Seifert, et al., (1978).

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

[f] Whitehead (1973a); Kimble, et al., (1974a).

[g] Seifert and Moldowan (1979).

Resolution of the terpane distribution is considerably better than that possible for the steranes and permits conclusions to be made as to maturity and general character of the oils. Seifert and Moldowan (1978) have introduced techniques to determine the maturity level of a sequence of oils on the basis of terpane distribution. Although only four oils are available here, one of Seifert and Moldowan's (1978) techniques for maturity appears to be applicable. These authors note the presence in crude oils of two particular hopanes, 17a(H)- and 18a(H)-22,29,30-Trisnorhopane, both of formulae $C_{27}H_{46}$ and molecular weight 370. On the basis of correlation with other parameters that change in a predictable manner with maturity, they concluded that 18a(H)-22,29,30-Trisnorhopane is more stable in the geologic environment than is 17a(H)-22,29,30-Trisnorhopane. Thus a ratio of 17a(H) to 18a(H) ("T_m/T_s" of Seifert and Moldowan, 1978) will decrease with "maturity," and the ratio will ultimately attain a value of zero. It was shown that this ratio decreases to zero when the saturate hydrocarbon content of a particular sequence of Jurassic oils reaches 57.7% (of the oil).

Similar results were found for the four oils of the present study. A very minor amount, if any, of 17a(H)-22,29,30-Trisnorhopane is present in these oils, indicating a 17a(H)/18a(H) ratio approaching zero. Interestingly, the average saturate hydrocarbon content of these four oils is 62.8%. Thus it is possible to conclude, on the basis of the terpane distribution, that these oils are thermally mature. Although Seifert and Moldowan (1978) suggest other maturity parameters based on terpanes, the low concentrations of these compounds precluded

their use in the present study.

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 the presence of 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 177, 191 and 205 (Figure 23) shows only minor 205 peaks, corresponding to fragments from norhopane (Hills and Whitehead, 1966), hopane (Whitehead, 1973b; Kimble, et al., 1974a) and two epimers of homohopane (Seifert and Moldowan, 1979). These are peaks 4, 5, 6a and 6b of Figure 22, respectively. On this basis, it is concluded that the concentration of methylhopanes in these oils is insignificant.

Observation of the m/e 177 scan (MAP for crude oil 11, Figure 23) 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 23, co-elutes with the peak 5 group of steranes (Figure 20 and Table 7). A mass spectrum of compound B reveals the following: 163 (100%), 177 (67%), 341 (20%), 355 (6%), 370 (M^+; 29%). Although identification of the compound is not possible with only this information, it is informative to compare this 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, et al., 1978), called demethylated 17a(H)-28-Noradiantane. Careful measurement of the C_{27} compound's fragments in

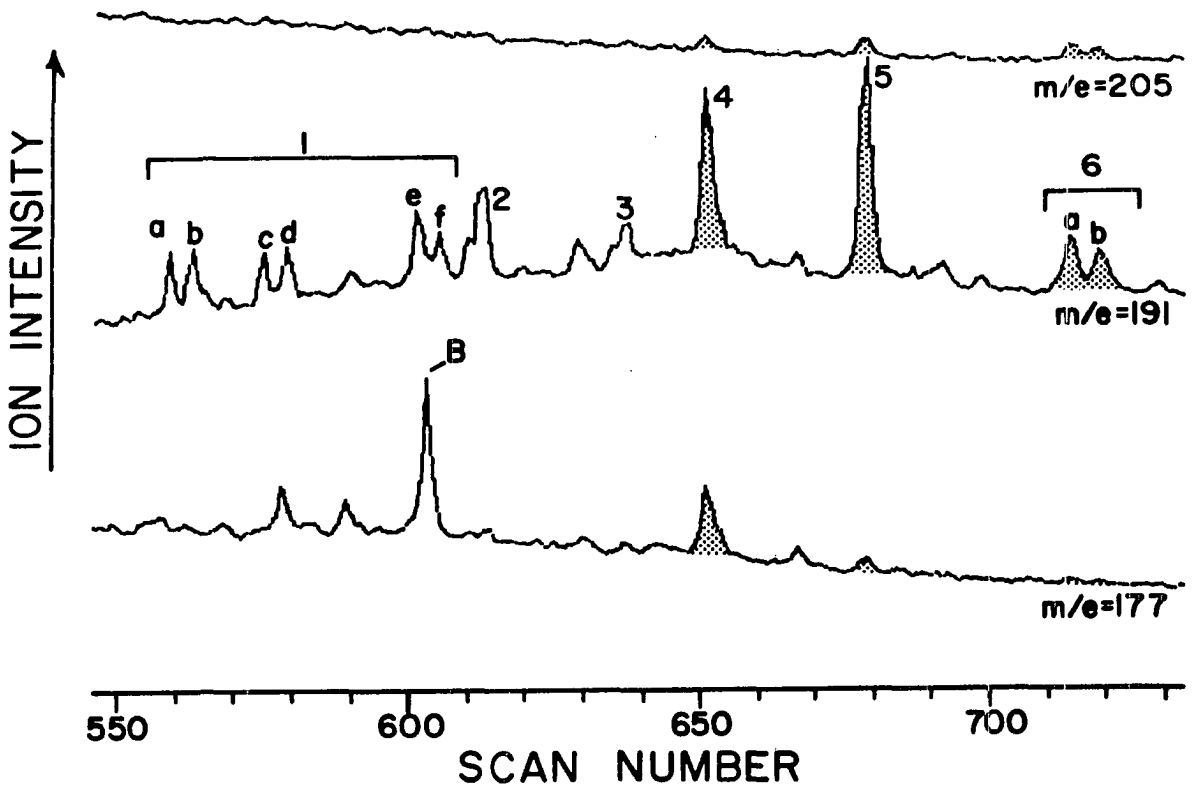


Figure 23. MAP of m/e 177, 191 and 205 of oil 11. C_{29}, C_{30} and C_{31} hopane fragments are shaded. Peak numbers correspond to assignments in Table 8.

the MAP diagram in Figure 5 of Seifert and Moldowan (1979) suggests a mass spectrum of: 149 (37%), 163 (100%), 177 (81%). This compound has a larger 177 fragment than that of compound B of the Ouachita oils (see above). 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, while the Ouachita oils show no evidence of strong biodegradation. However, it should be noted that the methylated analog of this compound (Seifert, et al., 1978) was found in the undegraded oil analyzed by Seifert as well, and also appears to be present in the Ouachita oils (see Table 8).

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%), 177 (84%), 341 (12%), 355 (3%) and 370 (48%). They assign a moretane rather than a hopane structure because the m/e 163 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 is also a moretane, while B of the present study is a hopane. Nevertheless, neither the compound of Seifert and Moldowan (1979) nor that of Bjoroy and Rullkotter (1980) appear to be identical with compound B of the Ouachita oils. Unfortunately, in the absence of a model compound for co-injection, or

proton NMR and X-ray data, B remains an unknown.

Oil-Oil Correlation Techniques

Each of the physical and chemical characteristics discussed in the previous sections has been evaluated to determine if the four oils in this study belong to the same oil family, i.e., if they were sourced by the same source rock or sequence. Differing subjective weights were assigned to each of the characteristics of the oils. Physical parameters were immediately discounted as correlation tools, on the basis of considerable evidence suggesting that, for example, API gravity ranges may coincide for three distinctly different oil families (Williams, 1974). Consequently, the chemical characteristics of the whole oil, and particularly the paraffinic hydrocarbon fraction, were examined more closely. Each of the relevant tools of correlation will be discussed in order of least important to most important in the present study.

Vanadium:Nickel Ratios. The use of the vanadium:nickel ratio as a correlation parameter for oils has received sporadic interest in the past (Shirey, 1931; Hodgson, 1954; Bonham, 1956; Stone, 1967). The "theoretical" basis for such use is the presence of these metals as part of the porphyrin complex (e.g., Treibs, 1934). Considering the V/Ni ratio as a constant in a single family of oils derives from the presumed relative equivalence of migrational loss for the nickel- and vanadium-porphyrins. This presumption is implicit in most correlations using this ratio, as is the assumption that these metals do, in fact, exist predominantly as porphyrin complexes. If

either of these conditions does not hold, then use of the ratio as a correlation tool loses its validity.

It has been shown that the vanadium and nickel ranges of these oils (Table 5) are 8.8-20.2 ppm and 2.1-7.0 ppm, respectively, while the ratio of vanadium to nickel (w/w) ranges from 2.15 to 3.59. Tissot and Welte (1978, p. 364) provide data for vanadium and nickel content of oils worldwide, in which the V/Ni ratio ranges from less than 0.05 to greater than 10.0. Therefore, the range for oils of the present study is approximately 14% 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% of the worldwide oils, while the nickel range is 4%. On this basis, the concentration levels of vanadium and nickel as well as the V/Ni ratios of these oils, indicates that they are of the same oil family.

On the basis of a successful correlation of the oils based on vanadium and nickel content, it is tempting to conclude that the above assumption is valid, namely that the metals exist in these oils as porphyrins. However, such a conclusion must be postponed until such time as a source is determined for the oil. This is especially critical because an early Paleozoic source may rule out the presence of porphyrins (Tissot and Welte, 1978, p. 365).

Elemental Analyses and Ratios. Attempts at correlation of oils based on carbon, hydrogen and oxygen content are rare in the literature. Reported atomic ratios of H/C for crude oils range from 1.65-1.84, while oxygen contents range from 0.06-0.87% (Ball, et al., 1959; Rubinstein, et al., 1977). Data in Table 5 indicate that, on

this basis, the H/C ratio is relatively high for the Ouachita oils, having a numerical range (1.79-1.90) that is about half that for the values reported above. Thus the H/C ratio appears to have little value as a correlation parameter in the present study. However, the oxygen content of the Ouachita oils, ranging from 0.44-0.58%, is only 17% of the range reported in the literature (above), suggesting a possible correlation. However, limitations imposed by the relative lack of previous data in the literature preclude more definite conclusions.

Correlation attempts involving the nitrogen content of oils are also relatively rare (Barbat, 1967). Nitrogen concentrations of oils from several fields worldwide are reported by Costantinides and Arich (1967), and range from 0 to 0.88% by weight. The four oils of the present study range from 0.063-0.142. This is approximately 9% of the range reported by Costantinides and Arich (1967), suggesting a similarity among these four oils. Again however, lack of sufficient published data for comparison precludes more definite conclusions based on nitrogen content.

Several workers have shown that the sulfur content of an oil varies substantially with maturity (Thode, et al., 1958; Orr, 1974). Williams (1974) reported considerable overlapping of sulfur concentrations for all three oil families in his study of Williston Basin oils, although these families were shown to be clearly distinguishable on the basis of other correlation parameters. Consequently, sulfur content will not be discussed further as a correlation tool for the oils of this study.

N-Alkane and Isoprenoid Analyses. Use of n-alkane and isoprenoid distributions as a crude oil correlation tool has become somewhat routine, although care must be taken in comparison of biodegraded oils by this method (Deroo, et al., 1974). Williams (1974) was able to distinguish between three oil families in the Williston Basin on the basis of n-alkane distributions. Isoprenoid isoalkane distributions and isoprenoid/n-alkane ratios are commonly used as correlation tools (Welte, et al., 1975b). Examination of the n-alkane distributions for the oils of the present study (Figure 12) suggests that at least three oils (11, 17, 45) correlate very well on this basis, while the fourth (15) lacks only the minor predominance at n-heptadecane and n-nonadecane observed for the others. Figure 24 suggests that all four are similar enough to be considered a single family. Similarities in the ratio of pristane to phytane, and in the CPIs (Table 6), support this conclusion. Nevertheless, it is interesting that the ratios of n-heptadecane/pristane and n-octadecane/phytane for oil 15 (the oil lacking an n-C_{17} and n-C_{19} predominance) are significantly lower than those for the other three oils. This could have been caused by depletion of n-alkanes due to biodegradation of the oil. This possibility is further supported by the low saturate/aromatic ratio (1.76), which might be expected for a microbially-degraded oil (Bailey, et al., 1973a). In addition, the sulfur content of this oil is significantly higher than that of the other three oils (Table 5). The generally strong n-alkane peaks in Figure 10 (oil 15) suggest only limited biodegradation, if any. In summary, the n-alkane and isoprenoid data suggest either a single

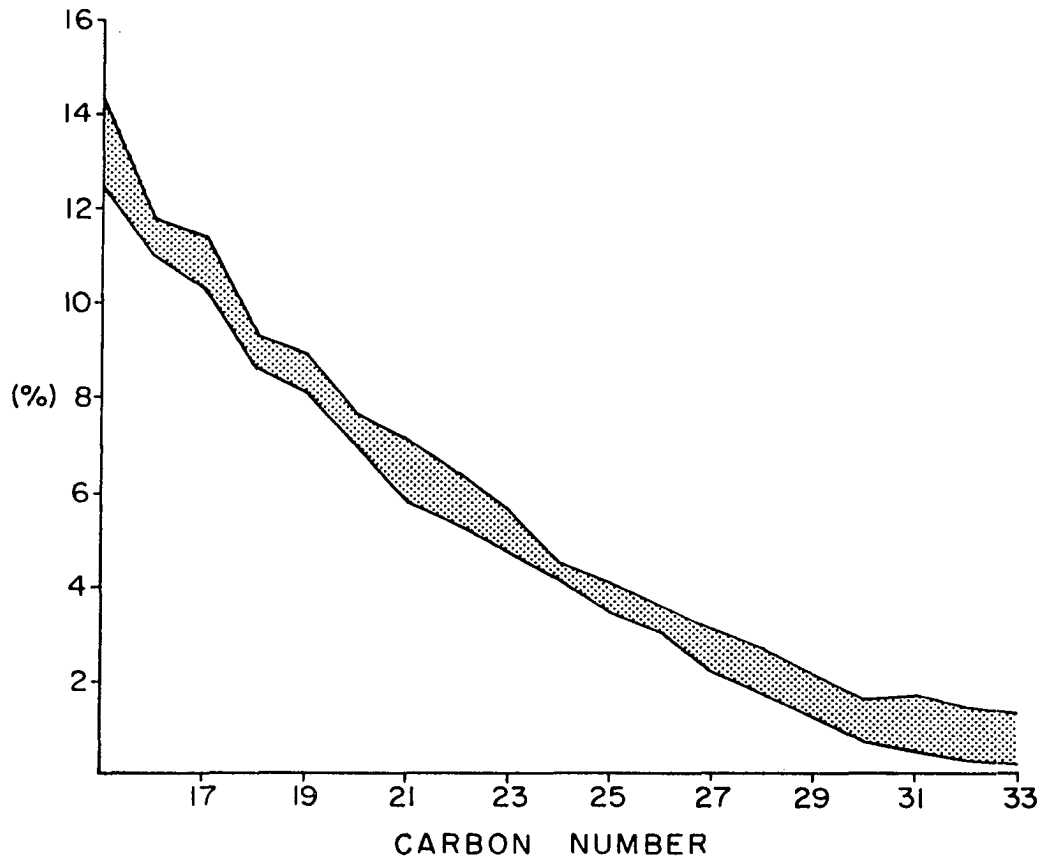


Figure 24. N-Alkane Distribution Overlap of Ouachita Oils. All four oil distributions plot within the dotted region.

source, or multiple sources with very similar organic matter content, for these oils.

Infrared Spectra. Infrared spectra of the aromatic and asphaltene fractions of the four Ouachita oils also suggest very similar sources (Figures 13 and 14, respectively). Despite possible microbial degradation of oil 15, as discussed earlier, note that the aromatic fractions of all four oil samples appear almost identical by IR (Figure 13). The IR spectrum of the asphaltene fraction of oil 15 however, differs from that of the other three oils. This difference is primarily in the band at approximately 1600 cm^{-1}, which has been tentatively assigned to aromatic carbon-carbon bond movement. This aromatic C-C band appears stronger in oil 15 than in the other three Ouachita oils, perhaps suggesting an increase in the aromaticity of the asphaltene fraction of a possibly biodegraded crude oil.

Stable Isotope Ratios. The use of stable isotope ratios as correlation parameters has increased rapidly in the last twenty years. Various attempts at the use of carbon isotopes as correlation tools were reviewed by Fuex (1977), who noted that changes in this ratio with maturity are possible (see also Orr, 1974). However, such variations are not a problem with the oil samples of the present study. Table 5 shows that the ratio for carbon for Ouachita oils ranges only from -29.8 to -28.9 $^{o}/_{oo}$, providing strong evidence that these oils are sourced from the same rock or from rocks having very similar organic matter (Vredenburgh and Cheney, 1971). This conclusion cannot be based solely on the carbon isotope data however, because it has been shown by Williams (1974) that two distinct oil families of the same basin can

exhibit similar carbon isotope values.

The use of sulfur isotope ratios of crude oils as a correlation tool has been attempted by several workers (Vredenburgh and Cheney, 1971; Orr, 1974). It is clear from these studies that the range of sulfur isotope values for the three Ouachita oils analyzed (+14.3 to +18.9 $^{o}/_{oo}$; Table 5) is small enough to again conclude that these oils are of the same family. However, too few samples are available to justify any conclusions concerning relative thermal maturity of these oils (Orr, 1974).

Sterane and Terpane Analyses. Use of sterane and terpane distributions in crude oil as a correlation parameter has now become common in the petroleum industry. These techniques have been discussed in detail by Leythaeuser, et al. (1975), Seifert and Moldowan (1978, 1979), and Seifert, et al. (1980). Several changes in ratios of specific biomarkers and in stereochemical groupings have been suggested by the above authors as indicative of changes in migration, maturation and source of the oils in question (Seifert and Moldowan, 1978). In addition, biodegradation is observable in biomarker changes as well (Seifert and Moldowan, 1979). For the purposes of the following discussion however, such detailed analyses of biomarker composition would be superfluous, because the sterane and hopane distributions for all four oils appear very similar (Figures 20 and 22, respectively).

Mass chromatograms for the m/e 217 ion are presented for the four oils in Figure 20. It can be seen that the sterane distributions are similar in all four samples. Variations appear in peak(s) 5, and in minor peaks (diasteranes) between peaks 2 and 3, as shaded in

Figure 20. Assignments for peak 5 (Table 7) indicate that this grouping consists mostly of C_{28} regular steranes. Oil 15, as shown in Figure 21, possesses the least C_{28} structures, and thus peak 5 is smallest in oil 15 (Figure 20). In addition, in view of the possible biodegradation of oil 15 as suggested by n-alkane data, it is interesting that the ratio of diasteranes to regular steranes (depicted roughly by the ratio of peaks 1-3 to peaks 4-9, respectively) appears slightly larger for oil 15. A relative increase in diasteranes would be consistent with observations of Seifert and Moldowan (1979) for a microbially-degraded oil. Unfortunately, adequate resolution is lacking in these chromatograms and therefore the true ratio of rearranged to regular steranes is not known.

Figure 22 presents the terpane chromatograms for each of the four oils examined. Again, differences in the oils are shaded. These are mostly differences in peaks 1a-1f (tricyclic terpanes?), while the hopanes present (peaks 2-6) are identical, with the exception of the depletion of peak 3 in oil 17, which is presently unexplained. However, similarity among the other hopanes suggests that these oils are of the same family.

In summary, the sterane and hopane data presented here support the previous conclusion that all four Ouachita oils examined are sourced from one formation, or from a source sequence containing very similar organic matter. This conclusion derives from examination of whole oil (carbon and sulfur isotopes; elemental analyses; vanadium and nickel content) and the saturate hydrocarbon fraction (n-alkane and isoprenoid distributions; sterane and hopane distributions). Each

of these analyses suggests that these oils are of a single family, although it must be emphasized that no single correlation parameter may be relied upon to the exclusion of the others. In the present case however, each of the parameters is useful in supporting the final conclusion.

Asphaltite Characterization

Physical Characteristics

Seven samples of grahamite and impsonite collected from six localities in the Oklahoma Ouachita Mountains were analyzed in this study. A single sample was collected from the following: Jumbo, South Bald, Bigfork Grahamite, Pumroy and Page. Two samples were collected at Sardis. Figure 2 and the tables in Appendix III have sample locations. In addition, a sample of gilsonite (an asphaltite from the Unita Basin) was analyzed for comparison.

All data pertaining to the physical characteristics of these eight samples is listed in Table 9. The specific gravities of the grahamites and impsonite agree generally with those in the published literature (see Tables 2 and 3). The solubility data describe a group of Ouachita solid bitumens on the basis of their solubility in methylene chloride. The range of solubilities of grahamite in this solvent (21.1% to 44.8%) seems to be characteristic for this asphaltite, since the solubilities of impsonite and gilsonite are considerably lower and higher than this, respectively (Douglas and Grantham, 1973). Note that there exists no apparent correlation between solubility and luster, even for different samples from the same deposit (e.g., Sardis samples

Table 9

Bitumen and Pyrobitumen -- Physical Properties

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+

3 and 7, Table 9).

Chemical Characteristics

Each of the seven solid bitumens, and gilsonite, was analyzed in a manner similar to that for the crude oils of this study. Both whole analyses and analyses of extracts (in methylene chloride) were made for the solid bitumens. Unfortunately, analysis of the fractions of the extract (paraffinic and aromatic hydrocarbons, NSO compounds and asphaltenes) was limited by the low yields of hydrocarbons, and the negligible content of n-alkanes (see Figure 25 for a chromatogram of the extract). This lack of n-alkanes in grahamite was also noted by Douglas and Grantham (1973). Consequently, fractionation data presented in Table 10 are primarily for use in discussion of the origin of the grahamite and impsonite in a later section. The remainder of the present discussion is generally confined to chemical analyses of <u>whole</u> grahamite, impsonite and, for comparison, gilsonite. The data for these analyses are presented in Table 10, and will be discussed in the same general order as that of the crude oils of the previous section.

<u>Elemental Analyses and Ratios</u>. Elemental analyses of six grahamites (sample numbers 3, 5, 6, 7, 8 and 21), one impsonite (sample 44), and a gilsonite are listed in Table 10. Several of the grahamites analyzed in this study have an H/C atomic ratio higher and an O/C ratio lower than those cited in the literature (see Table 2). The reason for this is unclear. It is possible that advances in analytical methods for determining hydrogen and carbon concentrations provide better data

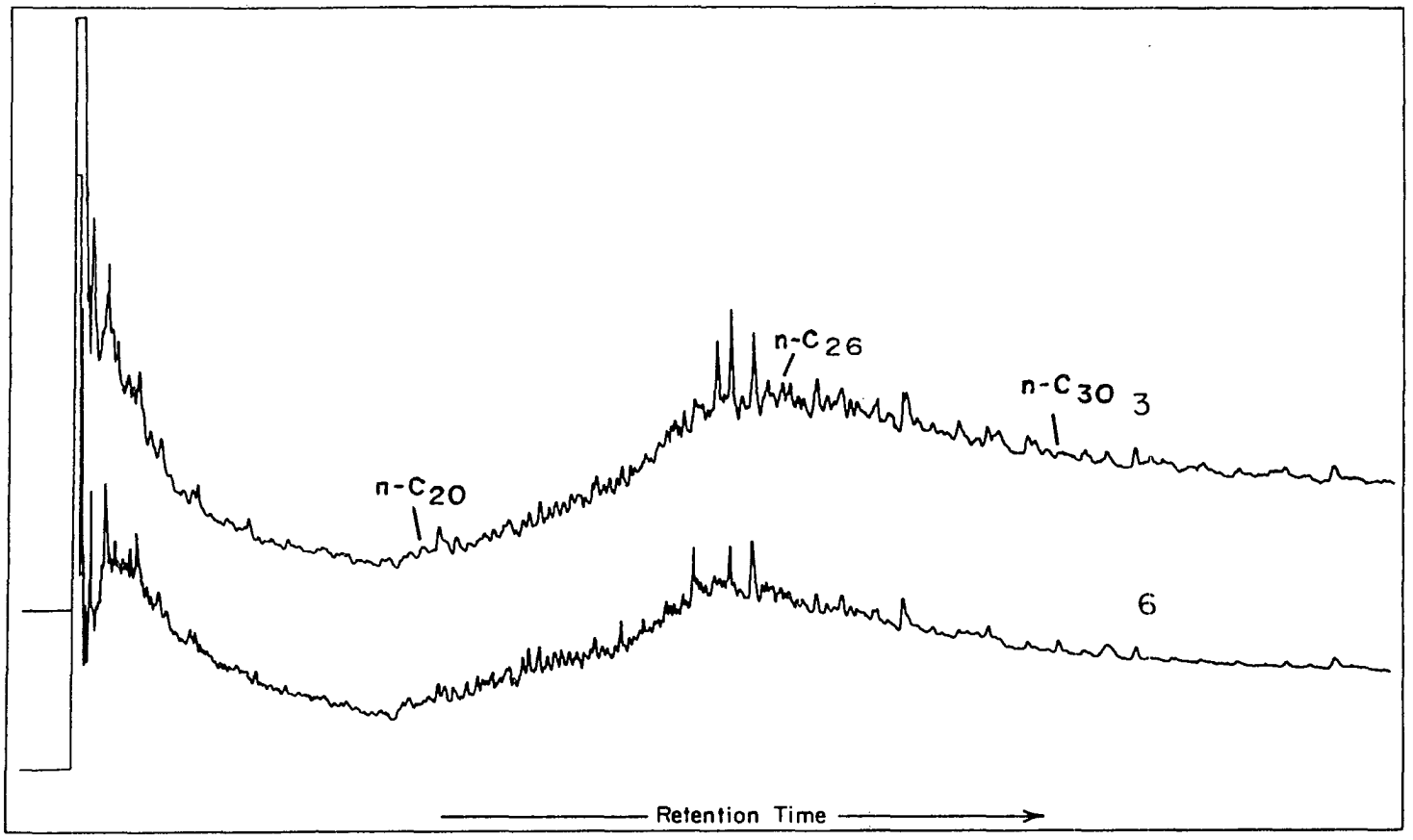


Figure 25. Gas Chromatograms of Typical Asphaltite Extracts. Relative retention times for three n-alkanes are as shown. Both samples run in methylene chloride solution. See Appendix II for further details of procedure.

Table 10

Bitumen and Pyrobitumen -- Chemical Data

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 %.

than did earlier studies (Table 2). The data listed in Table 2 (even that from Wen, et al., 1978) were compiled from studies completed at least thirty years ago. In addition, the discrepancy in O/C ratios is probably due to the computation of oxygen content by difference (as in King, et al., 1963, p. 4, for example) rather than more modern direct methods, as used in data presented in this study. Also, as was noted earlier in this report, the grahamite itself is somewhat variable in elemental content (note the range of sulfur present in asphaltite from the Jumbo deposit, Table 2). Finally, it should be mentioned that mineral matter may have contributed to the carbon, hydrogen, oxygen, nitrogen and sulfur content of these solid bitumens. This is indicated by the fact that up to 25% of the weight of these bitumens is unaccounted for by these elements (Table 10).

On the basis of H/C atomic ratios (Table 10), 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 and high fixed carbon (see Table 3). The H/C ratio for impsonite of the present study (0.73) agrees very well with that for Page impsonite found by King, et al. (1963), of 0.74. The S/C ratio in impsonite is lower than each of the grahamites examined. This phenomenon of decreasing sulfur content is commonly noted with increasing maturity of crude oils (Orr, 1974). However, the trend of decreasing S/N ratio going from grahamite to impsonite is opposite that expected in crude oils of increasing maturity (Orr, 1974).

Figure 26 presents a plot of nitrogen versus sulfur content 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 higher nitrogen concentrations in the gilsonite (see Figure 26). Consequently, it can be seen that, although both gilsonite and grahamite are listed as asphaltites by Hunt (1979), these materials are very different in terms of their elemental composition.

Metal Analyses and Ratios. Each of the grahamite samples in this study was analyzed for vanadium and nickel, and the results are listed in Table 10. Although several literature references exist attesting to the high vanadium and nickel content of impsonite (e.g., Ham, 1956), only one author has published data on the metal content of grahamite. Fay (in preparation) reports that analysis of a sample of grahamite from Sardis (luster unknown) indicated vanadium and nickel contents in the ash of 3.2% and 0.86%, respectively. If one assumes all of these two metals reside in the "ash" of the grahamite, calculations suggest 704 and 189 ppm levels for V and Ni, respectively, in the original grahamite. Samples 3 and 7 (Table 10) have a much lower content of vanadium and a much higher content of nickel in the whole grahamite than values calculated from ash determinations. In the case of nickel, this suggests that a large percentage of the nickel present in the grahamite is in the volatile (non-ash) portion of the grahamite. The discrepancy in the case of the vanadium, analyzed by x-ray fluorescence (as reported by Fay, in preparation) and by atomic absorption

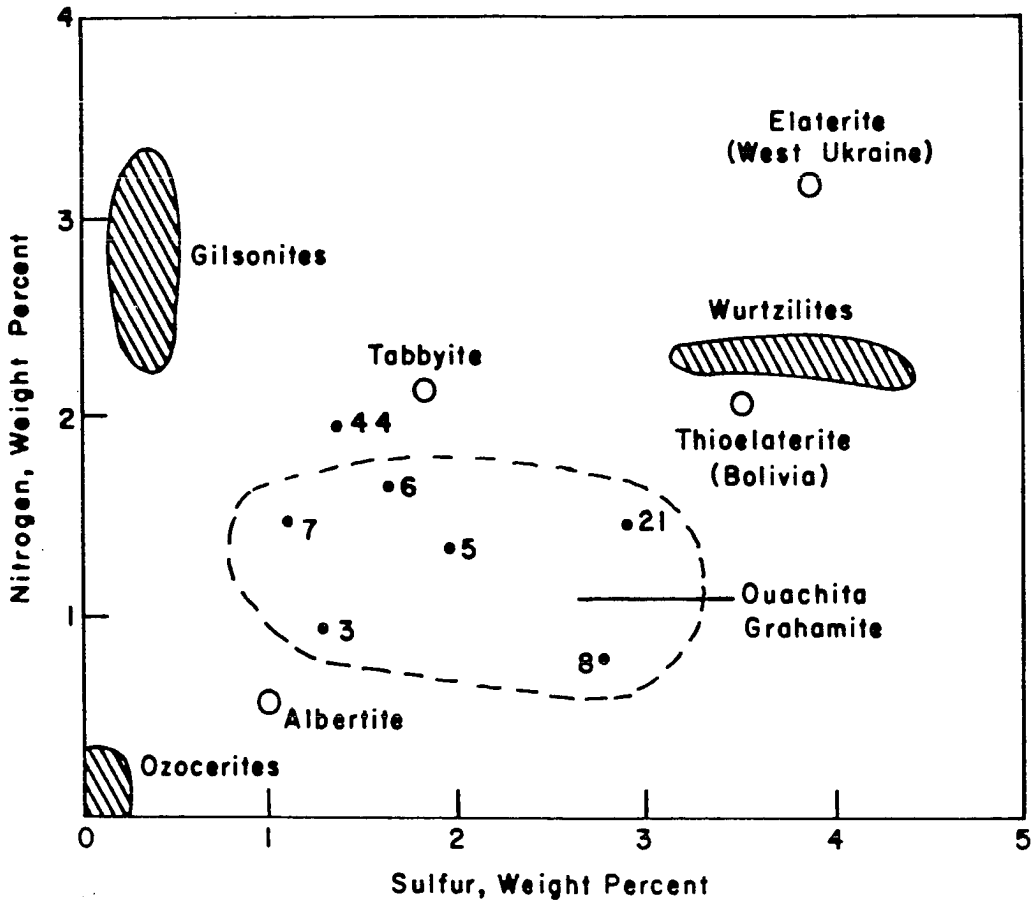


Figure 26. Graph of Nitrogen versus Sulfur for Solid Bitumens. Data for non-Ouachita materials is from Hunt (1979). Grahamite and impsonite fields as shown (impsonite = 44).

spectrophotometry (as reported here), remains unexplained.

The ratio of vanadium to nickel (w/w) of whole grahamite is reported in Table 10 also. With the exception of data for sample 5, there appears to be a correlation between the ratio and the S/C atomic ratio, as indicated in Figure 27 (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, et al. (1963) suggested that a relationship exists between sulfur and vanadyl pigments in crude oils, while Branthaver and Dorrance (1978) showed that, for several U.S. tar sand deposits, extracts having a high sulfur content usually have a V/Ni ratio greater than one. The results in Table 10 and Figure 27 of this paper suggest that this relation may hold for Ouachita grahamite as well.

Examination of the data for sample 5 in Table 10 indicates that this sample does not conform to the relation suggested in Figure 27 for the five other grahamites. Although the reason for this is unknown, it is interesting to consider that sample 5 is the only Ordovician-reservoired sample examined; all others are reservoired in the Carboniferous. Further, all other solid bitumens examined were sampled from large veins in shales up to 25 feet thick, while sample 5 is from a small fracture in a chert. At present no explanation is available for the lack of vanadium-sulfur relation in sample 5.

Isotopic Analyses. Table 10 also lists carbon and sulfur isotopic data for the grahamites, and impsonite and gilsonite of this study. The carbon isotopic ratios range from -30.2 to -29.6 $^{o}/_{oo}$. The sulfur isotopic ratios range from +15.5 to +20.3 $^{o}/_{oo}$, and are very

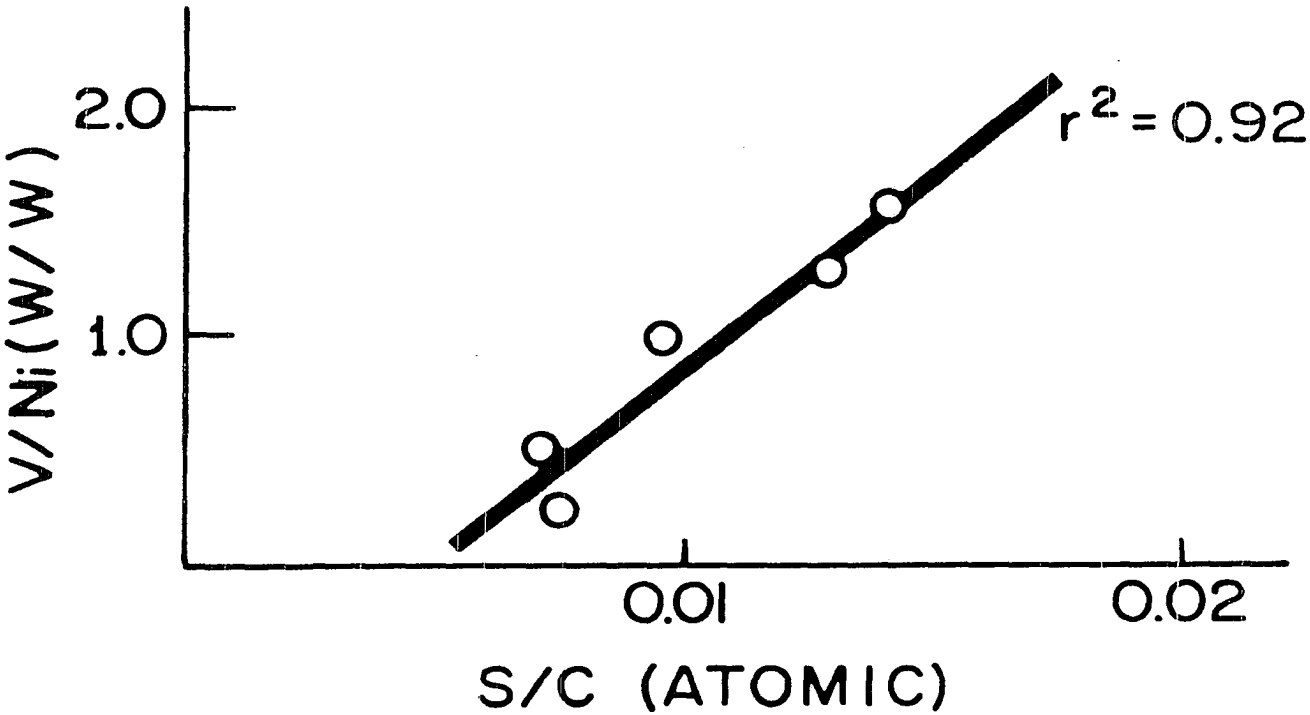


Figure 27. Graph of V/Ni (w/w) versus S/C (atomic) for Solid Bitumens. Correlation coefficient for the regression line (r^2) is as shown. Solid bitumen sample 5 is not plotted, for reasons discussed in the text.

similar to the oils. Unfortunately, there are no other published isotopic analyses of grahamite and impsonite in the literature with which to compare the results of this study. However, published isotopic data on gilsonite does exist. Silverman and Epstein (1958) report a value of -29.9 °/oo for a carbon isotopic ratio of gilsonite, while Mauger, et al. (1973) report a sulfur isotopic ratio for gilsonite of +28.0 and +29.6 °/oo, on duplicate runs of the same material. The carbon ratio of Silverman and Epstein (1958) is similar to that determined for gilsonite (this study) and is strikingly similar to the grahamites and oils of this study as well.

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 impsonite were pyrolyzed, and the chemical characteristics of the pyrolyzate were studied. Pyrolysis experiments involved continuous-flow high-temperature, as well as closed tube-low temperature techniques. Detailed techniques are listed in Appendix II.

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 28, and indicate a homologous series of doublets. Such doublets have been noticed by numerous workers studying volatile products of high-temperature pyrolysis, and have been attributed to alkane/alkene pairs (Scrima, et al., 1974; Martin, 1977; Sugimura and Tsuge, 1978). Of

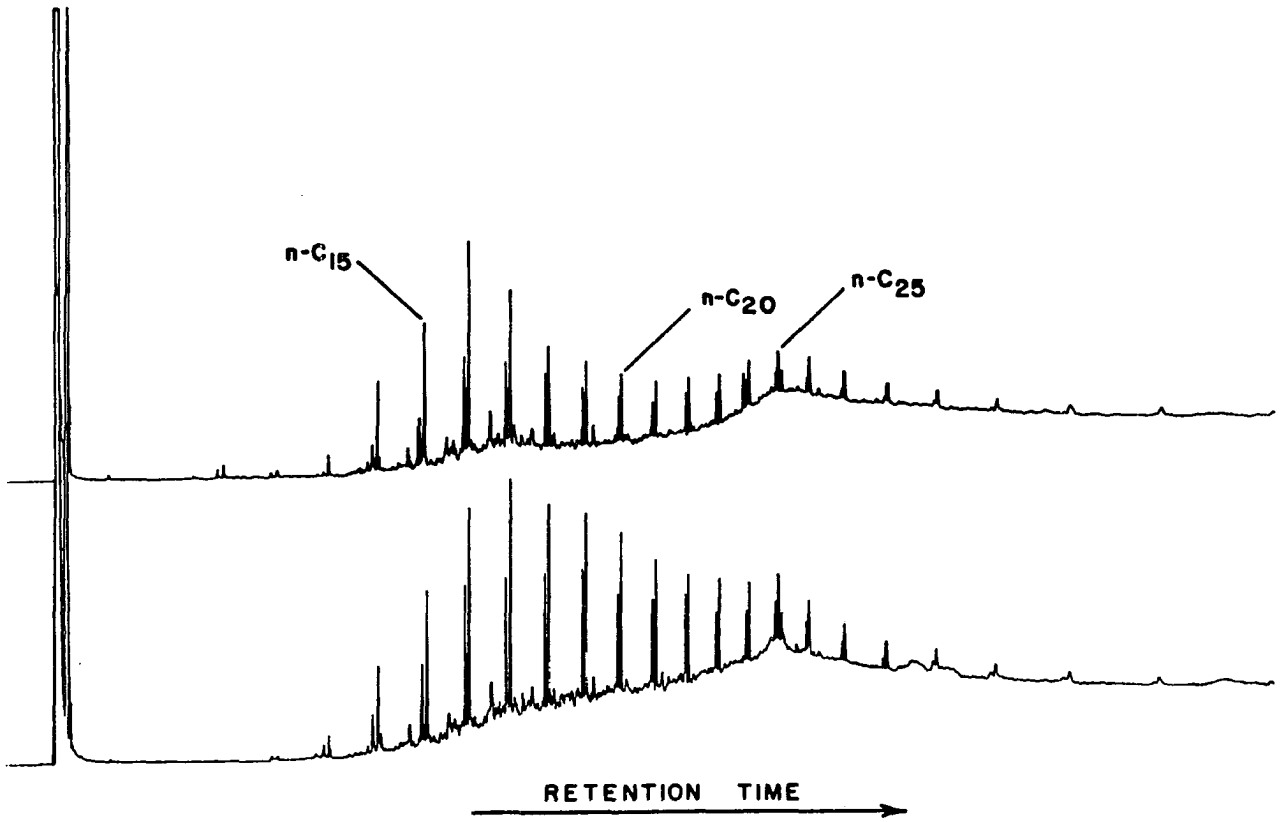


Figure 28. Gas Chromatograms of typical High-Temperature Pyrolyzates. Conditions same as in Figure 10. Doublets represent alpha-olefin/n-alkane pairs, as discussed in the text. Pyrolyzates are from sample 5 (top) and sample 7 (bottom).

the doublets generated in this study, the early eluting peak was identified as the alpha-olefin, while the late eluting peak was identified as the corresponding (same carbon number) n-alkane. Determinations were made by co-injection 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 (Figure 28). An attempt to generate a quasi-n-alkane distribution (C_{15} to C_{31}) by summing the area of each alkane with that of its corresponding olefin, generated a distribution for each pyrolyzate similar to that of a typical mature crude oil (Figure 29). The distributions show a predominance in the light end, with relatively high concentrations of the C_{19} and C_{25} alkane/alkene pairs in some of the samples (see Table 20 in Appendix V). Carbon preference indices for the range 22 to 30 are listed in Figure 29 also, indicating slight odd carbon preference in this range for most of the samples analyzed.

The production of alkanes and alkenes on pyrolysis of grahamite and impsonite at high temperature is of interest because of the possible conclusions concerning the chemical structure of these materials. The long-chain hydrocarbons present in the pyrolyzate suggest 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 Figure 25), suggesting that these long-chain compounds do not exist in an easily removable form. Similar

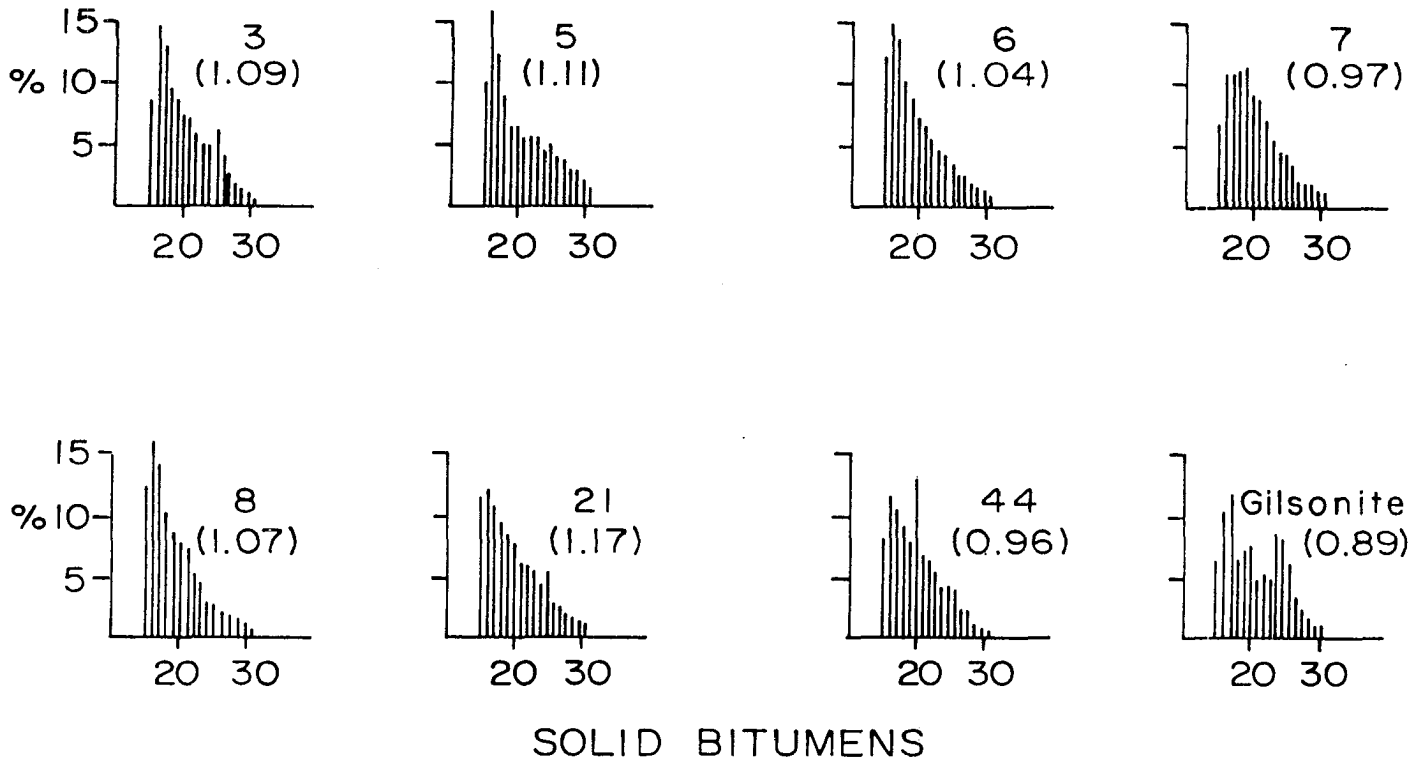


Figure 29. (Quasi-)N-Alkane Distributions of High-Temperature Pyrolyzates. Carbon Preference Indices, as defined in Table 6, are in Parentheses.

results were noted by Simm and Steedman (1980), who pyrolyzed crude oil asphaltenes and produced n-alkanes with up to 30 carbon atoms per molecule. Exhaustive extraction of the asphaltenes, in this case with diethyl ether, followed by pyrolysis, yielded similar results. This suggested to the authors that "...long alkyl chains are present in these asphaltene structures and are not due to residual absorbed resin" (Simm and Steedman, 1980, p. 669).

Urov (1980), in a study of kerogen pyrolyzates, suggested that short-chain alkenes are actually products which 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 in the case of the solid bitumens also. 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 of 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 (see Appendix II for details). 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, Figure 30). This is a result of the pyrolysis interval, which is too short to result in 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.

The sterane distributions of the five closed-tube pyrolyzates (CTPs) are shown in Figure 31. It can be seen immediately that the ratio of rearranged (dia-) steranes to regular steranes (shaded) increases in sample order 7, 5, 6, 3, 44, being greatest in impsonite, sample 44. Changes within the diasteranes themselves however, do not appear significant (e.g., the ratio of peak 1 to peak 2, both C_{27} diasteranes, does not change appreciably from sample to sample). Each of these observations is suggestive of biodegradation of a crude oil, as will be discussed later.

Figure 32 shows the distribution of (possible) tricyclic terpanes and hopanes for the CTPs. Three general observations can be made on the data presented in Figure 32. First, it is evident that the concentration of peaks 1a-1f is minimal in the pyrolyzates. Secondly, it is also evident that one of these peaks, peak 1e, represents a significant portion of the m/e 191 mass chromatogram. Previously, peaks 1a-1f have been tentatively assigned to the tricyclic terpanes (Table 8). Examination of the mass spectrum for peak 1e in pyrolyzate 5 however, shows strong fragment peaks (greater than 50% of the 191 base peak) at m/e 55, 69 and 365, suggesting co-elution of a

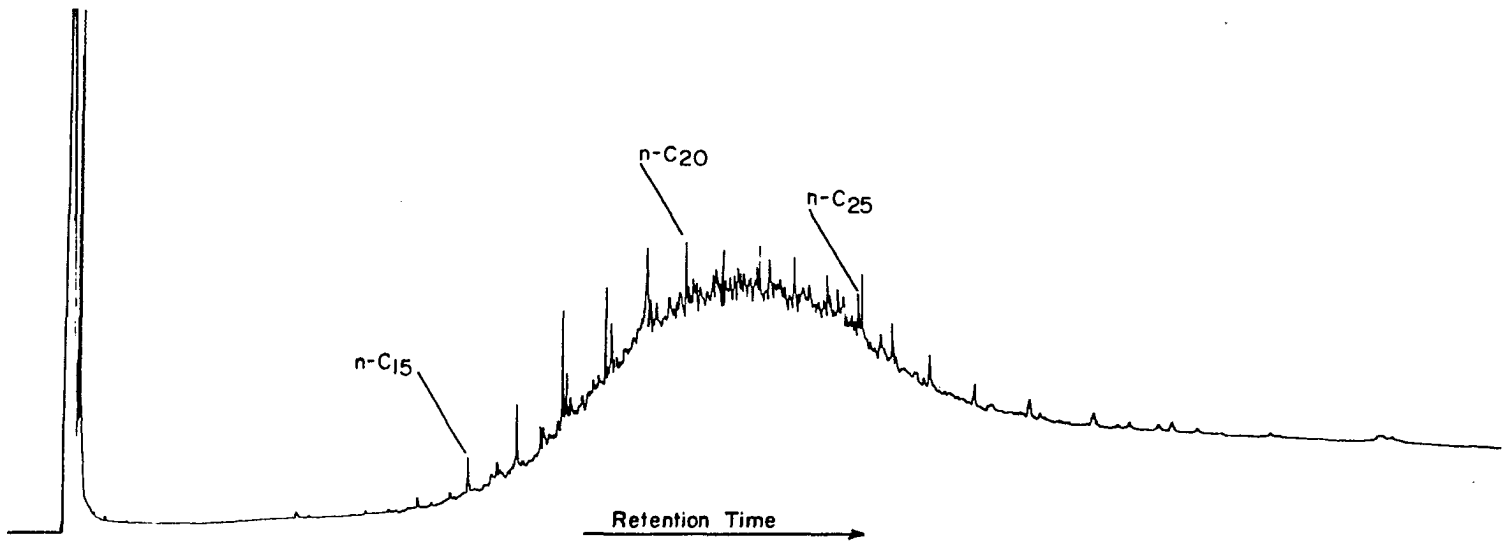


Figure 30. Gas Chromatogram of Typical Low-Temperature Pyrolyzate. Closed-Tube Pyrolyzate 3 is shown. Conditions as in Figure 10.

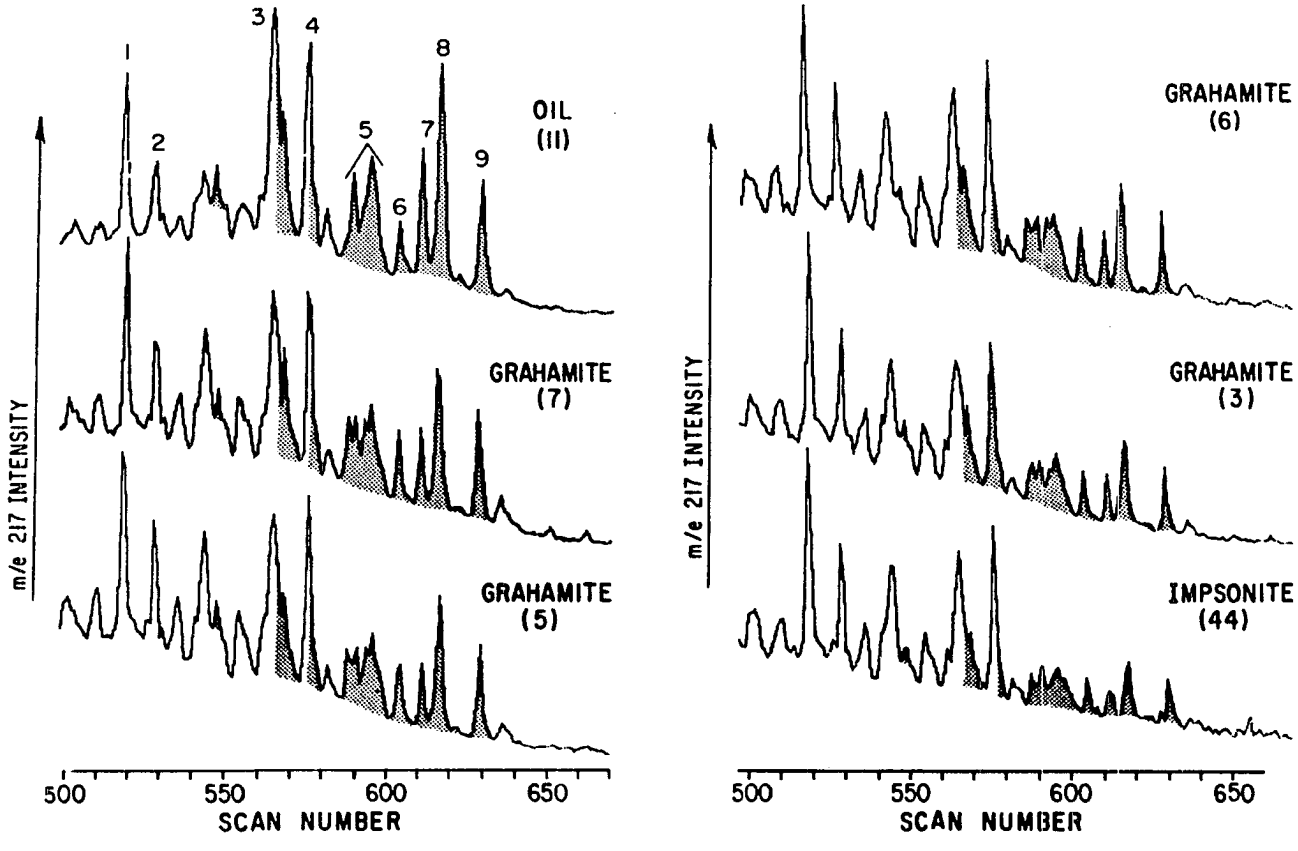


Figure 31. m/e 217 Ion Chromatograms of Low-Temperature Pyrolyzates and Oil 11. Regular steranes are shaded, although shading is not meant to indicate elution order or the amount of each compound present. See Table 7 for peak identifications.

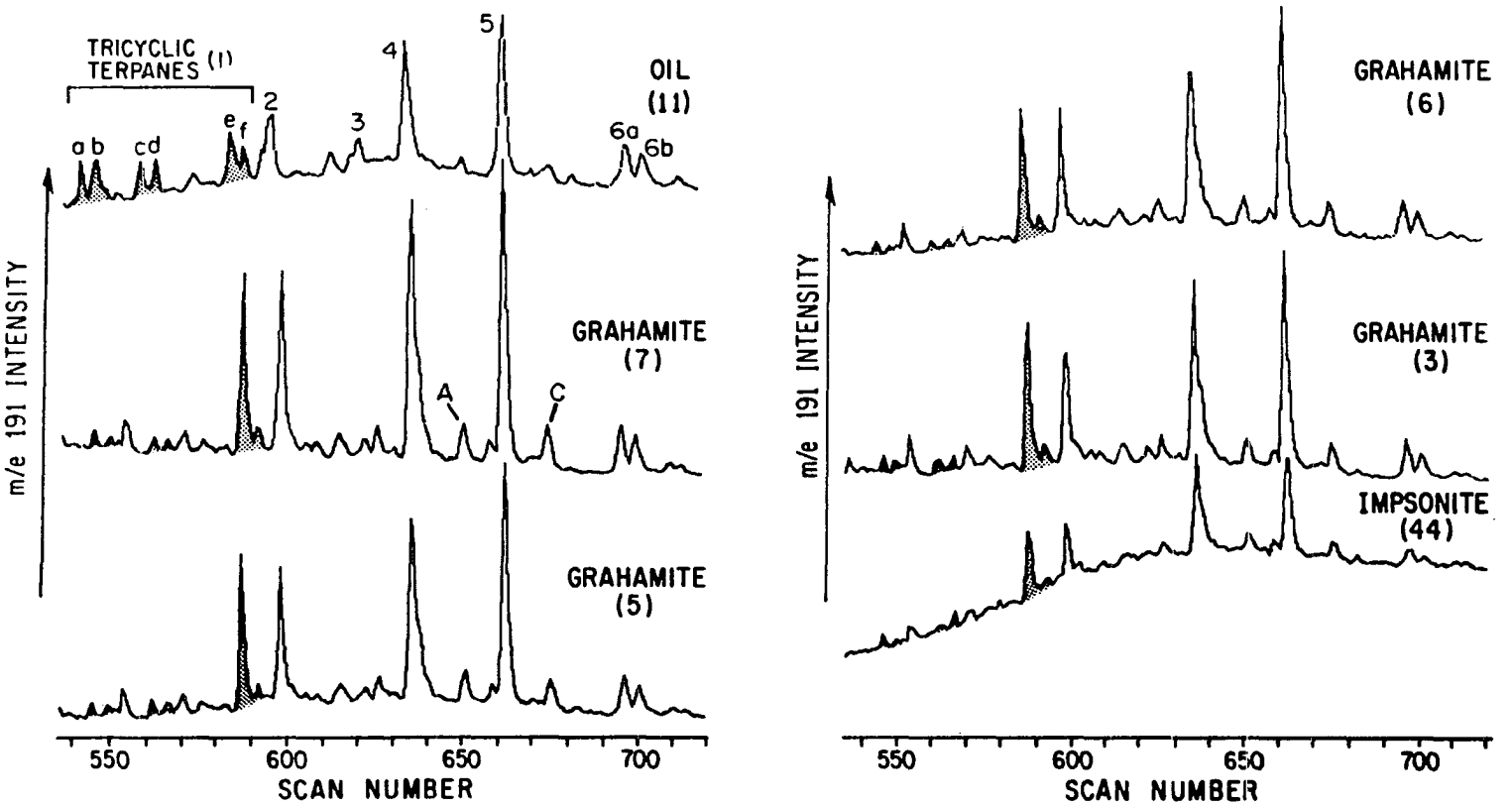


Figure 32. m/e 191 Ion Chromatograms of Low-Temperature Pyrolyzates and oil 11. Peaks 1a-1f are shaded. See Table 8 for peak identifications.

mono-aromatic compound (Bendoraitis, 1974); such a compound was not detected in either the oils or the rock extracts, which were treated to remove aromatic compounds prior to analysis. Nevertheless, a base peak of 191 in this spectrum strongly suggests the presence of 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. Thirdly, while peaks 2, 3, 4, 5 and 6 (the C_{27}, C_{28}, C_{29}, C_{30} and C_{31} hopanes, respectively) are present in all these samples, significant peaks eluting before and after peak 5 (C_{30} hopane) are present as well. These are labelled A and C in Figure 32. Peaks A and C have been identified by their mass spectra (Whitehead, 1973a; Kimble, et al., 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 have presumably been released by pyrolysis, although the mode of occurrence of these compounds in the original solid bitumen (i.e., occluded or chemically bound) is unknown.

Examination of the m/e 177 ion chromatogram for the closed tube pyrolyzates revealed the presence of unknown peak B (Figure 23) 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, 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, it appears that peak 1e in the pyrolyzates consists of three co-eluting compounds:

a tricyclic terpane (as also found in the oils), the monoaromatic species discussed above, and the unknown peak B, also found in all oils. Relative amounts of each of these compounds are impossible to determine by available techniques.

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 in a later section of this dissertation.

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 in order to determine whether the materials are co-genetic. Aside from the microscopy work of Jacob (1976) discussed earlier, very little information bearing on this question is available in the literature. A notable exception is the study by Erickson, et al. (1954) of the uranium content of various organic substances worldwide. These authors found "black asphalt" from the Stanley shale, Oklahoma (probably grahamite), and impsonite from the Page mine (mistakenly named grahamite) to each have 0.7 ppm uranium. In view of the large fluctuation in uranium content for worldwide organic substances, the similarity noted here between grahamite and impsonite is remarkable, and suggests a common source.

Selecting other suitable parameters from the present study for correlation is difficult, because of the unusual chemical nature

(e.g., the insolubility) of these solid materials. Further, as a result of evidence suggesting biodegradation (see above), such correlation parameters as are used to relate grahamite and impsonite must not change with chemical alteration, or must change in a predictable manner. Isotopic ratios of bulk material, n-alkane, sterane and terpane distributions of pyrolyzates appear to satisfy these conditions, and have been selected as parameters of correlation. Thus these data are used for comparison of grahamite and impsonite.

Both carbon and isotopic ratios suggest that these solid materials are genetically related (Table 10). 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 relative to ranges for these ratios in carbon- and sulfur-containing materials worldwide. The small isotope ranges of both elements suggest that the materials in question are commonly sourced. Thus gilsonite, although similar to grahamite and impsonite in carbon isotope ratio (Table 10, and Silverman and Epstein, 1958) is distinguishable from the Ouachita materials by its sulfur ratio (Mauger, et al., 1973).

Both high temperature-short term and low temperature-long term pyrolysis techniques are useful in relating the grahamites to each other, and to the impsonite. All of the quasi-n-alkane distributions of the high temperature pyrolyzates (Figure 29) of grahamites are similar to each other, and yet 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 striking resemblance to each other (Figures 31 and 32). The differences in the ratio of regular and rearranged steranes in these samples have been noted although, as will be discussed later, they do not negate conclusions of co-genesis of these materials.

In summary then, one may conclude on the basis of isotopic composition and the distribution of specific compounds in the pyrolyzates, that all Ouachita grahamites and impsonite examined in this study are genetically related. This conclusion is significant in that it points out the inadequacy of the commonly-used classification scheme for solid bitumens and pyrobitumens (Figure 3), which classifies grahamite as an asphaltite and impsonite as a pyrobitumen. It is evident from the co-genetic relationship pointed out above that such a classification can be very misleading.

SOURCE ROCK POTENTIAL AND TEMPERATURE HISTORY OF THE OUACHITA FACIES

Previous Investigations

Several studies of oil and gas source rock potential have been published for numerous basins around the world. These investigations have been reviewed in detail by Hunt (1979, pp. 261-350) and Tissot and Welte (1978). A few of the more important studies will be discussed briefly here. Prior to this discussion however, it will be helpful to review the general kerogen classification scheme of Tissot and Welte (1978), which divides most kerogens into three basic types.

The basis for the kerogen classification scheme in common use today is derived from coal petrology. Petrologists have historically classified coal on the basis of carbon, hydrogen and oxygen content. Van Krevelen (1961) originally plotted atomic H/C ratios versus atomic O/C ratios, in a successful attempt to classify coals into alginites, exinites and vitrinites, based on their positions in the H/C versus O/C field. It was soon discovered that kerogens isolated from rocks may be classified in the same fashion, and that the "Van Krevelen" plot for kerogens bears a striking resemblance to that for coals (Tissot and Welte, 1978). By analogy to the three coal groups above, kerogens can be classified as Type I, Type II or Type III. Although these groupings are not as distinctive as in the case of coals,

they have proved useful in discussions of kerogen classification. In the following paragraphs, examples of each of these kerogen types will be discussed, with an emphasis on the basic conclusions of each of the studies involved.

The source rock potential of the Paleocene-Eocene Green River Formation of the Uinta Basin has been recently studied by Tissot, et al. (1978). These workers used elemental analysis and infrared spectroscopic analysis of the kerogen to demonstrate that the Green River Formation organic matter consists predominantly of long aliphatic chains. Thus the kerogen is classified as Type I. Further detailed analysis of the extractable organic matter (EOM) suggests that oil generation has occurred below 13,000 feet, where vitrinite reflectance measurements have values of 0.7% and greater. The authors conclude that significant generation of petroleum from Type I kerogens requires a higher maturity level than does generation from Type II kerogen. Type I kerogen requires a maturity level equivalent to an R_o value of 0.7, whereas Type II kerogen may generate petroleum at a maturity level equivalent to an R_o value of 0.5. This difference is attributed to the greater energy requirements for the rupture of carbon-carbon bonds, which are more prevalent in Type I kerogens (Tissot, et al., 1978).

A classic study of a Type II kerogen is that of Tissot, et al. (1971), involving the Jurassic Early Toarcian Shales of the Paris Basin. Although infrared spectroscopy and spore carbonization techniques were utilized in an attempt to assess the quality and maturity levels of organic matter in the Toarcian Shales, analytical techniques were not sufficiently advanced for this portion of the study to be very

useful. However, Tissot, et al. (1971) have thoroughly discussed the chemical characteristics of the EOM in these shales, and these data are quite informative. Changes in n-alkane distribution, relative isoprenoid content, distribution of mono- through pentacyclic compounds, and composition of the aromatic, resin (NSO) and asphaltene fractions appear to vary systematically with maturity level. The authors reach the conclusion that "...temperature rise promotes the formation of petroleum compounds...." (p. 2188). The kerogen of the Lower Toarcian Shales has subsequently been described by Tissot, et al. (1978) as Type II.

Analysis of a Type III kerogen and products generated from such a kerogen has been presented in two excellent studies of the organic matter of the Douala Basin (Cameroon, West Africa) by Albrecht, et al. (1976) and Durand and Espitalie (1976). In general, changes in the EOM with increasing depth (i.e., temperature) are also recognized in this basin. In addition, changes in composition of the aromatic component of the EOM were also noted, such as disappearance of naphtheno-aromatics, and generation of diaromatics with depth (Albrecht, et al., 1976). Detailed study of kerogen maturity was possible because of advances in analytical techniques and because of a high geothermal gradient in the basin which resulted in a wide range of maturity levels. The Upper Cretaceous Logbaba Series, the primary hydrocarbon source sequence in the basin, is somewhat unusual in that it appears to be an oil source, despite a landplant origin for the organic matter. This suggests that Type III kerogens, although having a much lower potential for oil generation, cannot be completely eliminated as sources for oil.

In addition to this brief review, it will be useful to review the methods of source rock evaluation, with emphasis on those criteria necessary to qualitatively "rank" petroleum source rock potential. The three characteristics of organic matter in a potential source rock which must be assessed are the quantity, quality and maturity level.

The amount of organic carbon in a rock is one of the most basic considerations in the evaluation of petroleum source rocks, although the amount of total organic carbon (TOC) necessary to generate oil is open to debate among organic geochemists. Studies reviewed by Hunt (1979) suggest that a minimum of 0.4 to 1.0 percent total organic carbon in a rock is necessary to generate commercial oil. This range may be somewhat lower for carbonate source rocks. Another important parameter is the fraction of the organic carbon that is soluble, or the bitumen/TOC ratio. Of greater importance still is the amount of hydrocarbon in the sample, expressed variously as hydrocarbons/TOC or hydrocarbon content as a fraction of total rock weight. Each of these ratios is presented (in a table to be introduced later) for samples of the present study, although most published studies cite ppm hydrocarbons in the rock as a measure of hydrocarbon quantity. Classification of a rock as a "good" or "bad" source rock on this basis is somewhat dubious, in the writer's opinion, although a rock with greater than 500 ppm hydrocarbon content is often cited as a "good" source rock (Philippi, 1957). Current thinking about source rocks however, tends to deemphasize the importance of absolute and relative quantities of hydrocarbons (Hunt, 1979, p. 263). Both the quality and maturity of organic matter in a rock are often regarded as being more critical

to the classification of a rock as a source for oil.

Discussion of the quality or type of organic matter generally focuses on the type of kerogen within the rock (Burgess, 1974). Kerogen is classified on the basis of the type of living organic matter which served as precursor material. Although classification of kerogen is generally discussed in terms of Types I, II, III (Tissot and Welte, 1978), examples of mixtures of each of these types are common in the literature. In general kerogen types correspond to an aquatic origin (Types I and II) and a terrestrial origin (Type III). Since a terrestrial environment contains organic matter that is chemically and structurally distinct from that resulting from an aquatic environment, the ultimate organic product of diagenesis and catagenesis of each type of organic matter will be different. Specifically, marine environments and terrestrial environments tend to produce products rich in paraffinic hydrocarbons and polyaromatic structures, respectively, as shown by the pyrolysis experiments of Giraud (1970). Crude oil, being rich in paraffinic molecules, is thought to result predominantly from a marine-type kerogen (generally Type II). Consequently, it is important to determine the type, or quality, of organic matter present as kerogen in a potential source rock.

In addition to kerogen study, analysis of bitumen of a rock can provide information as to the type of organic matter present (Tissot and Welte, 1978). Specifically, geochemical fossils (the "biomarkers" discussed in the previous section) are direct indications of biochemical input. Unfortunately, due to problems in identifying such material as being indigenous to rock, their use as type indicators is

not common. Furthermore, changes in the chemical structure of these geochemical fossils can result during maturation. Nevertheless, all attempts to correlate oils to rocks based on biomarker analysis are in fact attempts to type the kerogen in the rock as an oil-generator.

The final major consideration in source rock analysis is the maturity of the organic matter in the rock. It is generally conceded that a rock must be "thermally mature" in order to generate and expel significant quantities of crude oil. Various empirical methods have been employed to assess such maturity (Dow, 1977). The best estimates of maturity are based on the elemental analysis (for carbon, hydrogen and oxygen) of kerogen. It is suggested that the ratio of hydrogen to carbon must attain some minimum value (depending on kerogen type) before significant generation will occur (Tissot and Welte, 1978). Other analyses of kerogen, such as a percentage of light reflected from vitrinite particles within the kerogen matrix, and coloration of spores and pollen, are also useful as maturity indicators. Finally, bitumen analyses are also useful in assessing the maturity level of a rock, although one must be cautious of non-indigenous bitumen in the rock. Specific details of these assessments will be presented later in this section, where appropriate.

Two of the foregoing topics, quantity and quality of organic matter, will be discussed below for the Ouachita samples in terms of procedural aspects of rock analysis. Specifically, these topics are presented in terms of whole rock, kerogen and bitumen analysis. The purpose of this section is therefore to evaluate the source potential and temperature history of rocks of the Ouachita Facies.

Whole Rock 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 (see Appendices for sample information). Initially, 115 subsurface and 11 outcrop samples were analyzed for total organic carbon (TOC) and, where necessary, for total carbonate carbon (TCC). Results are presented in Table 11 and in Figures 33 and 34. The data in Table 11 indicate that, in general, outcrop samples are considerably richer in TOC than cuttings samples. Because of the leanness of many of the cuttings samples, errors of interpretation due to the presence of recycled carbon and uphole caving are a possibility.

Each stratigraphic interval studied has an average TOC value in excess of 0.76%. Relatively few Missouri Mountain and Polk Creek Formation samples were analyzed for TOC content. Nevertheless, the TOC levels reported here are high enough to justify further study of all six formations as potential source rocks for oils and solid bitumens which occur in the Ouachita Mountains.

Also listed in Table 11 are total carbonate carbon (TCC) values for the rocks of this study. Note the pronounced decrease in TOC with a TCC increase in the Arkansas Novaculite of well 40. TCC values reach a maximum at approximately the depth at which TOC values reach a minimum (sample 40-8600-8700). However, as can be seen from Table 14 (to be introduced later), the hydrocarbon content as a percentage of total organic carbon in this well does not change appreciably from 7200 feet to 9100 feet. Similar observations by Hunt led

Table 11

Total Organic Carbon (TOC) and Total Carbonate Carbon (TCC) Contents of Ouachita Rocks

Sample Number	Stratigraphic Interval	TOC (%)	TCC (%)
24-3400-3500		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	Stanley	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 11 (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 11 (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.

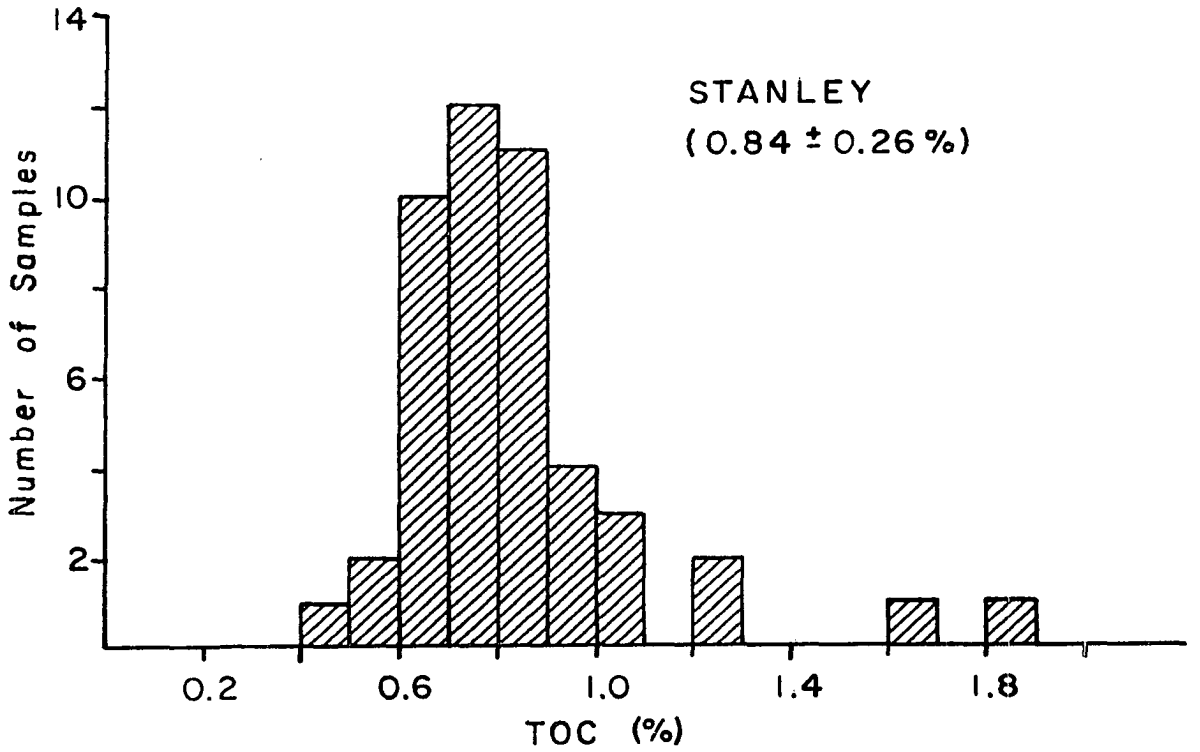


Figure 33. Total Organic Carbon Histogram for Stanley Group samples. Only subsurface samples are plotted. Number in parentheses is the average, with standard deviation.

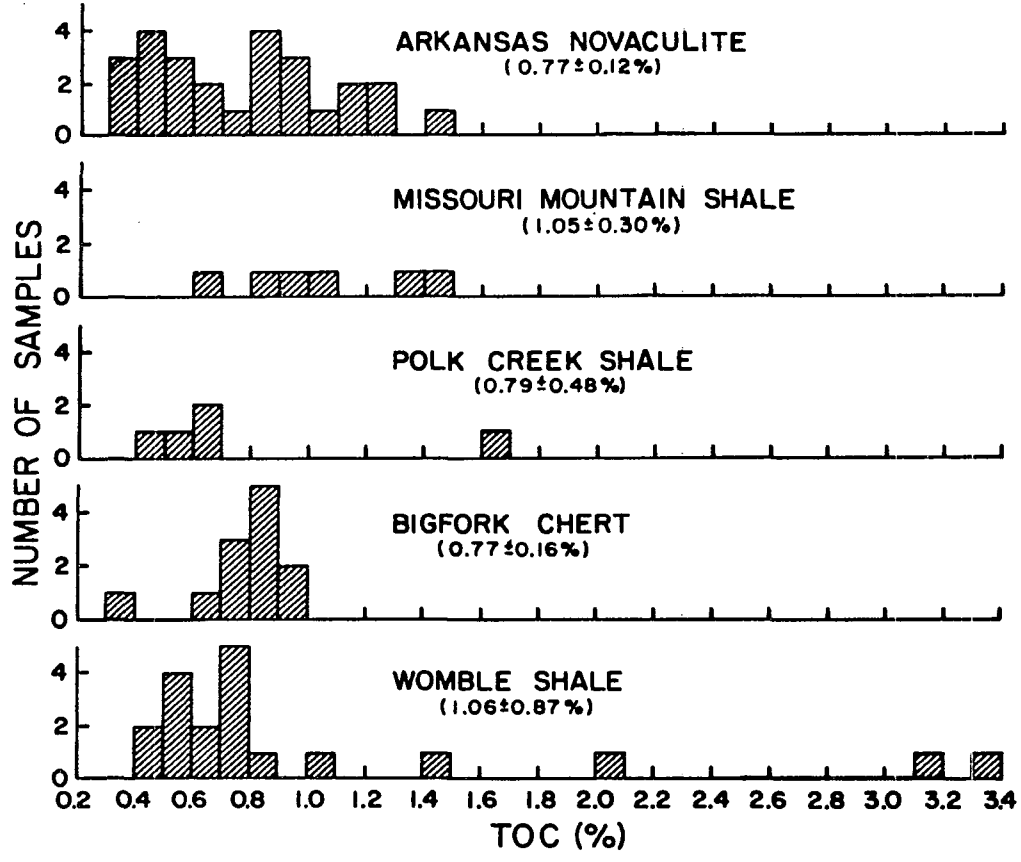


Figure 34. Total Organic Carbon Histograms for Arkansas Novaculite through Womble samples. See Figure 33 for further information.

him to conclude that "...fine-grained carbonate rocks generate more hydrocarbon for the same amount of total organic matter, so as little as 0.3 percent organic carbon may be sufficient for some carbonate source rocks" (Hunt, 1979, p. 270). Although the samples from well 40 are not carbonates, an increase in TCC to 7% is accompanied by a reduction in TOC by more than a factor of two, while the HC/TOC ratio does not fluctuate nearly as drastically. As a result of these observations, a few Arkansas Novaculite and Polk Creek Formation samples that were relatively high in carbonate content were chose for further chemical analysis (i.e., extraction and fractionation). A total of 57 samples was selected for extraction.

In addition to total organic carbon and total carbonate carbon determinations, at least one sample of each formation and group was analyzed to determine the carbon isotope ratio (Table 12) of its total organic carbon (TOC). The range of $\delta^{13}C$ values observed is -28.9 to -24.5 $^{o}/oo$. Although these values, particularly -28.9 $^{o}/oo$, suggest a terrestrial source (Sackett, 1964), values this light have also been noted in pre-Silurian rocks (Welte, et al., 1975a). A survey of the literature indicates that the Ouachita section organic matter is of both marine and terrestrial origin. Silverman and Epstein (1958) list two determinations of total organic matter in shales from the Miocene in California and the Eocene Green River Shale of -22.8 and -31.9 $^{o}/oo$, respectively. The Miocene sample is listed by these authors as a marine shale, while the Green River Formation is of non-marine (lacustrine) origin. Craig (1953) reports isotope ratios for the organic carbon of twelve shales, ranging from -30.8 to -18.0 $^{o}/oo$,

Table 12

Extractable Organic Matter (EOM) and Isotopic Data

Sample Number	Stratigraphic Interval	EOM (ppm)[a]	EOM/TOC (%)	^{13}C (‰)[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 12 (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 = $\pm$ 0.10.

[c] Outcrop sample.

[d] Not determined.

with an average value of -28.0 °/oo. Unfortunately, no distinction was made between marine and non-marine origin by Craig. This range overlaps with and is slightly heavier than the range for organic carbon in clastic rocks indicated by Fuex (1977) of -32.0 to -23.0 °/oo. Hunt (1979, p. 26) suggests an average value for the earth's crust of -27 °/oo, a value close to the average for the samples of the present study.

In summary, samples of the present study apparently cannot be categorized as marine or non-marine in origin on the basis of the isotopic content of their total organic matter. Ouachita samples appear to contain organic matter derived from both terrestrial and marine sources. In addition, samples of this study do not exhibit an isotopic ratio-geologic time relation, as shown by Welte, et al. (1975a) for some Paleozoic sediments, although a time span in excess of 150 million years is represented.

Kerogen Studies

Selected rock samples were demineralized after extraction of soluble organic matter and the resultant kerogen concentrates were analyzed for carbon isotope ratios.

Carbon isotope studies of kerogen have been reviewed by Galimov (1980), and this review provides data for comparison with the range observed in the present study (-29.7 to -25.5 °/oo). Of 32 Paleozoic kerogens reported by Galimov (1980), a range from -28.2 to -21.5 °/oo is observed. These values are somewhat greater (isotopically heavier) than the range reported here. This is in contrast to

data presented by Stahl (1978) for 14 kerogens from different ages, and locations throughout the world, which range from -33.8 to -22.2 °/oo.

Galimov (1980) noted a general decrease (lightening) of the carbon isotope ratio with age for rocks of the Phanerozoic sequence of the Russian Platform. A similar observation was reported by Welte, et al. (1975a) for Paleozoic kerogens of northern Germany. The data in Table 13 however, indicate that no such trend is evident for the Ouachita section, although it is perhaps noteworthy that the lightest kerogens analyzed are from the upper Ordovician.

The carbon isotope values for kerogen (Table 13) are similar to those for organic carbon in the whole rock (Table 12). This is to be expected, because the bulk of organic matter in an ancient non-reservoir rock is kerogen (Tissot and Welte, 1978). However, the range for kerogens is from -29.7 to -25.5 °/oo, making this material isotopically lighter than the whole rock. This is an anomalous finding, since thermal maturation cleaves isotopically lighter material from a kerogen (Silverman, 1964). Thus whole-rock organic carbon should be lighter than kerogen isolated from it. The opposite is observed here in the four samples whose kerogen and total organic carbon isotope ratios were determined (see Table 12). However, the isotopic ratios of extractable organic matter (EOM) are lighter in all cases than their corresponding kerogen or total organic carbon in the rock, as would be expected (Table 12). It is possible that 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 (see Appendix II). This would result in anomalously heavy isotope ratios for TOC.

Kerogen concentrates are also useful in determining the type, or quality of organic matter in a rock. Such analyses are usually visual and are somewhat subjective. Kerogen concentrates, as well as four whole rock samples of this study, were examined microscopically for evidence of organic matter type. Microscopic examination of the kerogen concentrates revealed only two samples containing morphologically distinct organic matter. One sample from the Stanley Group and one sample of Arkansas Novaculite contained several trilete spores. These spores were identified on the basis of the trigonal suture and their size (approximately 60 microns). However, with such limited information, it was not possible to type the kerogen on this basis.

Examination of four whole rock samples prepared for reflectance measurements show that almost all of the recognizable organic matter in these Stanley and Arkansas Novaculite samples consists of the maceral vitrinite. Tissot and Welte (1978, p. 452) state that "Vitrinite is abundant in type-III kerogen,...moderately abundant in type-II kerogen, and mostly absent in type-I." On this basis it is suggested that the kerogen contained in these four samples is predominantly of Type III. It must be stressed however, that analysis of two samples each of the Stanley Group and the Arkansas Novaculite Formation is insufficient to characterize organic matter type of these rocks throughout the Frontal and Central Regions of the Ouachita

Mountains of Oklahoma.

Bitumen Studies

Selected rock samples, chosen on the basis of TOC contents, were subjected to soxhlet treatment in methylene chloride in order 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 12. These data are presented graphically in Figure 35. Average EOM values, in parts per million parts rock, for the Stanley, Arkansas Novaculite, Missouri Mountain, Polk Creek, Bigfork and Womble are 1150, 871, 1183, 925, 732 and 2640, respectively. These values are all high enough to suggest that each of these stratigraphic intervals has hydrocarbon source rock potential. Such data however, can be misleading unless interpretted with other measurements. For instance, an EOM yield of 10,000 ppm may be "average" for a shale with 6 percent organic carbon. The same yield would have drastically different meaning if the sample was a sandstone with 0.1 percent organic carbon. Table 12 contains data which relate EOM to TOC.

Carbon Isotopic Analysis

Also listed in Table 12 is the carbon isotope ratio for the EOM, of 13 selected samples. As discussed earlier, these values are isotopically lighter than those of their corresponding kerogen or total organic carbon (TOC), where comparisons are available. In the case of kerogen-EOM pairs, samples 40-9100-9200, 31-9665-9715 and 28-1750-1800 possess kerogen which is isotopically heavier than the corresponding EOM by 1.6, 5.7 and 1.3 $^{o}/_{oo}$, respectively, suggesting

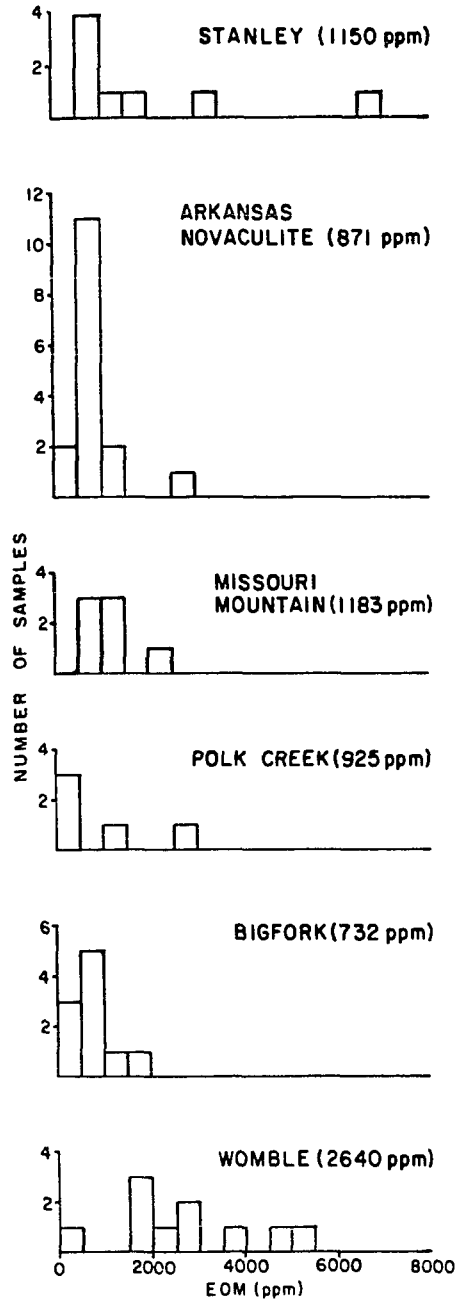


Figure 35. Extractable Organic Matter Histograms for Stanley through Womble samples. Numbers in parentheses are average EOM values. Average for Stanley samples excludes the richest sample, due to the presence of non-indigenous organic matter (see text).

either difference in thermal maturation or, perhaps, differences in original organic input.

The range of isotope ratios for bitumens of the present study (-41.2 to -29.3 °/oo) is considerably lighter than that reported by Galimov (1980) for Paleozoic bitumens (-30.0 to -24.0 °/oo). Silverman and Epstein (1958) report a Pliocene extract (marine) value and a Green River Formation extract (non-marine) value of -22.2 °/oo and -30.5 °/oo, respectively. Comparison of these values, and those of Galimov (1980), with ratios of EOM of the present study can be misleading however, since the maturity levels of samples from the two cited studies are unknown.

Metal Analysis

In an attempt to establish characteristic metal concentrations of the EOM of each stratigraphic interval studied, vanadium and nickel determinations of at least one sample from each stratigraphic interval were made (Table 13). The data suggest that the highest concentration of vanadium (greater than or equal to 3.0 ppm of extract) was found in the Missouri Mountain, Polk Creek and Bigfork Formations. Pre-Devonian samples are highest in nickel content (all greater than or equal to 1.0 ppm of extract). The vanadium:nickel ratio (w/w) of EOM appears highest in samples collected from Silurian and upper Ordovician rocks. In general, these data suggest that distinction between samples of different ages on the basis of the metals vanadium and nickel is not possible. The outcrop sample of the Bigfork Formation appears to have lost nickel "faster" than vanadium, suggesting an

Table 13

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) = $\pm$ 15%.

increase in the V/Ni ratio with weathering. Such an interpretation must be made with caution, since only two samples of Bigfork Formation EOM were analyzed. Furthermore, such a difference in V/Ni is not noted between the outcrop and subsurface samples of the Polk Creek Formation (Table 13).

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 (EOM). Each of these was fractionated into paraffinic hydrocarbons, aromatic hydrocarbons, nitrogen-, sulfur-, and oxygen-containing compounds (NSO's) and asphaltenes. In addition, each paraffinic hydrocarbon fraction was analyzed by gas chromatography. Table 14 lists the results of these analyses.

Hydrocarbons typically constituted less than 50 percent of the total EOM. Paraffinic and aromatic components usually comprised 40-60 percent of the total hydrocarbon fraction. The hydrocarbon content of the rock is particularly important, because hydrocarbons constitute the majority of the compounds in most crude oils, comprising more than 80% of the crude oils of the present study (Table 6). Table 14 lists hydrocarbon (HC) yield of whole rock and of the total organic carbon of the rock (HC/TOC). Figure 36 shows the relation between HC yield and TOC on a log-log graph (Baker, 1962). Various fields noted in Figure 36 are after Hunt (1979, p. 266), and suggest that most of the samples in Table 14 contain indigenous EOM. A single possible exception is sample 24-3600-3700, an unusually dark shale

Table 14

Extractable Organic Matter Fraction Data

Sample Number	Stratigraphic Interval	Fraction (%)[e]				TOC[f]	HC[a]/rock	HC[b]/TOC	pris/phyt	n-C_{17}/prist	n-C_{18}/phyt	CPI[c]
		Sat HC	Arom HC	NSO	Asph							
24-3600-3700[d]	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	26.3	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[d]		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[d]		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 (Table 6).

[d] Samples analyzed for sterane and hopane distributions.

[e] Reproducibility data given in Appendix II.

[f] Total organic carbon.

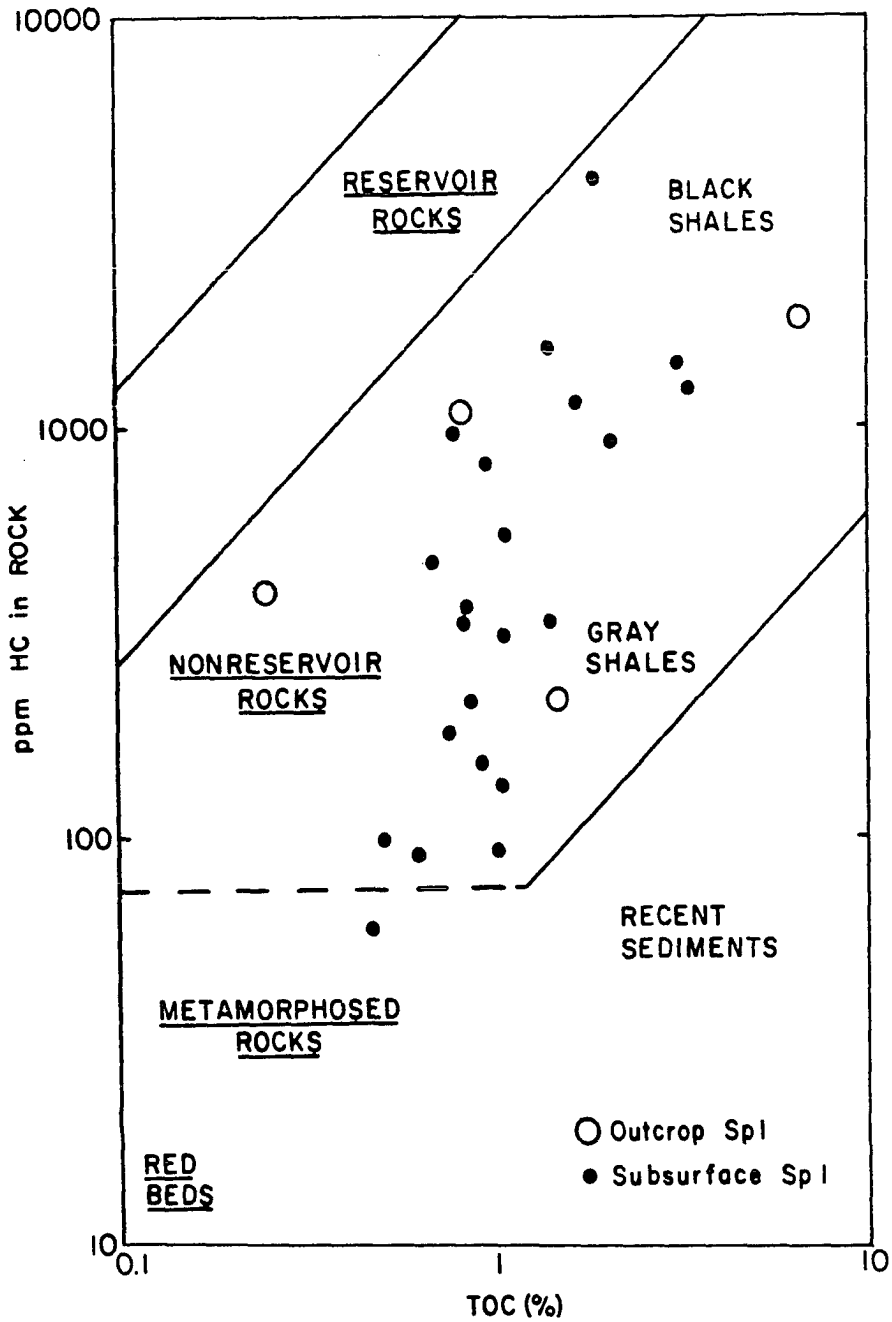


Figure 36. Graph of Total Hydrocarbon versus Total Organic Carbon for selected rock samples. Plot format and fields are from Baker (1962) and Hunt (1979).

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 unambiguously classified as a rock whose organic matter is totally indigenous, and was not used in calculating average EOM values for Stanley Group samples.

Philippi (1957) has classified source rock "quality" on the basis of parts hydrocarbon per million parts rock. A fair source rock thus contains in excess of 150 ppm HC in the rock, while a good source rock has over 500 ppm HC in the rock. By this measure, at least one sample from each formation in this study can be established as a "fair" source rock, while "good" or better source rocks are restricted to the Stanley, Polk Creek and Womble stratigraphic intervals. However, caution must be exercised because this scheme does not consider maturity level of potential hydrocarbon source rocks or total organic carbon content.

The implications which result from screening criteria such as total EOM and total HC content in a rock can be better assessed if accompanied by a molecular description of the paraffinic hydrocarbon fraction of the EOM. Consequently, 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 present in some of the samples will also be discussed.

N-Alkane and Isoprenoid Data

Typical gas chromatograms of the paraffinic hydrocarbon fraction are shown in Figure 37. N-alkane distributions for the Stanley Group, the Arkansas Novaculite through Bigfork Formations, and the Womble Formation, are depicted in Figures 38, 39 and 40, respectively. As noted in these figures, different samples from the same formation and the same well exhibit similarities (e.g., Figure 38, well 25; Figure 40, well 28). However, different samples from the same formation, but different wells, exhibit some differences (e.g., Figure 40, wells 25 and 28). In general though, similarities are noted among samples from the same stratigraphic interval. For example, all Missouri Mountain Formation samples (Figure 39) 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 the organic matter of these intervals.

Note the predominance of the 22-carbon n-alkane in EOM of all Arkansas Novaculite Formation samples and in the two unweathered Bigfork Formation samples. The strong occurrence of n-C_{22} in these formations suggests a lithologic dependence. A dominance of n-C_{22} in rock extracts was noted by Schenck (1968) in rocks which ranged 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 (1968) also suggests that, because an n-C_{22} predominance has never been documented in a crude oil, then such a predominance

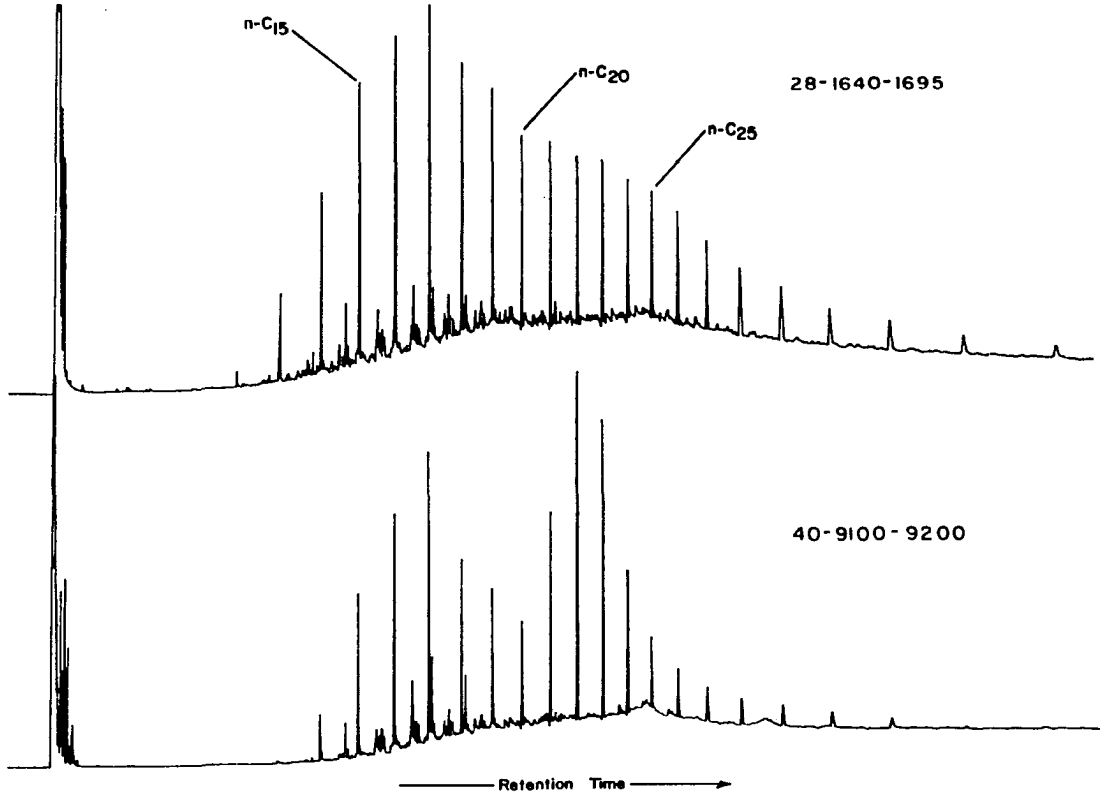


Figure 37. Typical Gas Chromatograms of Paraffinic (Saturate) Hydrocarbon Fractions of two Potential Source Rock Extracts. Conditions as in Figure 10.

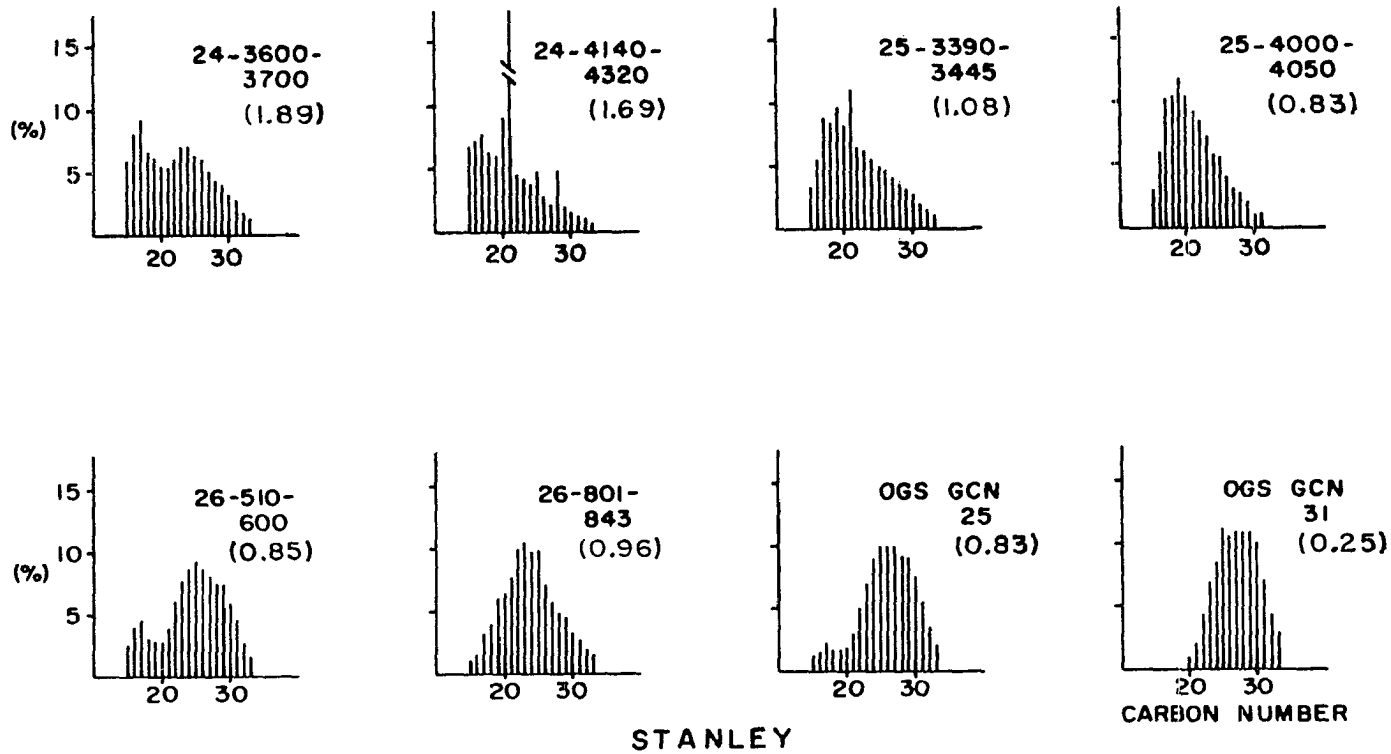


Figure 38. N-Alkane Distributions of Stanley samples. High "n-C_{21}" concentration in sample 24-4140-4320 may be due to co-elution of an unknown compound in the saturate hydrocarbon fraction. Total organic carbon values (%) are given in parentheses.

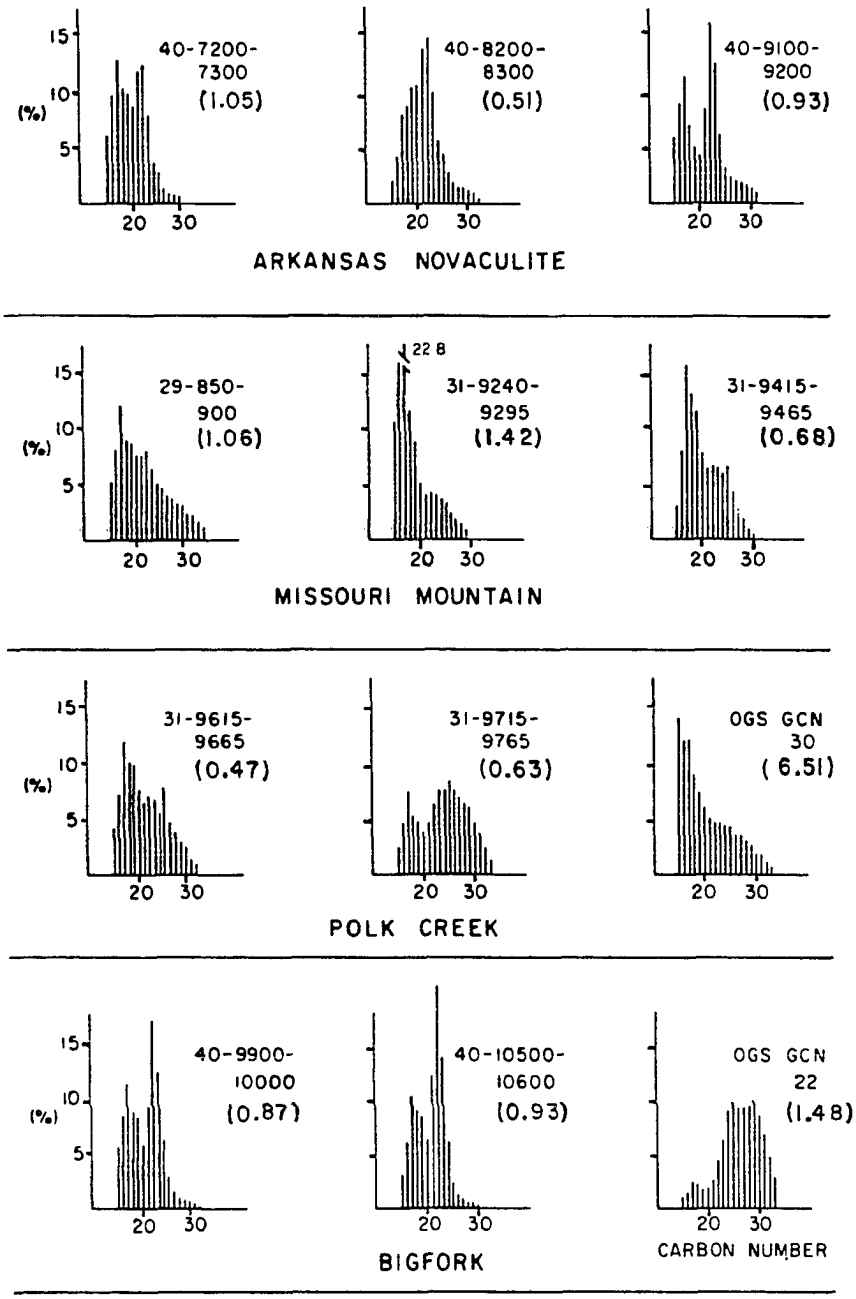


Figure 39. N-Alkane Distributions of Arkansas Novaculite through Bigfork samples. Total organic carbon values (%) are given in parentheses.

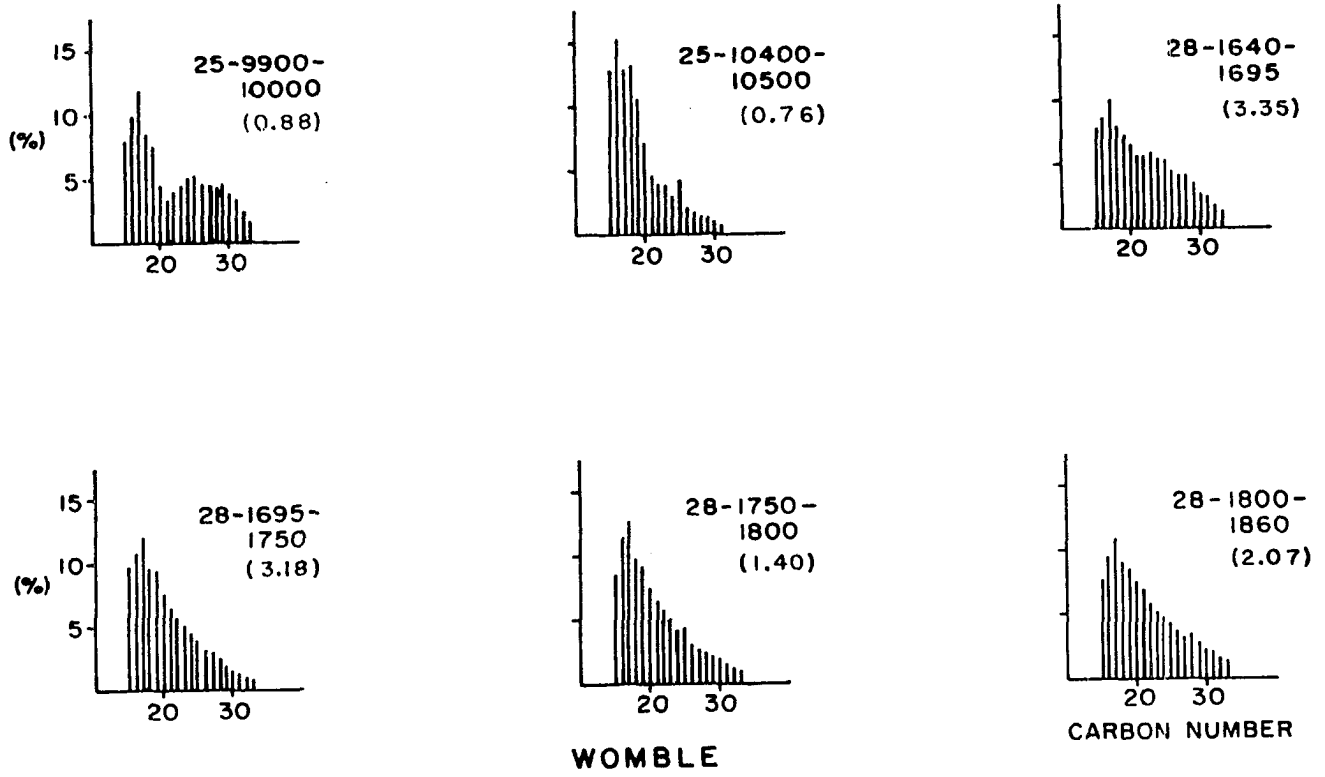


Figure 40. N-Alkane Distributions of Womble samples. Total organic carbon values (%) are given in parentheses.

in a rock extract implies immaturity of the rock. It appears that this conclusion is unwarranted, at least in the present study, because of the thermally-mature nature of several samples which demonstrate the n-C_{22} predominance.

In addition to the distribution of various chemical fractions in the EOM of selected rock samples, Table 14 also lists the carbon preference index and three isoprenoid and n-alkane ratios: pristane/phytane, n-heptadecane/pristane, and n-octadecane/phytane. All these parameters have been presented in a single histogram-type plot for each sample. These plots are shown for the Stanley Group, the Arkansas Novaculite through Bigfork Formations, and the Womble Formation, in Figures 41, 42 and 43, respectively. Although these diagrams will be more useful in the correlation phase of this study, certain of their aspects will be discussed here as well.

As is the case with the n-alkane distributions, similarities between samples from the same formation in the same well are noticeable (e.g., Figure 41, well 25; Figure 43, well 25). Also, in some cases all samples from a single formation exhibit similarities (e.g., Missouri Mountain Formation, Figure 42). Some of the other factors evident in Figures 41-43 are: (1) The Womble is the only formation which has an n-heptadecane/pristane and an n-octadecane/phytane ratio greater than 3.25 (see Table 14); (2) The Stanley Group and the Womble Formation (Figure 41 and Figure 43) contain EOM with a paraffinic hydrocarbon/aromatic hydrocarbon ratio significantly greater than one; (3) The asphaltene content is consistently in excess of 24% in <u>all</u>

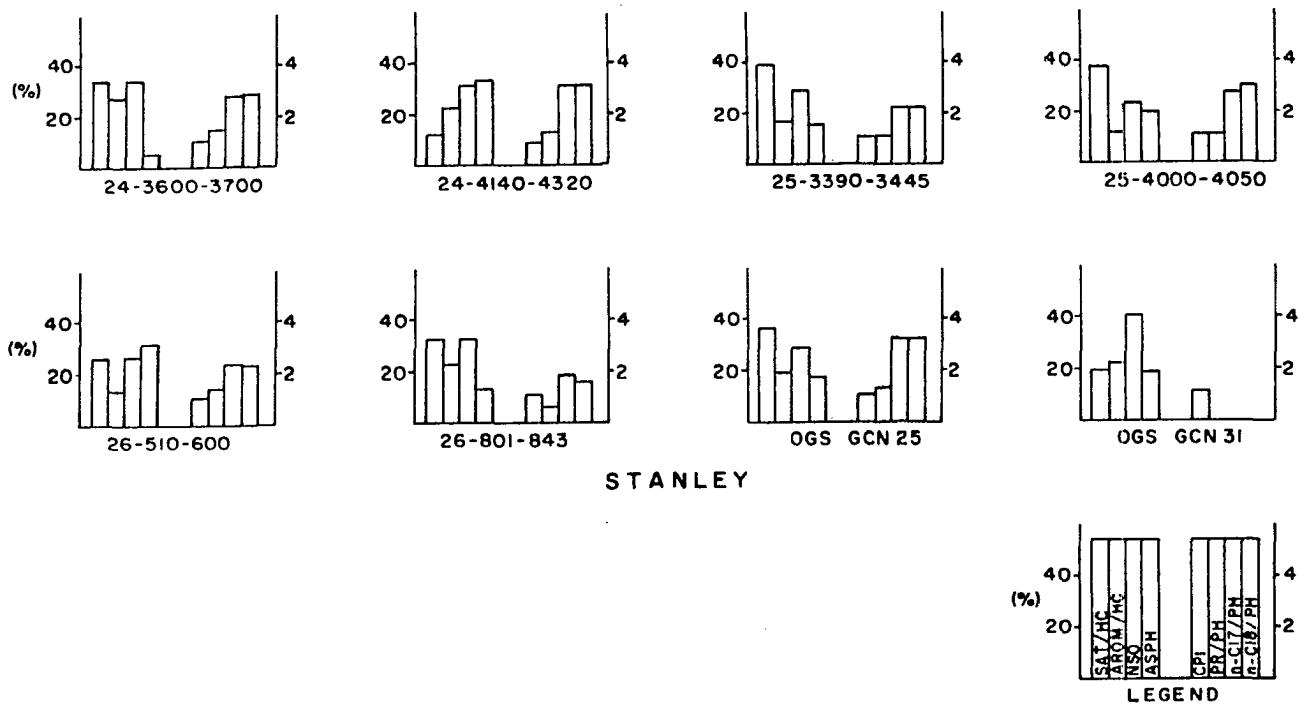


Figure 41. Graphic Display of Fractions and N-Alkane/Isoprenoid Ratios of Stanley Samples.

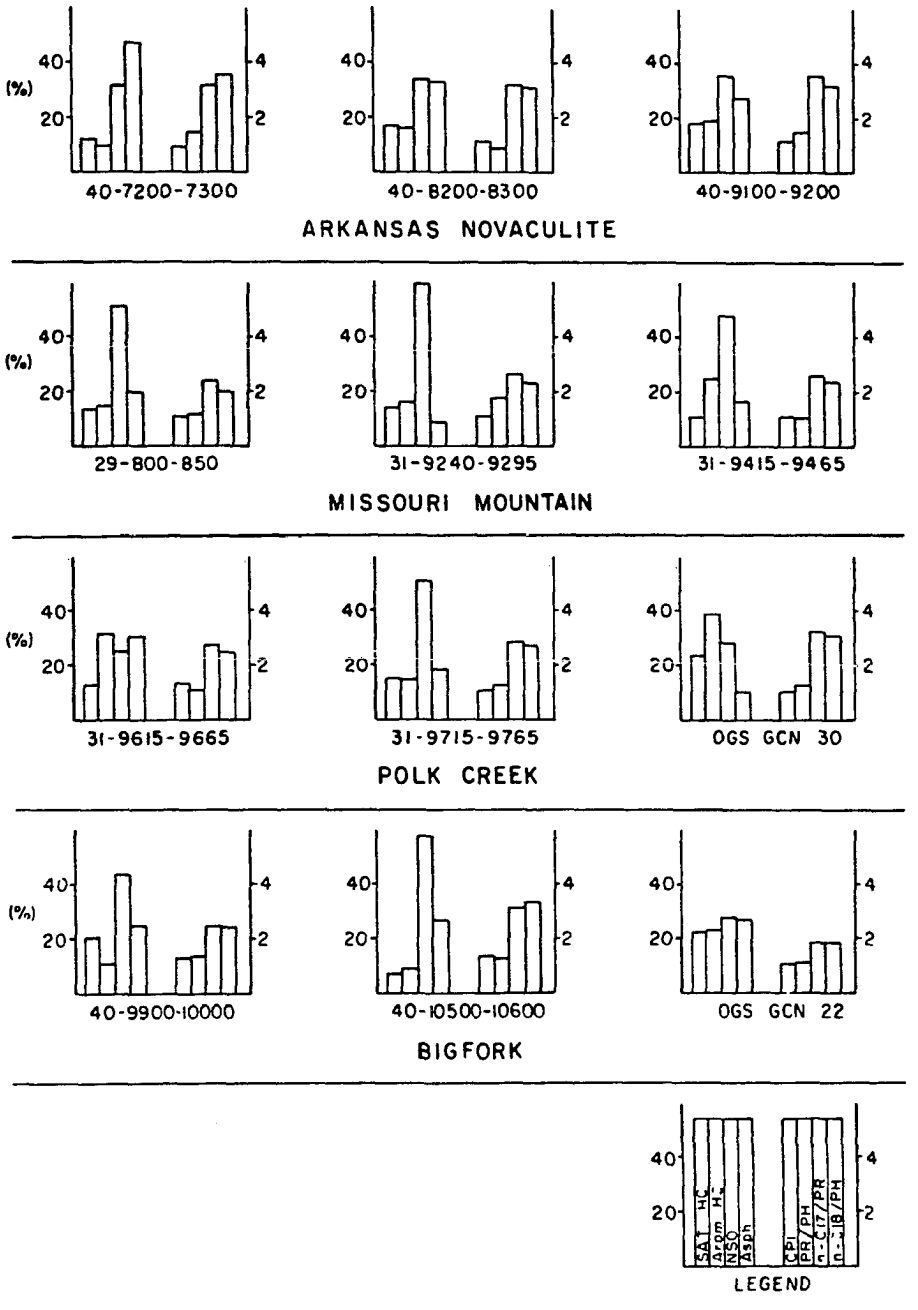


Figure 42. Graphic Display of Fractions and N-Alkane/Isoprenoid Ratios of Arkansas Novaculite through Bigfork samples.

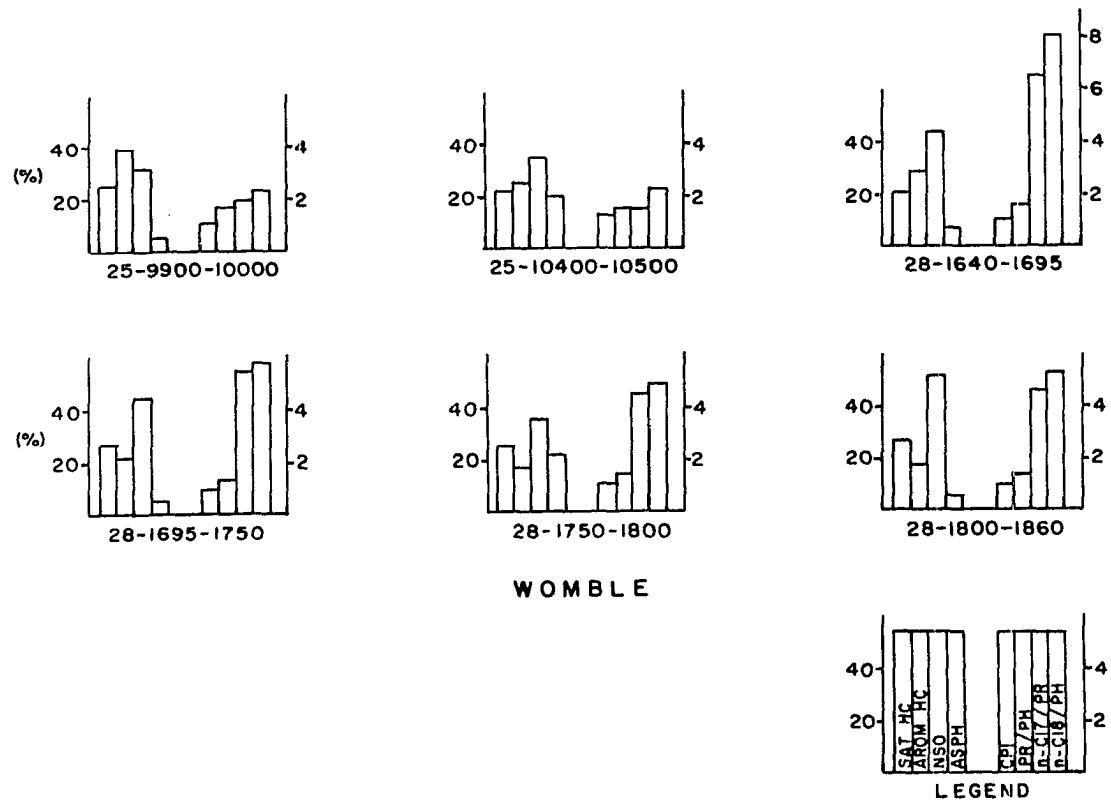


Figure 43. Graphic Display of Fractions and N-Alkane/Isoprenoid Ratios of Womble samples.

samples of Arkansas Novaculite and Bigfork Formations; and (4) The NSO fraction typically comprises a higher percentage of EOM than either the hydrocarbon fractions or the asphaltene fraction. These observations are somewhat difficult to explain. Observations (1) and (2) are probably functions of maturity level in these samples, although detailed conclusions from the available data are unwarranted. Observation (3) is most likely a consequence of lithology, 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 level of maturity of these samples.

Sterane and Hopane Data

The branched and cyclic fraction of EOM of samples containing a large quantity of 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 very minor. Interpretation was further complicated by the fact that the mass chromatograms were not of the quality most desirable, owing to the low content of these compounds. Nevertheless, some conclusions based on these biomarkers are still possible. Two samples of each of the six stratigraphic intervals involved in this study were analyzed for sterane and terpane content; these are noted in Table 14, footnote d. The characteristic ion fragments 217 and 191 were monitored for sterane and terpane content, respectively. These scans are shown in Figures 44-49 (steranes) and Figures 50-55 (terpanes). In addition,

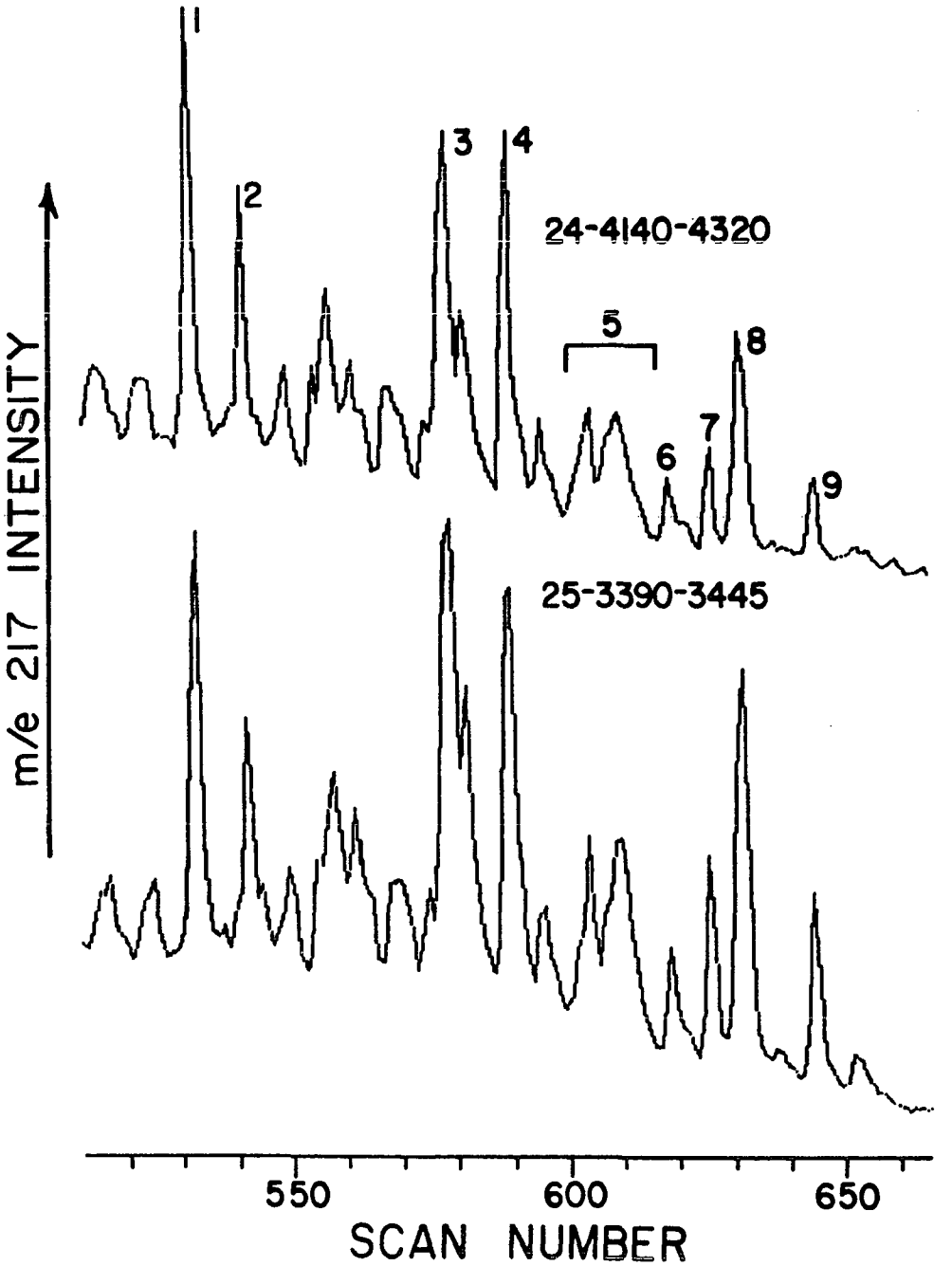


Figure 44. m/e 217 Ion Chromatograms of Stanley samples. See Table 7 for peak identifications.

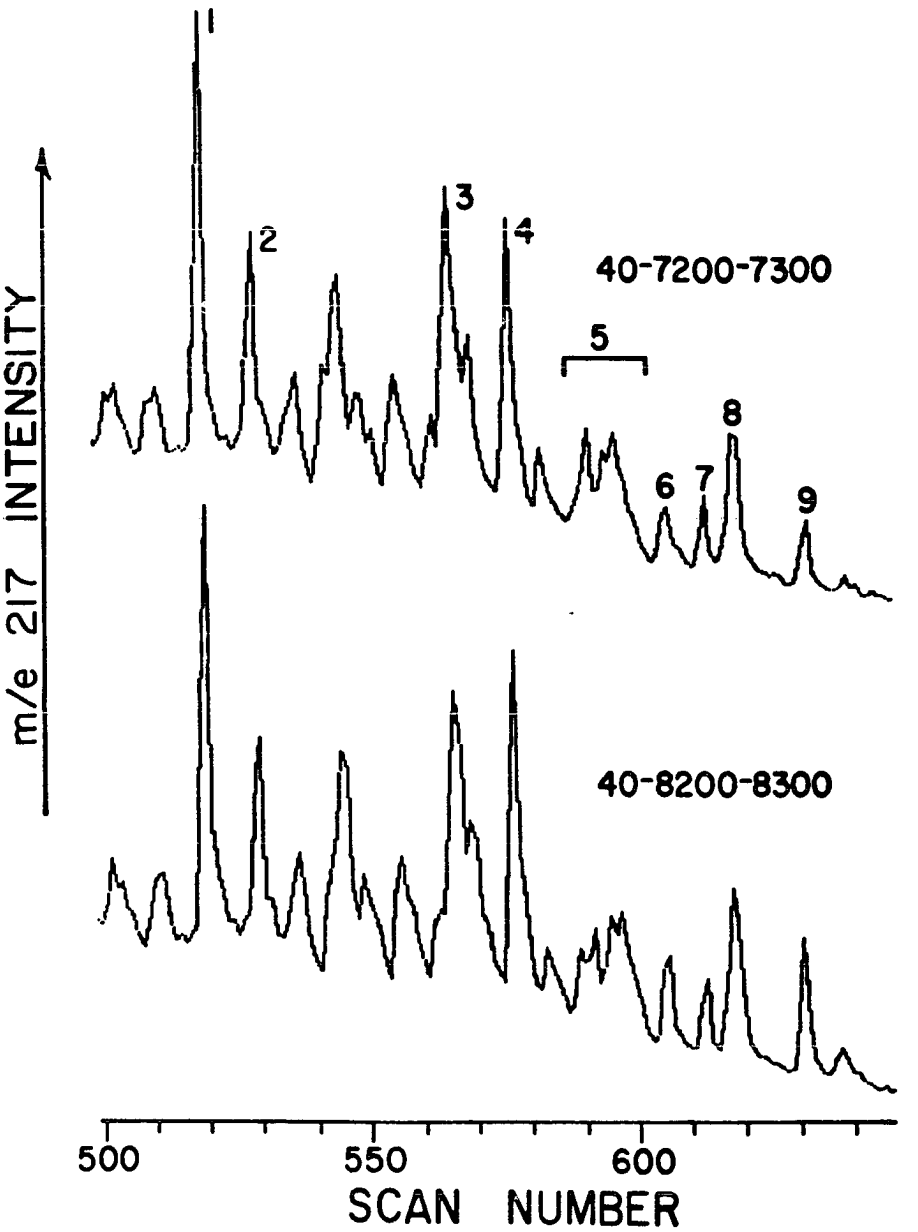


Figure 45. m/e 217 Ion Chromatograms of Arkansas Novaculite samples. See Table 7 for peak identification.

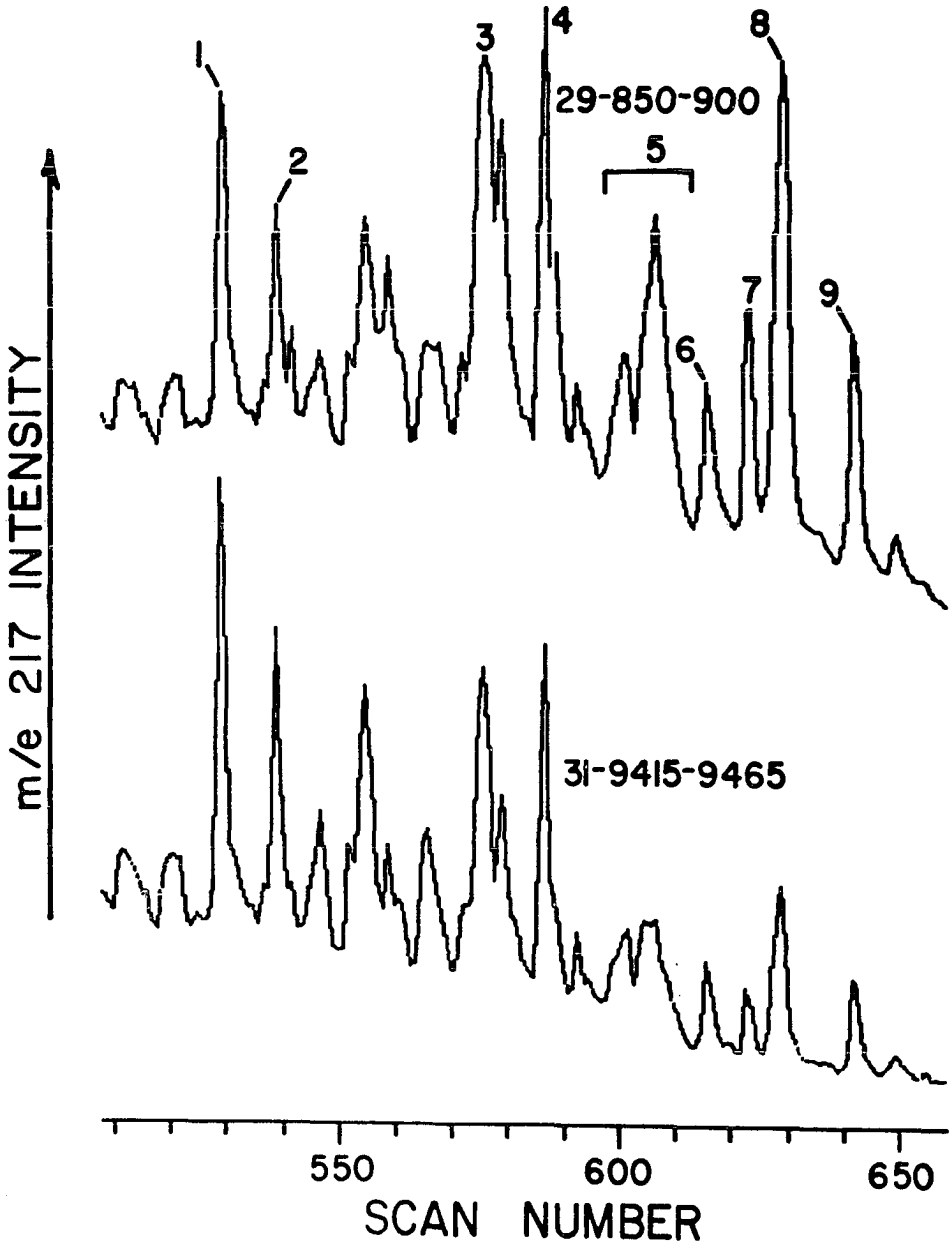


Figure 46. m/e 217 Ion Chromatograms of Missouri Mountain samples. See Table 7 for peak identification.

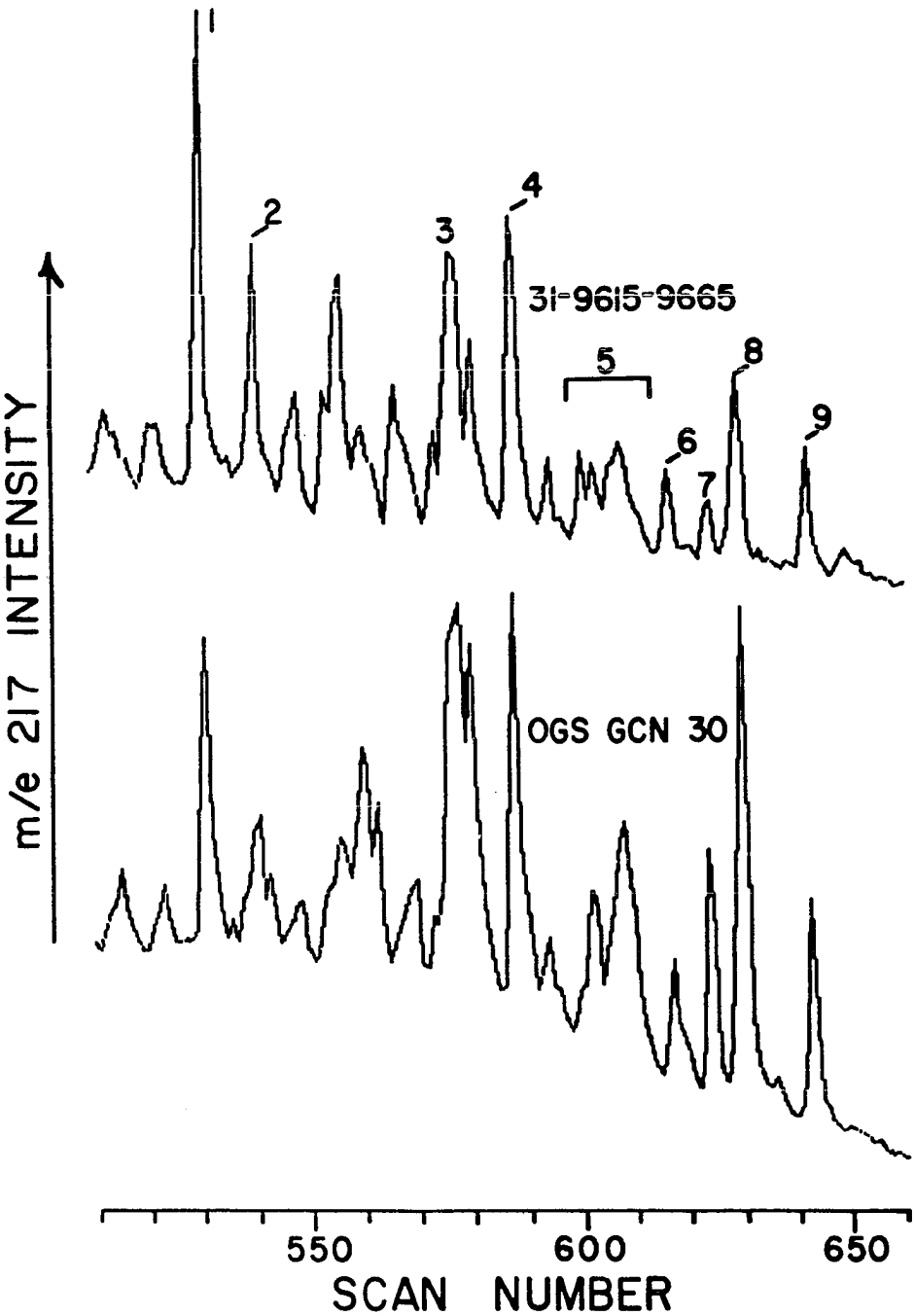


Figure 47. m/e 217 Ion Chromatograms of Polk Creek samples. See Table 7 for peak identifications.

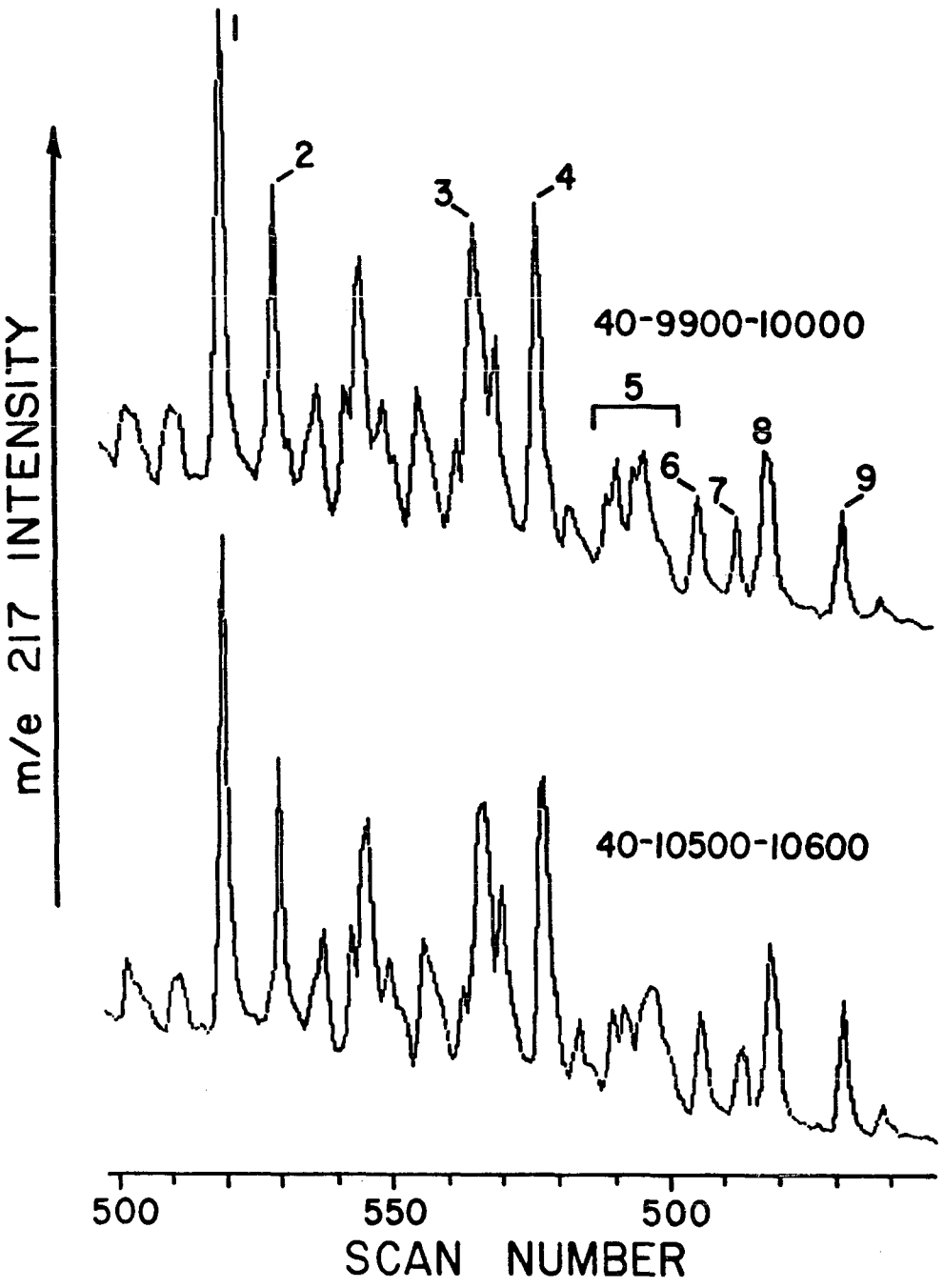


Figure 48. m/e 217 Ion Chromatograms of Bigfork samples. See Table 7 for peak identification.

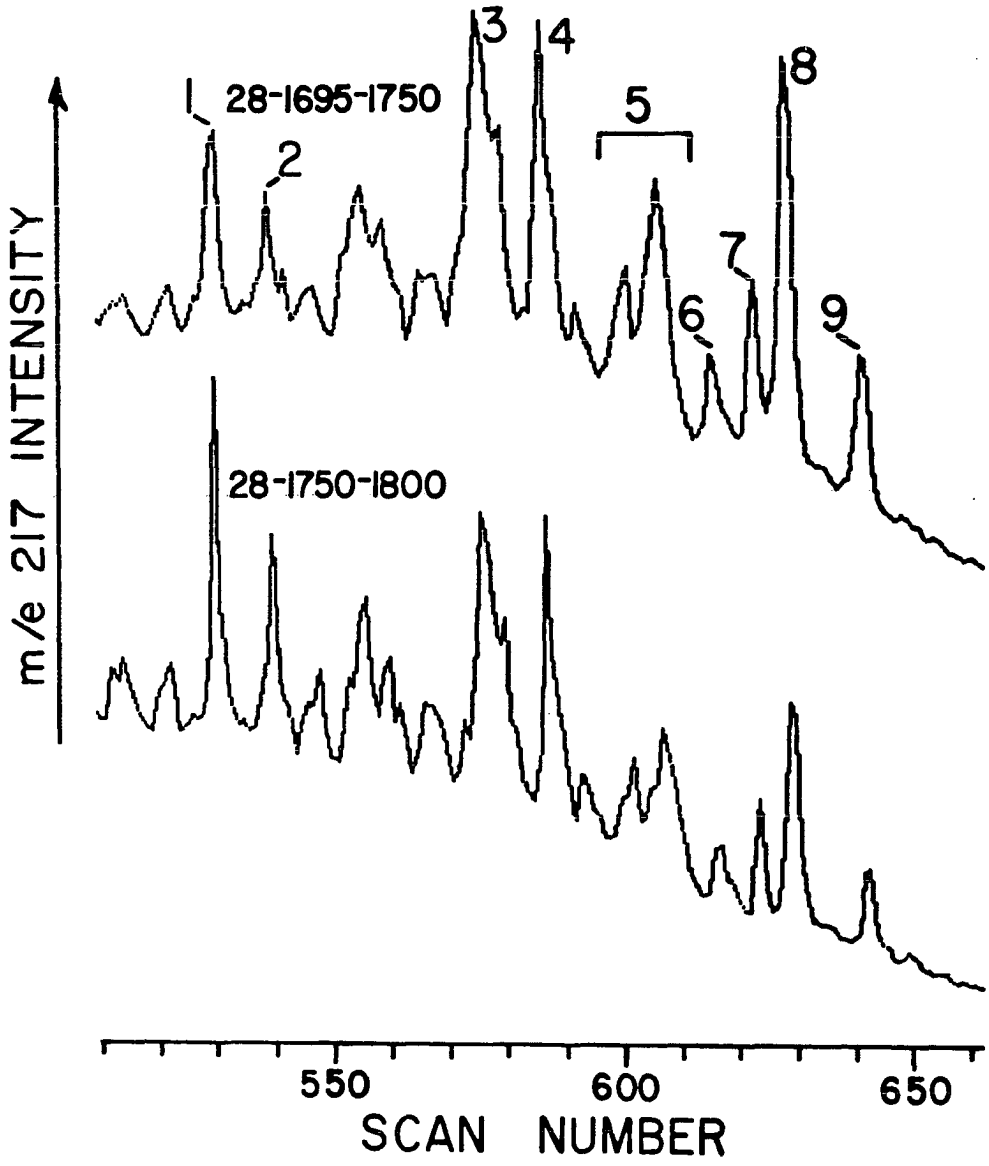


Figure 49. m/e 217 Ion Chromatograms of Womble samples. See Table 7 for peak identifications.

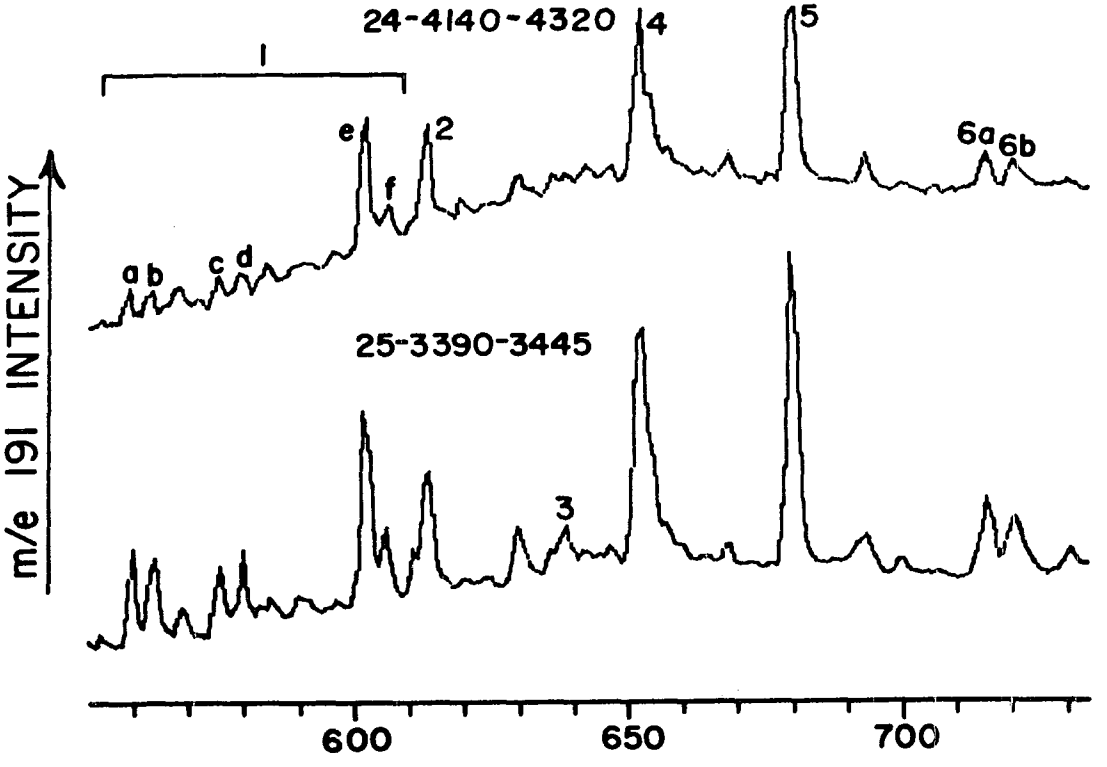


Figure 50. m/e 191 Ion Chromatograms of Stanley samples. See Table 8 for peak identifications.

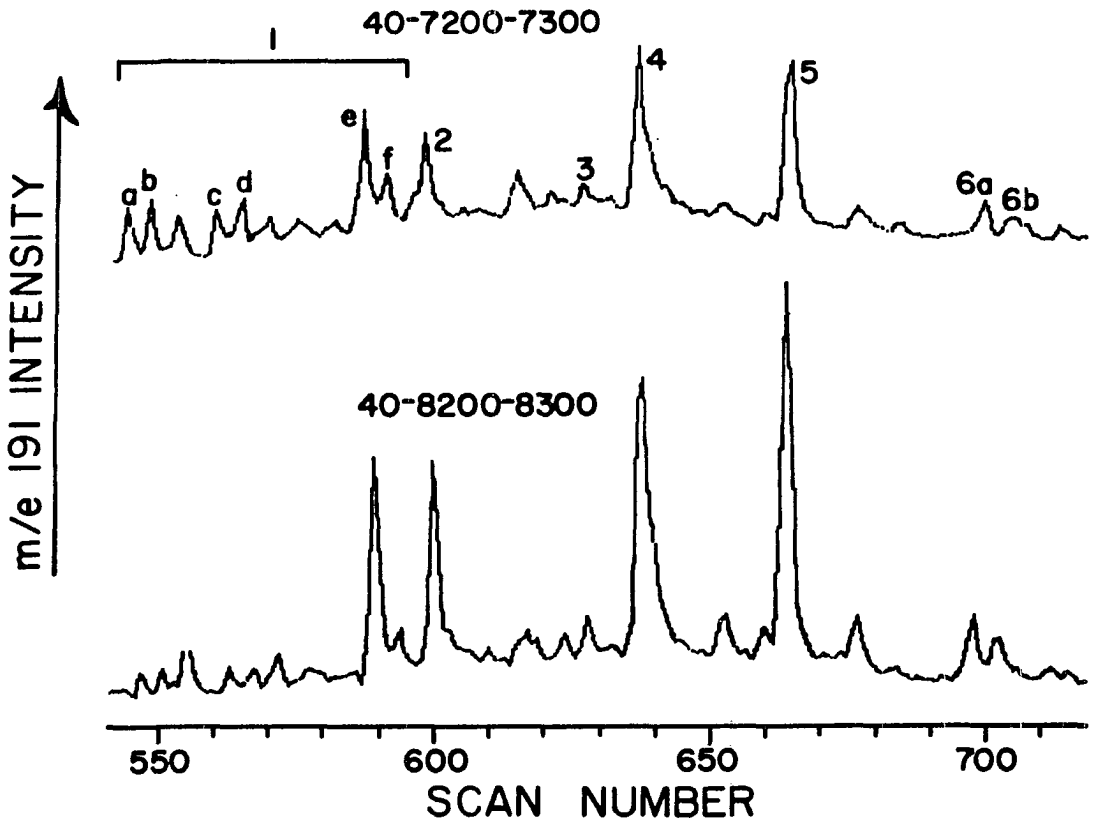


Figure 51. m/e 191 Ion Chromatograms of Arkansas Novaculite samples. See Table 8 for peak identification.

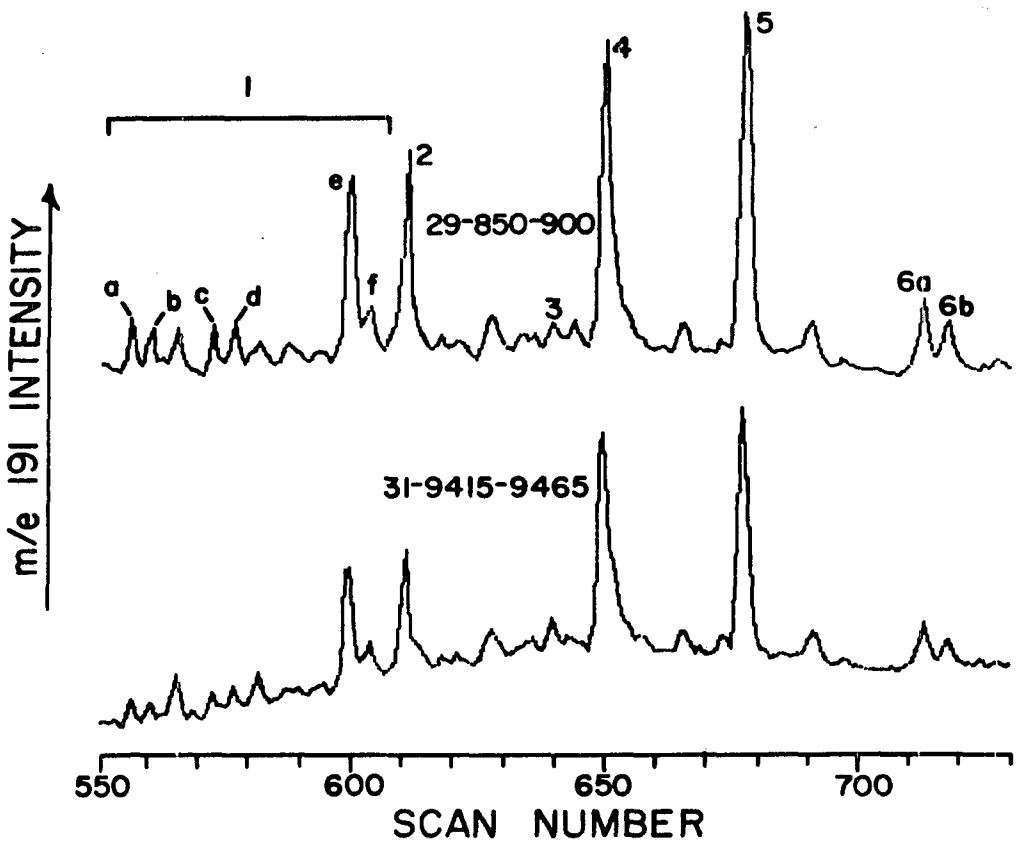


Figure 52. m/e 191 Ion Chromatograms of Missouri Mountain samples. See Table 8 for peak identifications.

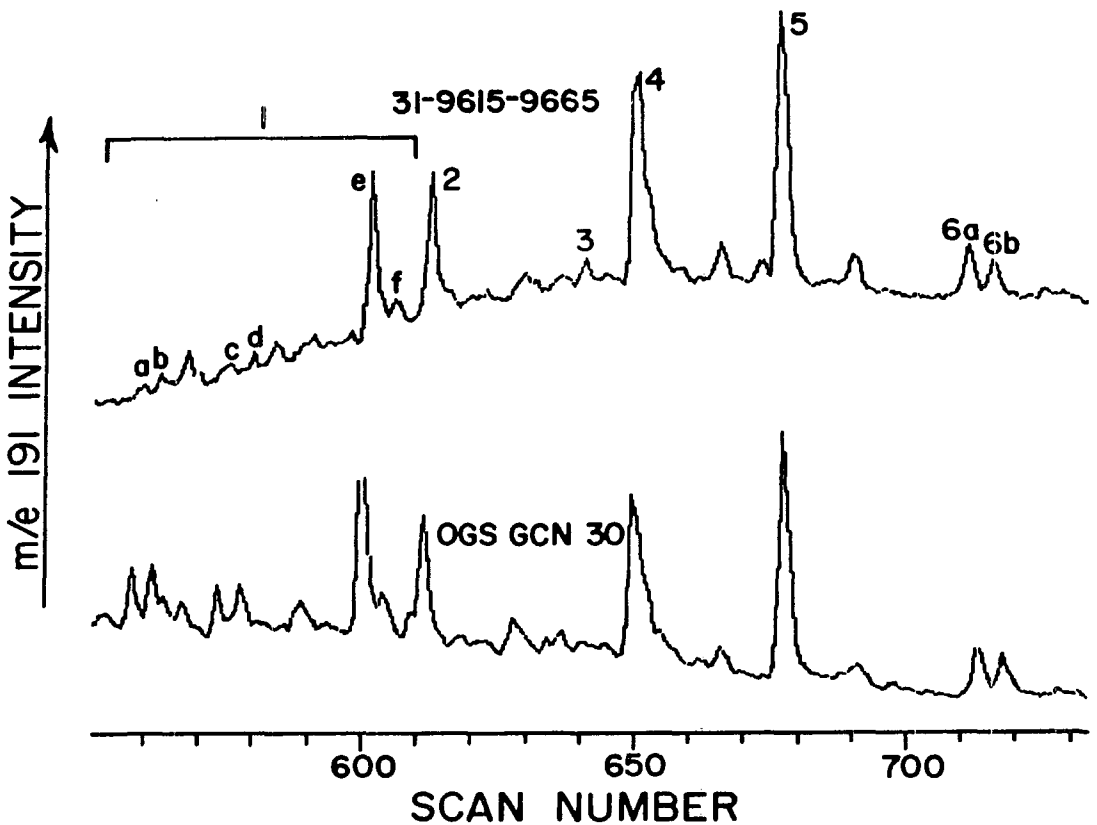


Figure 53. m/e 191 Ion Chromatograms of Polk Creek samples. See Table 8 for peak identifications.

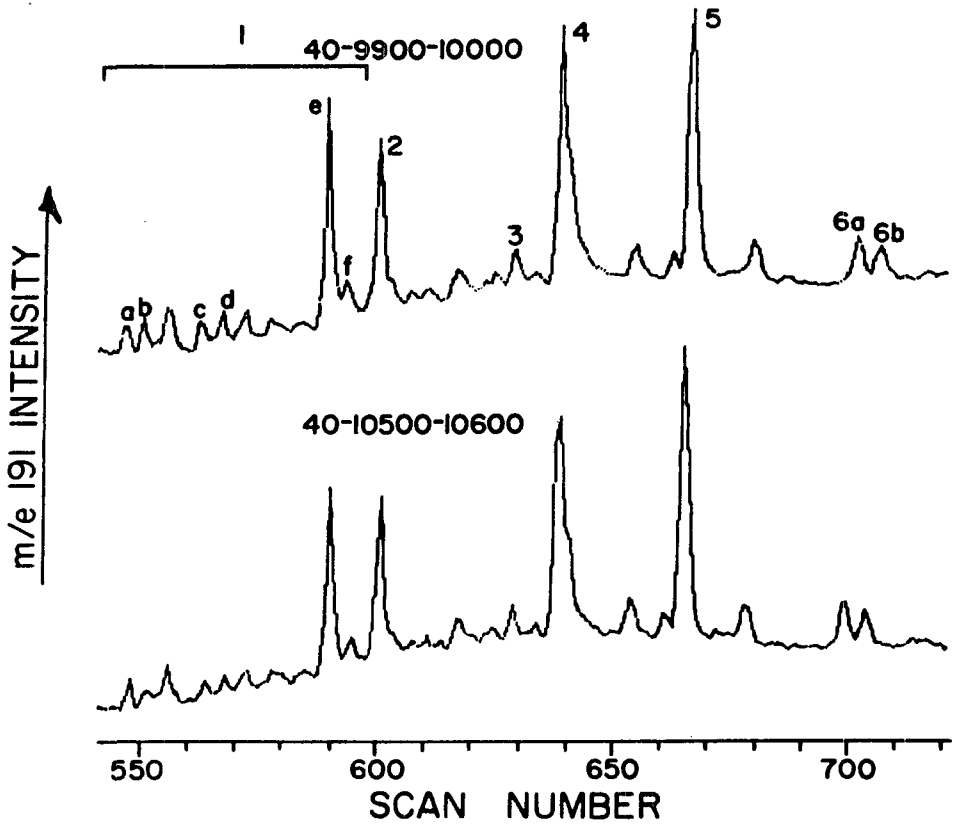


Figure 54. m/e 191 Ion Chromatograms of Bigfork samples. See Table 8 for peak identifications.

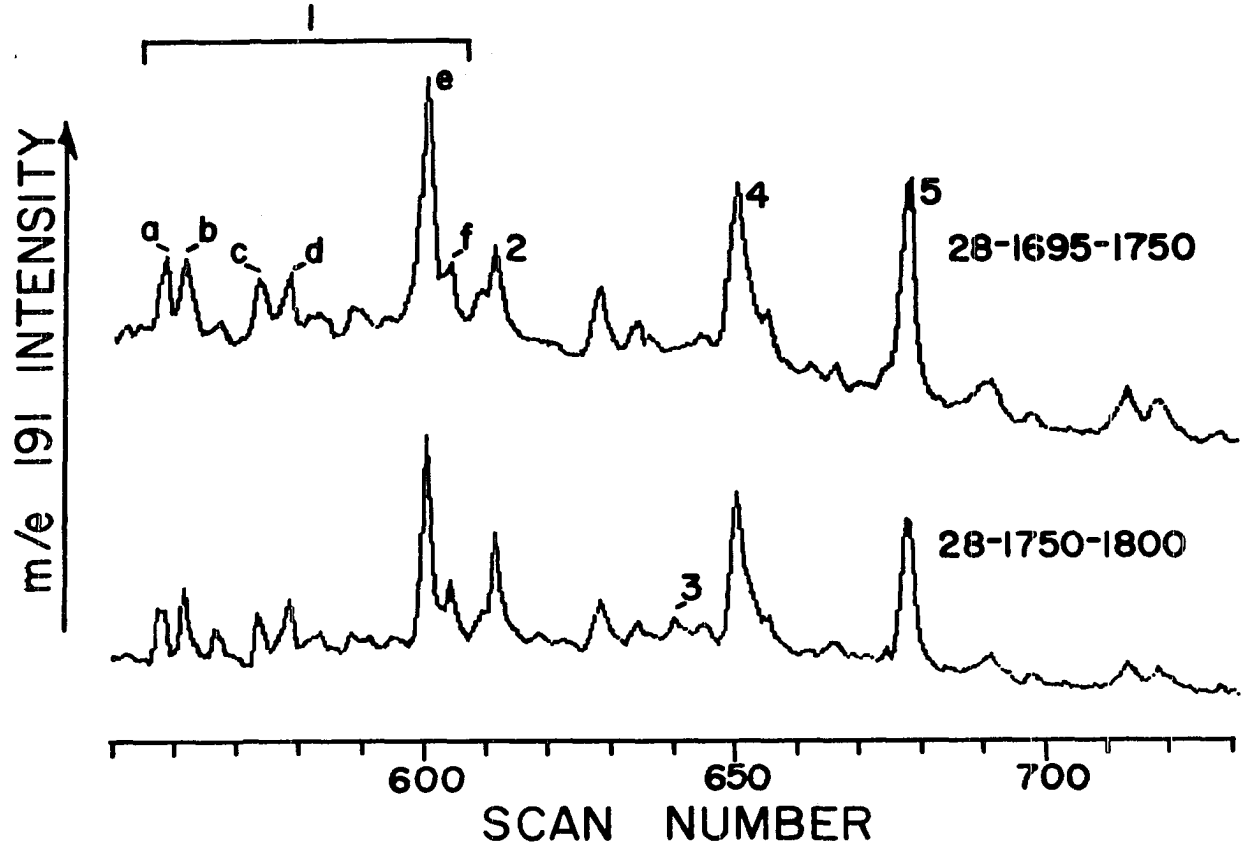


Figure 55. m/e 191 Ion Chromatograms of Womble samples. See Table 8 for peak identifications.

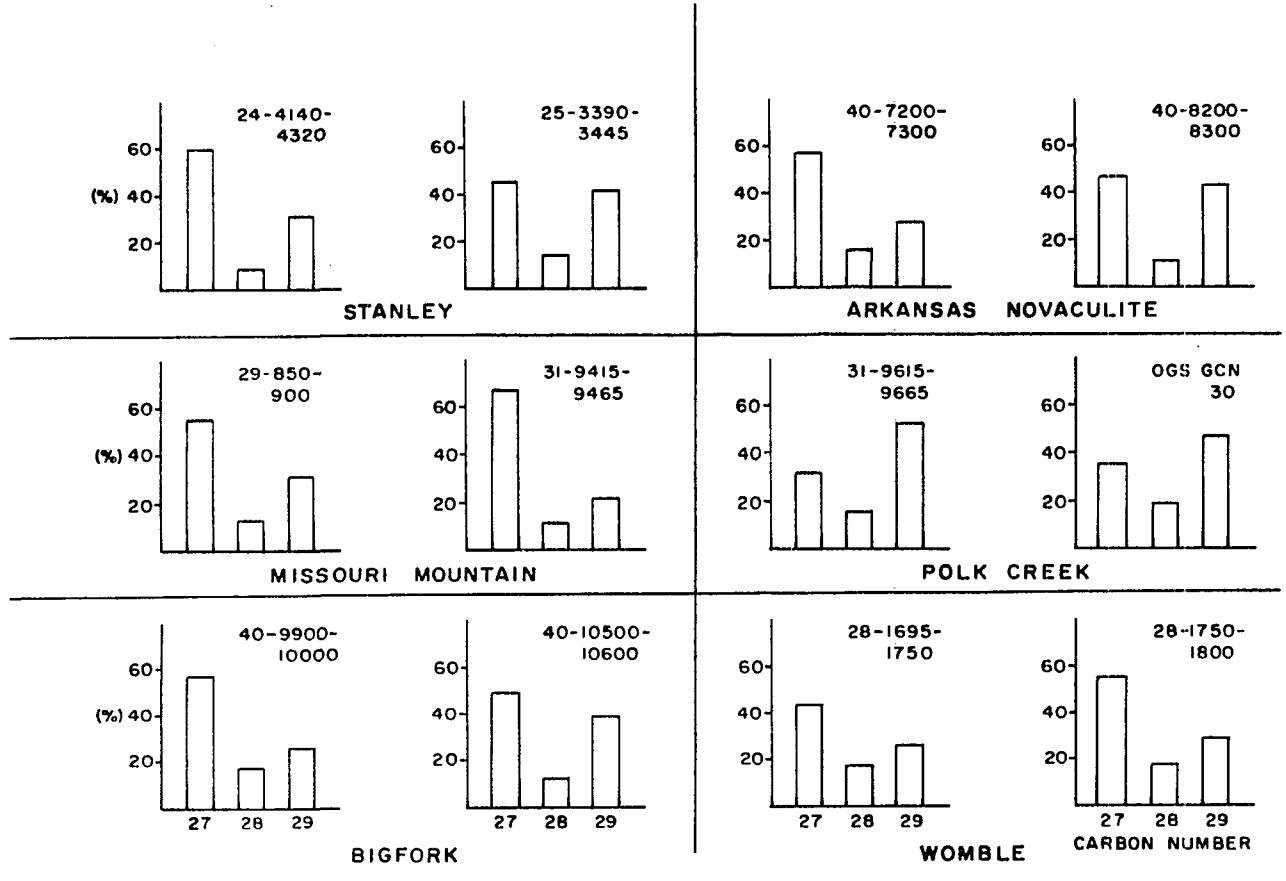


Figure 56. Distribution of steranes by carbon number, in rock samples. Obtained as described in the caption to Figure 21. Numerical data presented in Appendix V, Table 22.

Figure 56 presents the C_{27}, C_{28} and C_{29} distributions of the steranes, as in the case of the oils. Characteristics of the content of each of these biomarker groups will be discussed briefly for each of the stratigraphic intervals.

Sterane and terpane mass chromatograms obtained from Stanley Group samples (24-4140-4320 and 25-3390-3445) are shown in Figures 44 and 50, respectively. Figures 44 and 56 suggest that, while the content of C_{28} steranes is low in both of these samples, the ratio of C_{29}/C_{27} steranes is much higher in sample 25-3390-3445, where it approaches one. If steranes are products of sterol degradation, and if deposition, diagenesis and subsequent catagenesis do not alter the number of atoms in the sterane structure, one may conclude that a lower content of C_{29} steranes indicates a greater input of marine-type organic matter. Unfortunately, other information regarding depositional environment of these samples is unavailable. However, recognition of much of the Stanley as a flysch facies indicates the very heterogenous nature of organic matter that is to be expected throughout the Group (Morris, 1974). It is therefore not surprising that the two samples differ in their sterane distributions.

These differences are also noted in the terpane distributions (Figure 50). Sample 25-3390-3445 exhibits a relatively high content of "tricyclic terpanes" (peaks 1a-1f), as well as the presence of 17a(H),18a(H),21b(H)-28,30-Bisnorhopane (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 Figure 50) revealed the presence of unknown compound B, which was discussed earlier as 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 which exists in the crude oils, suggests a source rock-oil relationship between the Stanley and the oils of the Ouachitas. However, examination of 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 3666-3786 foot interval, while so-called "dead stains" were noted from 3991 to 4021 feet, and from 4031-4056 feet. Furthermore, in the interval closest to the sample in question, a drill stem test from 3676-3786 feet recovered gas cut mud, with a trace of oil. It therefore seems clear 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. This explains the observed similarities, and further invalidates the "differences" noted earlier in the sterane distributions of the two Stanley samples examined.

The sterane distributions of two Arkansas Novaculite samples are shown in Figure 45. Terpane distributions for the same samples are shown in Figure 51. Both sterane and terpane distributions are very similar, with the major difference being fewer "tricyclic terpanes" (i.e., peaks 1a-1f) in sample 40-8200-8300 (Figure 51). This suggests a similar depositional environment over this 1000 feet of well 40. However, beds in this well are very steeply dipping, indicating that much less than 1000 feet of Arkansas Novaculite section is involved.

Examination of Figure 45 suggests that steranes of carbon number 27 and 28 predominate in the Arkansas Novaculite, as was the case in the Stanley sample (Figure 44, 24-4140-4320). This again suggests less of a terrigenous plant input than in the oils examined in this study.

Examination of the m/e 177 chromatogram indicates the absence of unknown peak B in Arkansas Novaculite samples.

The sterane and terpane distributions of two samples of Missouri Mountain Formation, 29-850-900 and 31-9415-9465, were analyzed (Figures 46 and 52, respectively). Figure 46 indicates that both samples are unusually high in diasterane content (peaks 1 and 2, and most unnumbered peaks between peaks 2 and 3; Seifert and Moldowan, 1979). Sample 29-850-900 has higher C_{28} and C_{29} (peaks 5 through 9) regular sterane concentrations than does sample 31-9415-9465. This is evident in the histograms presented in Figure 56. Despite these differences in the sterane distributions, Figure 52 shows that the hopane distributions are similar for both samples. Sample 29-850-900 (Missouri Mountain) contains very minor amounts of unknown compound B.

The distributions of these biomarkers in the Polk Creek Formation, represented by samples 31-9615-9665 and OGS GCN 30, are shown in Figures 47 and 53, Figure 47 shows significant differences in the amount of C_{28} and C_{29} steranes present (see also Figure 56). The C_{29} steranes are minimal in sample 31-9615-9665. Figure 53 shows however, that the hopane distributions of these samples are similar; peaks 1a-1f are in significant concentration in sample OGS GCN 30.

Examination of the m/e 177 ion chromatogram for sample OGS

GCN 30 shows the presence of the unknown peak B in relatively high concentration. This fact, along with the distribution of steranes shown in Figure 47 for this sample, suggests a possible source rock-oil relationship.

Sterane and terpane distributions of samples 40-9900-10000 and 40-10500-10600 of the Bigfork Formation are shown in Figure 48 and 54, respectively. Both samples of the Bigfork Formation examined are very similar, having sterane distributions that are dominantly marine-influenced. The hopane contents (Figure 54) are also similar. The m/e 177 chromatograms indicated the absence of compound B in these samples.

Finally, the Womble Formation samples 28-1695-1750 and 28-1750-1800 were examined for sterane (Figure 49) and terpane (Figure 55) content. Figure 49 indicates that the diasterane and C_{27} and C_{28} regular sterane distributions of these samples are similar, although significantly higher relative amounts of C_{29} regular steranes are present in sample 28-1695-1750. The terpane mass chromatograms (Figure 55) are also similar for the two samples, although a larger norhopane/hopane (peaks 4 and 5) ratio is evident for 28-1750-1800, while 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 reveal the presence of minor, although observable, quantities of the unknown peak B, as observed in crude oils and in single samples of the Missouri Mountain and Polk Creek Formations.

Thermal Maturity of Frontal and Central Ouachita Rocks

Consideration of the quantity and quality of the organic matter of a rock are important in assessing hydrocarbon source rock potential. There is another factor however, which must be determined in order to evaluate whether such a rock may be capable of sourcing petroleum. This parameter is maturity level. In the present study, estimates of maturity level were made using a variety of methods: atomic H/C ratios, a palynological-color-estimate of fixed carbon, reflectance of the kerogen "maceral" vitrinite, and carbon preference index. Results of these assessments are listed in Table 15. In addition, examination of the EOM/TOC and HC/TOC contents (Table 14) also yields information concerning the thermal maturity of these samples.

Elemental Data

The atomic ratio of H/C of source rock kerogens is one of the most commonly used parameters of source rock maturity, when the kerogen type is known (Tissot and Welte, 1978). Thermal maturation of Types I and II kerogens results in depletion of kerogen side chains, which are relatively rich in hydrogen. Consequently, the remaining kerogen becomes concentrated in carbon and atomic H/C ratio values for Type II kerogen in the "liquid window" (Pusey, 1973) varies from about 1.25 to 0.50 (Tissot and Welte, 1978, p. 151). Hunt (1979, pp. 344-345) compiled results of several investigations and suggests a range of 1.35-0.75 for generation of oil from a kerogen of mixed type.

Values of this ratio for kerogen concentrates of the present

Table 15

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 Mt.	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.

study are listed in Table 15, and range from 1.25 to 1.02. These values may be slightly higher than true values because of hydrogen contribution from mineral matter (see Appendix II for details concerning the kerogen concentration technique used). Nevertheless, it is clear that, on the basis of the atomic H/C ratio, we can conclude that the four samples analyzed are within the oil-generation window, and are thermally mature, but not postmature.

Spore and Pollen Data

The second maturity parameter employed in this study was an estimate of the fixed carbon percentage in a kerogen based on the color of spores in the rock (Gutjahr, 1966). Wilson (1971) has shown that the level of fixed carbon (determined by proximate analysis) of coals is manifested in the color of spore and pollen of organic matter in associated non-coaly 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 attaches a more precise numerical figure to maturity than does, for example, the Thermal Alteration Index for kerogen color, proposed by Staplin (1969).

The two samples of kerogen concentrate of this study which contain recognizable spores exhibit fixed carbon values of 54-62% (using standard colors recommended by Wilson, 1971), having trilete spores that are orange to light brown in transmitted light. According to Dow (1977), kerogen with such fixed carbon levels would be

approximately in the middle of the oil generation window.

Vitrinite Data

One of the most commonly used maturity parameters is reflectance of the coal maceral, vitrinite. It has been shown that the reflectance of polished vitrinite specimens in oil (R_o) is a function of the temperature to which the sample has been subjected. This empirical correlation has proved useful in several studies, allowing one to propose maximum and minimum R_o values for generation and preservation of liquid petroleum. Typical of these is Dow's (1977) suggestion that oil generation begins at an R_o value of about 0.5, peaks at 0.9 and ceases about 1.35, although variations do exist (e.g., Heroux, et al., 1979).

Data from four samples of the present study yield average reflectance values ranging from 0.86-1.03%. As shown in Figures 57 and 58 for Stanley and Arkansas Novaculite samples, respectively, the spread in values is very large, perhaps reflecting the flysch-type deposition prevalent in the Ouachita Trough in Mississippian and Devonian time. (It should be noted that, in collecting R_o data for these four samples, no attempt was made to discriminate against possible reworked material.) It is clear from these data that the samples in question are situated in the middle to lower part of the oil window (Dow, 1977).

The samples whose R_o values were determined are not from great depths (Stanley average depth: 3940 feet; Arkansas Novaculite average depth: 7500 feet). Depths at which R_o values of 1.0 are

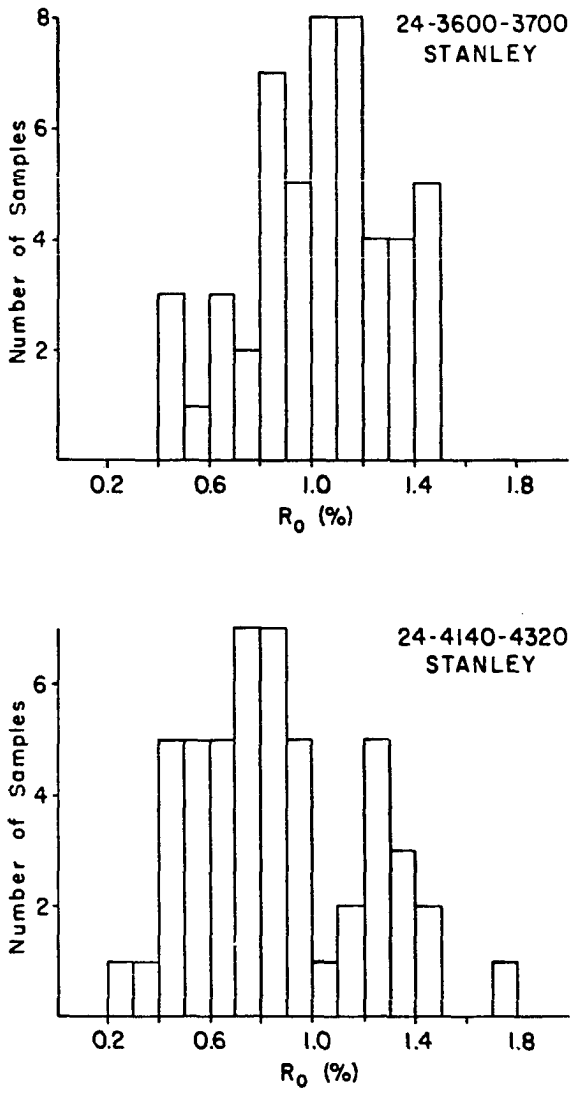


Figure 57. Vitrinite Reflectance Histograms for Stanley Group samples. Each histogram represents the distribution results of 50 random vitrinite particles. All reflectance data is derived by use of conventional immersion oils.

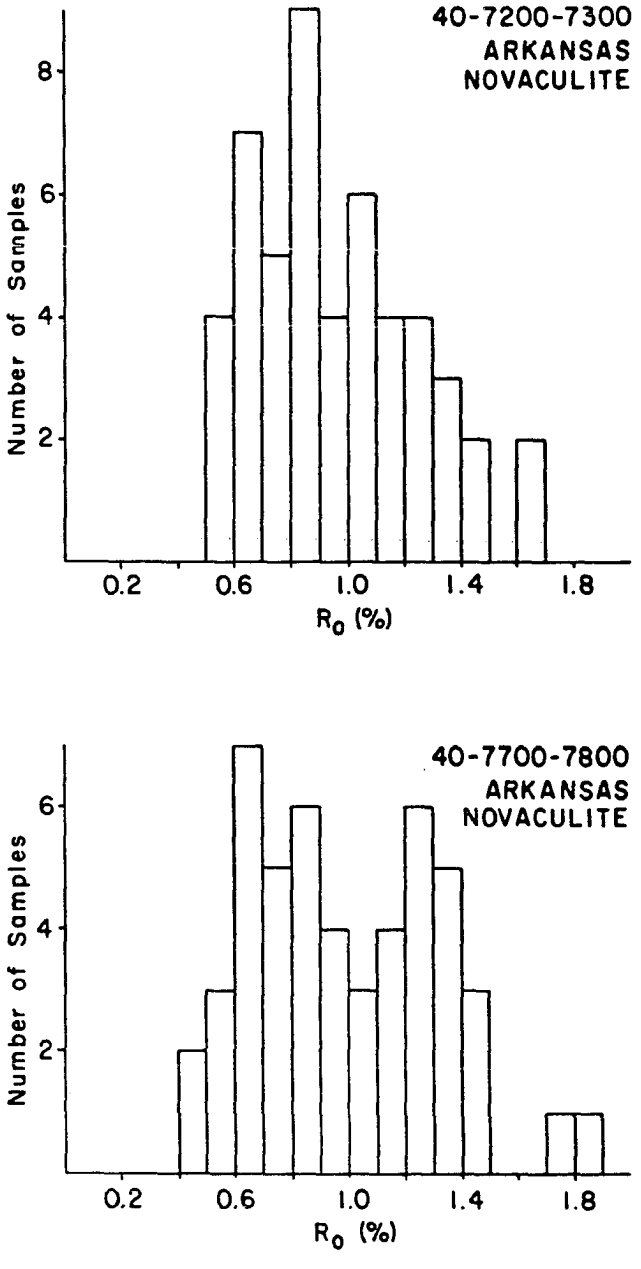


Figure 58. Vitrinite Reflectance Histograms for Arkansas Novaculite Formation samples. See caption for Figure 57 for further information.

attained in other basins are generally much greater, ranging from 9500-13000 feet in various North American basins (Dow, 1977; Hunt, 1979). Hunt (1979, pp. 344-345) suggests an average depth of 11000 feet before the vitrinite reflectance reaches 1.0%, given an average geothermal gradient of 1.5°F/100 feet (2.7°C/100 meters). Therefore, assuming an average geothermal gradient (as well as an average paleo-gradient), it is suggested that a minimum of 4000-7000 feet of over-burden has been removed by erosion at the sites of these two wells (T2S R15E; T1N R14E).

EOM Maturity Data

The three maturation parameters discussed previously have involved only the kerogen component of sedimentary organic matter. However, if one presupposes that the organic matter in a sample is 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, et al., 1979). In general, the CPI must attain values of about 1.13 to 0.92 before a Type I or II kerogen can be considered thermally mature (Bray and Evans, 1961). As shown in Table 14, most CPI values of the present study are less than 1.13. Furthermore, Hunt (1979, pp. 305-306), in evaluating a study by Albrecht (1970), suggests that when a rock

> ...has reached sufficient maturity to generate considerable oil, the alkane distribution within the rock will peak between C_{13} and C_{18} and will show a steady decrease in concentration of alkane with increasing chain lengths.

It is important to note that, in the present study, such criteria are met only by the Womble Formation (see Figure 40).

In addition to the CPI of the n-alkane distribution in a source rock, the HC/TOC and EOM/TOC ratios can be used to determine the depth of the "principal zone of oil formation" (Vassoyevitch, et al., 1969, in Albrecht, et al., 1976). Tissot, et al. (1978), in a study of the Green River Formation, observed the onset of hydrocarbon generation where the HC/TOC ratio exceeds 50 mg/g. It should be noted that this is for a Type I kerogen. Albrecht, et al. (1976) observed approximately the same value for the Logbaba series of the Douala Basin (Cameroon) in a kerogen of predominantly terrestrial origin. If we then accept a value greater than 50 mg/g (HC/TOC) as indicative of significant generation of hydrocarbons, it is evident from examination of values listed in Table 14 that several samples of the present study indicate temperature conditions sufficient to generate petroleum. In particular, Stanley, Polk Creek and Womble rocks have HC/TOC values of 50 mg/g or greater.

Analogous estimates based on the EOM yield (EOM/TOC) are also utilized to determine the onset of generation. Heroux, et al. (1979), after a thorough review of the literature, suggested that an EOM/TOC greater than 25% implies that oil-generating temperatures have been achieved. This minimum figure does not take into consideration the composition of the EOM. As a result, an EOM rich in heterocompounds and asphaltenes, and strongly depleted in hydrocarbons, may yield a high EOM/TOC ratio, suggesting the erroneous conclusion that oil generation has occurred. Alternatively, a rock having a low EOM/TOC ratio may be discounted as a source rock, even though the greatest portion of the EOM is hydrocarbon material. Thus the EOM/TOC ratio

appears to be of lesser importance to source rock evaluation than the HC/TOC ratio.

Reviewing the data of Table 12, and excluding sample 24-3600-3700 because of probable non-indigenous EOM, we see that only two samples (one from the Stanley Group and one from the Womble Formation) exhibit an EOM/TOC greater than 25%. It can be seen that there is a discrepancy between the number of "good" source rocks based on HC/TOC (a total of nine in Table 14) and the number based on EOM/TOC (a total of two in Table 12). This is resolved in light of the above discussion. Unaltered, mature oils consist predominantly of hydrocarbons, so the HC/TOC ratio must take precedence over the EOM/TOC ratio, in the writer's opinion.

Each of the numerical values suggested above (e.g., HC/TOC, EOM/TOC) for the onset of significant hydrocarbon generation is strongly influenced by the type of organic matter involved. An example of this is the CPI value. Hunt (1979, p. 310) states that CPI values are of no use in assessing maturity levels of early Paleozoic hydrocarbon source rocks. The reason for this is that the organic matter of these rocks is ostensibly lacking in long-chain odd-carbon number paraffins, thus limiting the usefulness of CPI values as maturity indicators. Nevertheless, use of EOM parameters as maturation indicators is often valuable, if only as corroborating evidence for the kerogen-derived parameters.

Finally, the terpane data obtained for each of the samples analyzed by GCMS is also of value as a maturity indicator for the organic matter in these potential source rocks. It has been noted

by Seifert, et al. (1980) 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, with the early-eluting epimer being predominant. Conversely, living organisms contain predominantly the second eluting epimer. Thus 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 it is to be expected that mature (as opposed to immature) petroleum source rocks will contain such an equilibrium mixture (Seifert, et al., 1980). On this basis then, because the terpane distributions (Figures 50-55) for the Ouachita rocks all possess a ratio of about 60/40 for the epimers in question, these rocks are thermally mature.

Summary and Conclusions

It is clear from the data presented in this section that formations of the Mississippian through Ordovician section of the Oklahoma Ouachita Mountains have the potential to be source rocks, and are mature enough to have generated liquid hydrocarbons. Total organic carbon levels of most samples are over 0.5%, while extract yields suggest that the EOM of samples from each formation is high enough to classify all formations as having source potential. This is particularly true for samples of the Stanley Group and Womble Formation. Finally, the hydrocarbon content of many of the samples is high; Philippi's (1957) classification indicates that the Stanley Group, and

Polk Creek and Womble Formations are "good" source rocks. By Philippi's classification, the Womble Formation is consistently the best source rock examined.

Examination of the type of organic matter in this mid-Paleozoic section indicates a mixture of marine and non-marine organic matter that is consistent with the known depositional environment of these rocks (Morris, 1974). This is suggested by carbon isotope ratios of the total organic carbon in the samples. These isotopic ratios for samples of the present study fall between those expected for marine and non-marine rocks. Furthermore, the sterane distributions show that there are roughly equal amounts of C_{27} and C_{29} steranes, also indicating a mix of marine and non-marine conditions, respectively. Finally, microscopic examination of four samples of Stanley and Arkansas Novaculite reveal large amounts of vitrinite, suggesting the presence of Type III kerogen, whose oil generation potential is low.

Thermal maturation data obtained in this study indicate that all formations and groups are mature enough to have generated oil. The H/C atomic ratios and coloration of spores of the kerogen indicate that the material is in the middle of the oil window. Vitrinite reflectance data indicate that these samples are in the middle or bottom half of the oil window (as described by Dow, 1977). These observations are also confirmed by the equilibrium ratio of the homohopane C_{22} epimers present in all potential source samples, which suggests that the samples examined are mature enough to have generated oil. Samples from the Stanley Group and Womble Formation had EOM/TOC values greater than 25%. Hydrocarbon content as a fraction of TOC, or the HC/TOC

ratios are highest in samples from the Stanley Group and Polk Creek and Womble Formations. Examination of the n-alkane distribution in the samples however, clearly suggests that the Womble Formation is the best hydrocarbon source sequence present in the section examined. Only the Womble exhibits distributions that have maxima between C_{13} and C_{18}, and decrease uniformly with increasing chain length. These criteria have been noted in mature source rocks (Tissot, et al., 1971; Hunt, 1979).

The sedimentary rocks in proximity to the Oklahoma-Arkansas state line (Figure 2) may be significantly more mature than most samples of the present study. This is suggested by the high fixed carbon and low H/C values for the impsonite sample (44) from this area (see also the following section). Unfortunately, no rocks from near this deposit were examined. However, samples examined from as far east as northern Pushmataha County (i.e., from near all the grahamite deposits) are clearly still within the liquid window (Appendix I).

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 Formation must be considered as a source by virtue of the high HC/rock ratio noted in one of its samples. Finally, the Stanley Group shales represent a potential source on the basis of extract yield, although type of organic matter suggests that this material should be considered a gas source.

CHEMICAL CORRELATIONS BETWEEN OIL AND SOLID BITUMEN

Previous Investigations

Relatively few studies have attempted to compare the chemical characteristics of solid bitumens with those of crude oil. Hunt, et al. (1954) studied relationships between different types of solid bitumens, including gilsonite, in the Uinta Basin. Infrared spectroscopy showed that various types of solid bitumens can be distinguished on the basis of their infrared spectra.

More recently Amit and Bein (1979) and Nissenbaum and Goldberg (1980) have investigated the chemical relations between asphalts and oils of the Dead Sea area. These workers suggested biodegradation as the dominant cause in altering crude oil to asphalt. However, the absence of conventional crude oil from the Dead Sea Basin has led Nissenbaum and Goldberg (1980) to also cite as a potential origin for the asphalt "...low temperature alteration of organic matter from a thermally immature source." Such a distinction was impossible to make, despite correlations between oil and asphalts based on vanadium:nickel ratios and sulfur and carbon isotope ratios.

One of the objectives of the present study is to determine the relation between Ouachita bitumens, petroleum produced in the area, and hydrocarbon source rocks. Knowledge of this relation would be valuable in terms of oil exploration in the area. However, before addressing the

problem of the origin of grahamite and impsonite, the chemical relation between oil and these materials must be established. The intent of the present section is to evaluate this relation, in order to determine if the two substances (oil and bitumen) are commonly sourced in the Ouachita Mountains. Such relations can be defined on the basis of bulk, or gross, correlations between solid bitumen and oil, or on the basis of molecular correlations between bitumen pyrolyzates and oils.

Bulk correlation parameters may be defined as those which involve the entire sample, rather than chemical fractions or distillation cuts of the sample. Examples include elemental, metal and stable isotope ratio analyses. Results of these analyses are useful both in characterizing the gross chemical properties of oils and bitumens, and in correlating one to the other. In addition, such parameters are useful in answering the question of genesis of the solid bitumens.

Correlation between oils and bitumens involving investigations more detailed than those involved in bulk parameters are also desirable. However, such correlations are impractical due to the high content of asphaltenes in the bitumens. Consequently, molecular-level correlations based on comparison of oils with solid bitumen pyrolyzates have also been attempted. Specifically, the n-alkane, sterane and triterpane distributions of solid bitumen pyrolyzates have been compared with those of Ouachita oils. Such comparisons also yield considerable information bearing on the origin of the solid bitumen material.

Bulk Correlation Parameters

Bulk comparisons between oils and bitumens can be based on elemental, metal and isotopic analyses. Results of this study show that

significant differences in elemental and metal content exist between oils and bitumens. Carbon and sulfur isotope ratios however, are very similar for the two materials.

Atomic H/C ratios versus atomic O/C ratios for oils and bitumens are plotted in Figure 59. These data show that, while there is no obvious relationship among the solid bitumens, each is clearly depleted in hydrogen and enriched in oxygen compared to the oils.

Differences in concentrations of vanadium and nickel are also obvious, as shown in the log-log plot of Figure 60. However, even though these metals are enriched in the bitumens by an average factor of 41, the vanadium:nickel ratio for oils and bitumens ranges 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 does not affect the V/Ni ratio as severely.

This indicates that one of these substances represents an alteration product of the other (Amit and Bein, 1979). However, the specific type of alteration involved cannot be determined from this data.

The relationship between sulfur and carbon isotope ratios for the oils and bitumens is shown in Figure 61 for three oils and five bitumens. 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).

Several papers in the literature suggest a common source for organic materials based on similarities in their stable carbon isotope ratios. Silverman and Epstein (1958) attempted to relate oils to their original biochemical source input, based on stable isotope ratios. Such

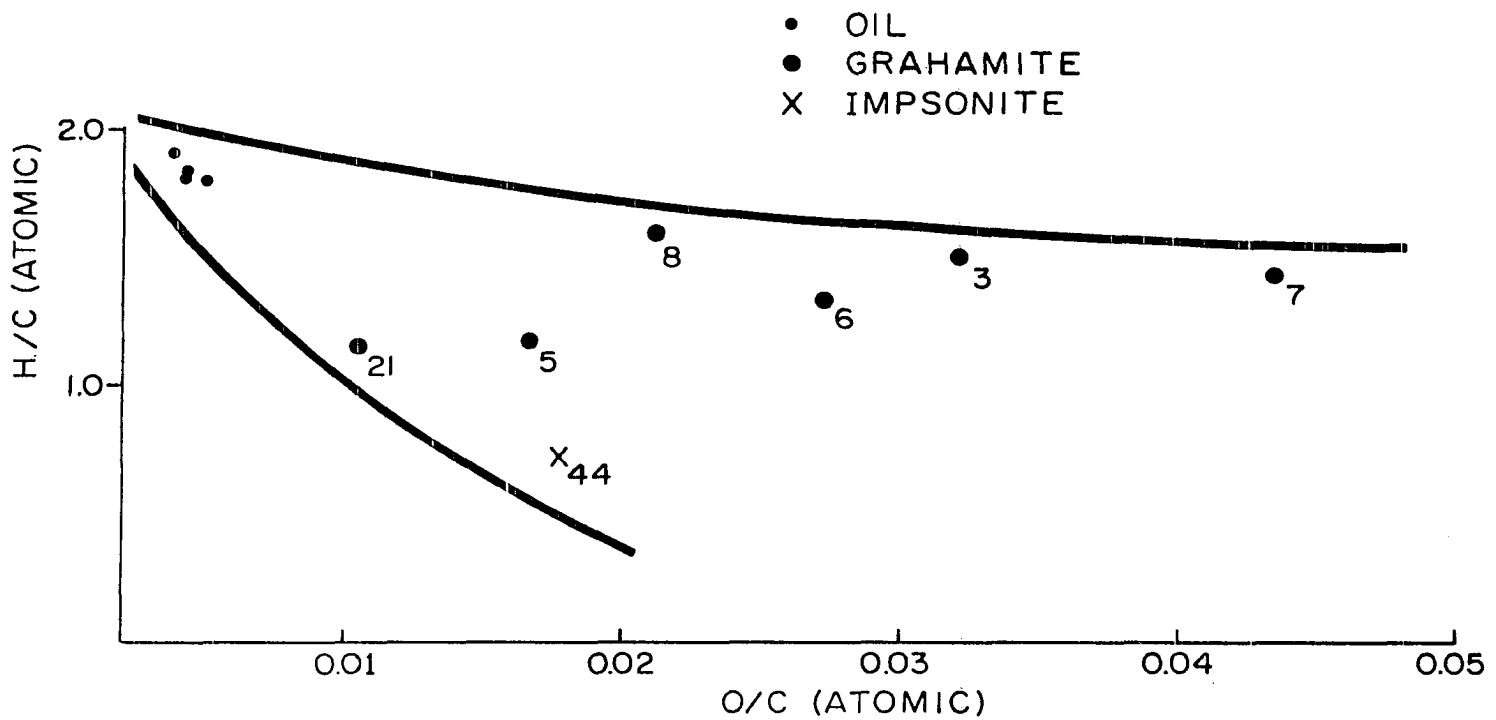


Figure 59. Graph of atomic H/C versus O/C for Crude Oils and Solid Bitumens.

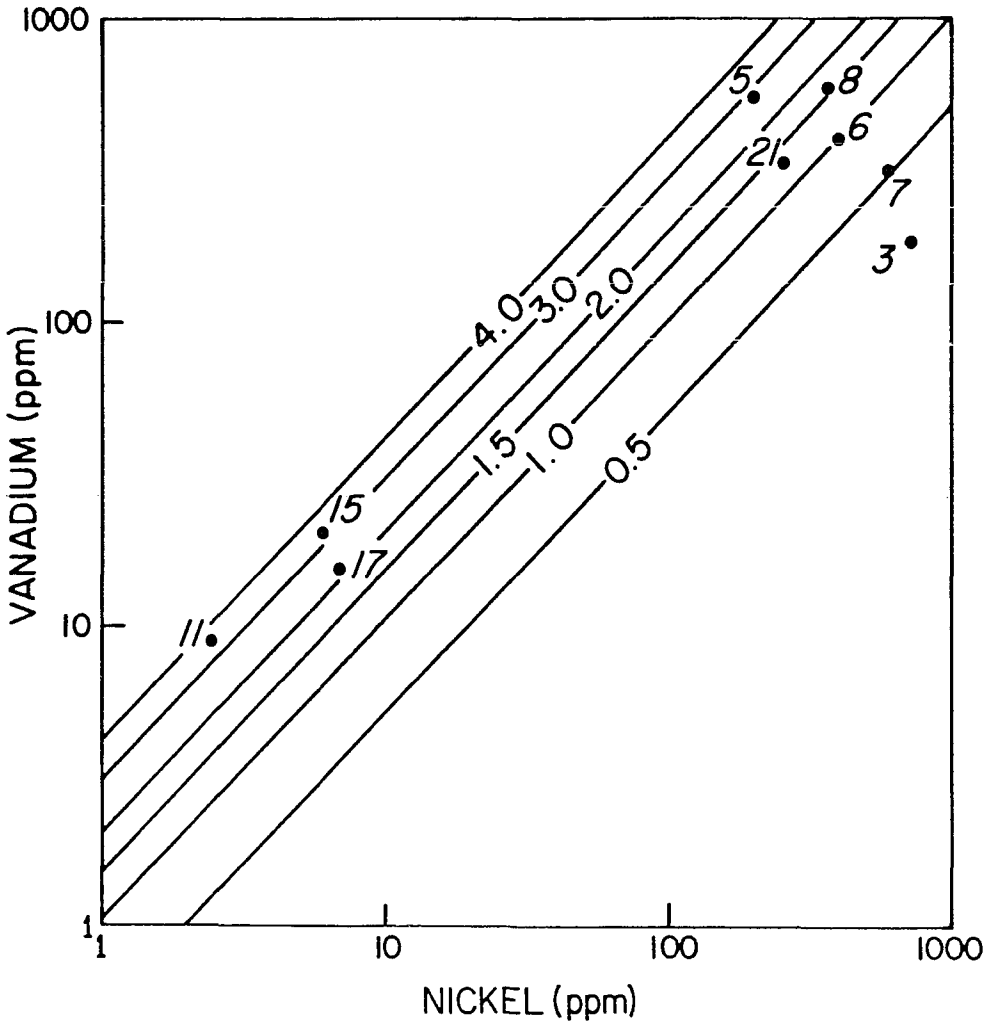


Figure 60. Graph of Vanadium versus Nickel for Crude Oils and Solid Bitumens. Diagonal lines represent lines of constant V/Ni ratio, as indicated. Axes are both logarithmic.

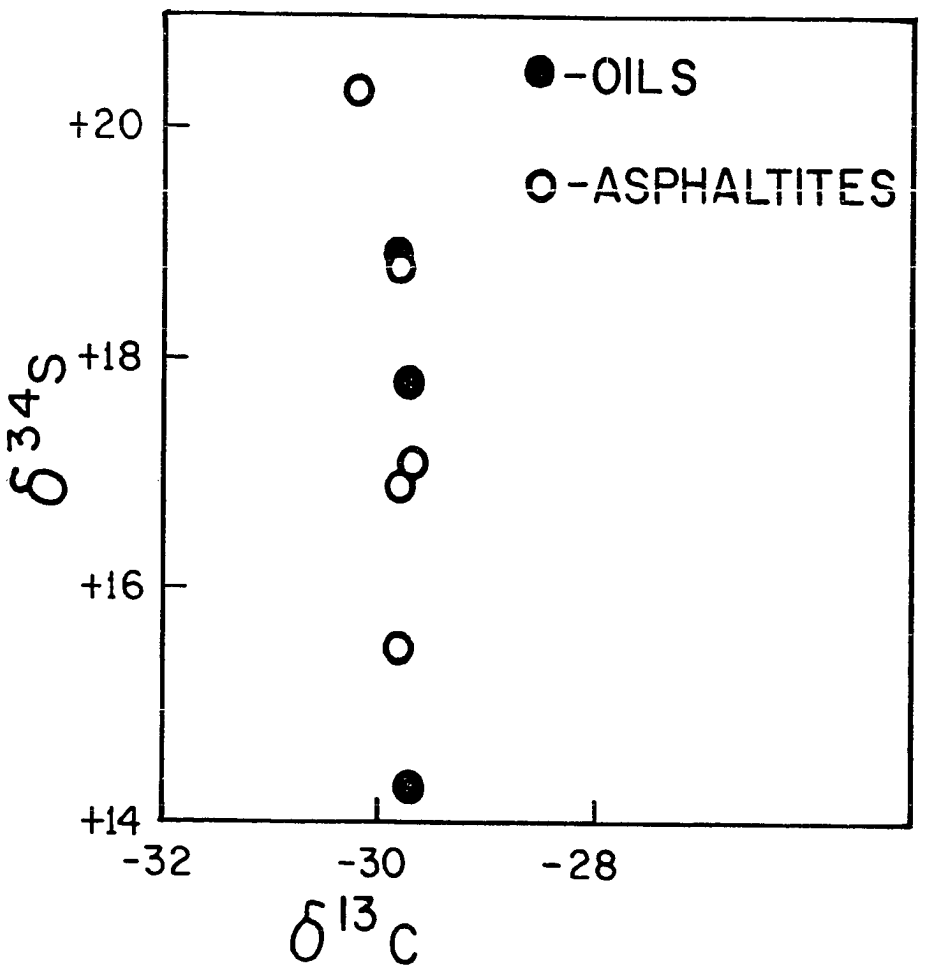


Figure 61. Graph of Sulfur Isotope Ratios versus Carbon Isotope Ratios for Oils and Solid Bitumens. Carbon isotopes are relative to PDB standard, and sulfur isotopes are relative to Canon Diablo troilite standard. This plot is not meant to indicate a functional relationship between carbon and sulfur isotope ratios.

attempts were continued by Silverman (1967), who suggested a lipid-source for petroleum based on carbon isotope similarities between many crude oils and the lipid fraction of marine organic matter. Fuex (1977) cites several successful oil-oil correlations based on the stable carbon isotope ratios of the oils, noting possible variations of this ratio with oil maturity. Fuex cites studies involving oil families from Wyoming, southeastern Mississippi and West Texas, whose isotope ratios have spreads of 3.6 °/oo, 1.2 °/oo and 3.3 °/oo, respectively. Although evidence exists that each of these oil families is commonly sourced, the (as yet) unknown effects of migration and maturity on the isotope ratio of an oil has apparently resulted in significant ratio spreads. In any event, the relationships between the carbon isotope ratios of carbon-containing materials established in the aforementioned studies suggest that the bitumens and oils of the present study are commonly sourced, because the ratio spread in these materials is only 1.3 °/oo (Tables 5 and 10).

A similar conclusion can be drawn from the sulfur isotopic data in Figure 61. The oils show a range from +14.3 to +18.9 °/oo, while the bitumens range from +15.5 to +20.3 °/oo. The range overlap here is +15.5 to +18.9 °/oo, which represents 74% and 71%, respectively, of the total range for oils and solid bitumens analyzed. This large overlap in the sulfur isotope ratio ranges again strongly indicates a co-genetic relationship between oil and solid bitumen. Because these materials are unusually depleted in light sulfur (Thode, et al., 1958), it is extremely unlikely that such a correlation is fortuitous.

Pyrolyzate-Crude Oil Correlations

In addition to correlation of oil and bitumen based on bulk chemical parameters, results of this study indicate the feasibility of bitumen-pyrolyzate:crude oil correlations. Both types of pyrolysis used to characterize the grahamites and impsonite (high temperature-short term and low temperature-long term) are useful in this respect.

High temperature pyrolyses of grahamite, impsonite and gilsonite created alpha-olefins as well as n-alkanes, as discussed in the section on solid bitumen characterization. Figure 29 presents the quasi-n-alkane distributions for each of these materials, while Figure 12 presents the n-alkane distributions for the four Ouachita oils. Grahamite samples yield pyrolyzates whose distributions are very similar to those of the crude oils. In addition, except for an anomalous peak at C_{20}, the impsonite sample is also 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 12 and 29 also suggest similarities between pyrolyzates and oils. The CPI range for crude oils (1.01-1.08) is included within the range for the grahamites and impsonite (0.96-1.17). The gilsonite however has a CPI value lower than both of these ranges (0.89). These data suggest that a correlation between oils and bitumens is possible on the basis of grahamite and impsonite quasi-n-alkane distributions. Such a correlation, while corroborating previous evidence that these materials are co-genetic, also places chemical restrictions on the possible mode of formation of grahamite and impsonite, as will be discussed later.

Low temperature closed-tube grahamite and impsonite pyrolyzates also show good correlation with the Ouachita oils examined, on the basis of sterane and terpane distributions. Figure 31 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 from 50-75% of peak 1 (by height) in both oil and pyrolyzates, while other diasterane ratios (e.g., 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 7), diminish greatly in the order: oil 11, and pyrolyzates 7,5,6,3 and 44 (the reasons for such a change will be pursued later in this section). 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 to that in oil 11, with peak 8 predominating in all cases.

Despite the features discussed above, the distribution of steranes (both regular and rearranged) by carbon number (Figure 62), suggests that these materials are commonly-sourced. In all samples examined, the amount of C_{28} steranes is less than 20% of all steranes present. Although the ratio of C_{29}/C_{27} (or roughly, the ratio of terrigenous/marine influence) varies somewhat, that ratio for pyrolyzates of samples 6, 3 and 44 is similar to that found in the crude oil. Based on similarities in the distribution of sterane carbon numbers, it can be concluded that oils, grahamites and impsonite are co-genetic.

Some similarity in the terpane distributions of oil 11 and the

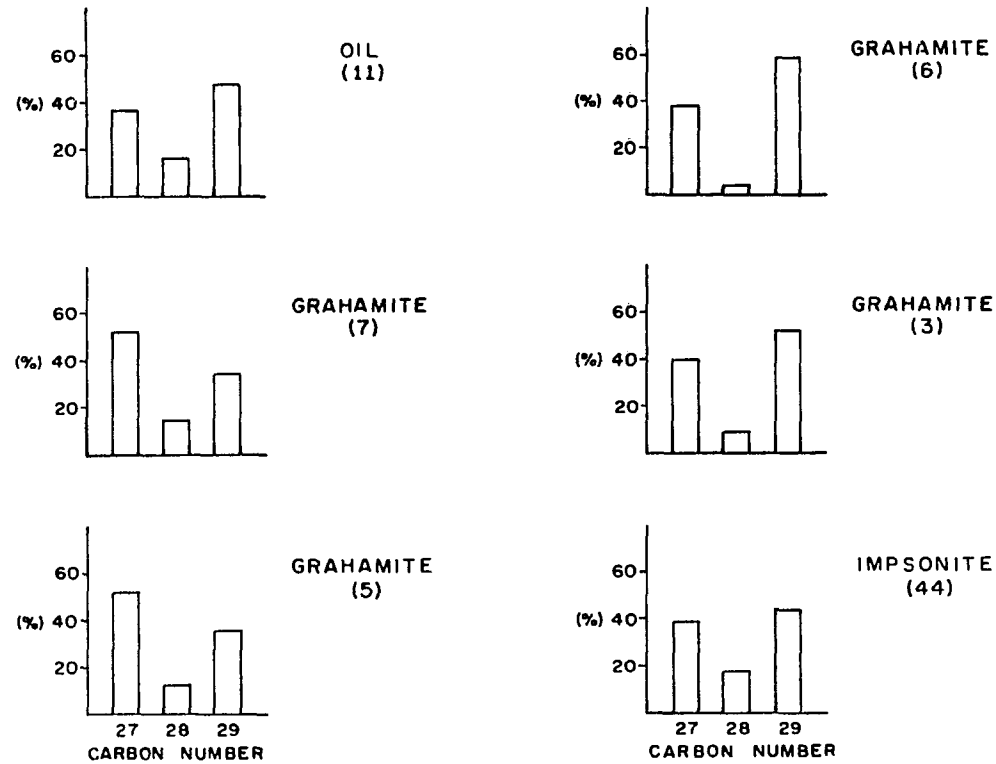


Figure 62. Histograms of Steranes by Carbon Number in oil 11 and Solid Bitumen Pyrolyzates. Obtained as described in Figure 21. Numerical data given in Appendix V, Table 22.

pyrolyzates is also evident (Figure 32). Peaks 4 and 5 (C_{29} and C_{30} hopanes; see Table 8) are present in roughly 1:1 ratios in both oil and pyrolyzates, while the ratio of peaks 6a and 6b (C_{31} homohopanes) is about 60:40 in all cases. Differences present 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, Figure 32) is more prominent in the pyrolyzates than in the oils. By comparison, the C_{28} bisnorhopane peak (peak 3, Figure 32) is more prominent in the oil. The anomalously strong presence of peak 1e (probably a co-eluting 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 Figures 50-55). The unknown peak B, eluting just after peak 1e in all of the crude oils, is also present in each of the solid bitumen pyrolyzates examined, albeit in small amounts. Its presence, as well as similarities between the C_{29}, C_{30} and C_{31} hopanes in pyrolyzates and oil, again suggests that oils, grahamites and impsonite result from either a common source or from sources having very similar types of organic matter.

Origin of Solid Bitumen

Assessment of several parameters determined for solid and liquid hydrocarbons (as well as pyrolyzates) suggests that the oils, grahamites and impsonite of the Ouachita Mountains have a common source. However, prior to establishing the identity of that source, the question of origin of the solid bitumen must be considered.

Solid bitumen has been ascribed to two modes of formation, which

are widely separated in the evolutionary scheme of bituminous materials. Some workers (Brooks, 1936) consider solid bitumen to be a primary product or "protopetroleum," whereas other investigators (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 (i.e., high temperature or low temperature alteration). Detailed discussion of these two questions will be presented below, in an attempt to establish a reasonable origin for grahamite and impsonite in the Ouachitas.

The concept of protopetroleum, being the first-generation product of a very rich, relatively immature source rock, has existed in the literature in one form or another for over forty-five years (Brooks, 1936). Such a material would consist of high molecular weight compounds, rich in heteroatoms and having minor, but measurable amounts of n-alkanes (Silverman, 1978). This material would therefore represent a source rock's primary product, which has not attained the physical and chemical characteristics of conventional crude oil (Welte, 1965; Silverman, 1978). Subsequent 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 such a primary material should be recognizable by (1) high heteroatom (O, N, S, V and Ni) content, (2) high molecular weight (i.e., very viscous, or solid; high melting point, etc.), (3) an isotopic enrichment in heavy carbon relative to its associate petroleum, and (4) minor quantities of n-paraffins.

The data in Table 10 clearly indicate 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, indicates that thermal maturation of an immature oil (e.g., protopetroleum) will yield "lower molecular weight daughter molecules" possessing an enrichment in ^{12}C. Thus a protopetroleum associated with a liquid oil would be isotopically heavier than that oil. Comparison of data in Tables 5 and 10 indicate no significant difference in the carbon isotope ratios of oil and solid bitumen, indicating a lack of isotopic fractionation in the creation of oil from solid bitumen.

Criterion (4) above is also not satisfied by either grahamite or impsonite. Examination of Figure 25, gas chromatograms of the methylene chloride extracts of two solid bitumens, shows a total absence of n-paraffins. Silverman (1978, p. 23-24) notes that a 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, even in minor quantities, indicates that Ouachita solid bitumens are not immature oils, or protopetroleums. Therefore, they must be secondary products, resulting from extensive alteration of once-liquid oil.

Having established the above relation, the question of high-temperature or low-temperature crude oil alteration must be addressed. The similarities in isotopic characteristics of oils and bitumens can be utilized to help resolve this question. Rogers, et al. (1974), in com-

paring 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 the enrichment of ^{13}C in the bitumen by up to 2 $^{o}/oo$. Thermal cracking of C-C bonds tends to remove isotopically lighter fractions, because ^{12}C-^{12}C bonds are cracked in preference to ^{12}C-^{13}C or ^{13}C-^{13}C bonds. The residual material is thus enriched in the heavier isotope. In the case at hand, thermal destruction of Ouachita oils should yield a residual material (i.e., grahamite or impsonite) that is isotopically heavier. However, as seen from the data in Tables 5 and 10, 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, in addition to grahamite and impsonite being products of oil alteration, the alteration itself was a relatively low-temperature phenomenon. Thus isotopic data 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 lines of evidence exist which independently support the conclusions that these solid bitumens are not primary, and do not result from thermal alteration 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) summarized this effect by stating "Palynomorphs disappear in extremely low-grade metamorphism."

(2) At several localities throughout the Frontal Ouachitas,

liquid oil is found within one mile of solid bitumens deposits. In the Redden Field area (see Figure 2) such 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) notes that:

> 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.

Again, 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, via dissolved molecular oxygen).

The deasphalting process has been discussed by several workers (e.g., Rogers, et al., 1974). They attribute natural deasphalting to the difference in solubilities of the compounds of crude oil 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 this lower-molecular weight oil (McKay, et al., 1978, p. 141). This effectively results in a concentration of asphaltene-like materials in the resi-

due which, presumably, would be chemically similar to the grahamites and impsonite described from the the Ouachita Mountain region of Oklahoma.

Geologic considerations appear to minimize the possibility that deasphalting was significant in the origin of solid bitumens in the Ouachita Mountain area. The following relations were considered: (a) Deasphalting is most efficient in a conventional reservoir. However, the grahamite and impsonite in the Ouachitas occur in large veins, which show no evidence of a continual precipitation (i.e., there is no layering evident in the vein); (b) 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 in the Ouachitas (Fay, 1976) represent all the resin and asphaltene material which precipitated from a crude oil due to deasphalting, and that the oil originally contained 18.5% resins and asphaltenes (a worldwide average: Tissot and Welte, 1978, p. 339), it is possible to 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, as is common in laboratory deasphalting procedures (Rubinstein, et al., 1979a), calculations suggest that over one trillion cubic feet of gas are necessary. Although recent re-working of old wells have resulted in the production of gas in the Frontal and Central Ouachitas, the extent of this gas is unknown. However, natural gas which may have migrated from the thermally metamorphosed core of the Ouachitas (Figure 2) could have contributed to natural deasphalting. Although such gas could have escaped at the surface in the past, such huge quantities of flowing natural gas cannot

presently be documented; (c) The phenomenon of grahamite becoming less viscous with depth (Ham, 1956) is inconsistent with a deasphalting origin, because one would expect a deasphalting process to precipitate asphaltenes from bottom-to-top, because natural gas is presumably migrating upward from depth.

These observations support an origin of grahamite and impsonite that results from near-surface alteration of crude oil. These are processes due to the many effects of meteoric water influx. These effects are, in order of presumed importance, biodegradation, devolatilization, water-washing and inorganic oxidation by molecular oxygen. There are several geologic arguments which are consistent with a near-surface alteration phenomenon. All major deposits of asphaltite known in the Frontal and Central Ouachita Mountains of Oklahoma are within 500 feet of the surface. Most deposits were initially discovered because they were exposed at the surface. Thus it can be seen that the geochemical evidence given below for low-temperature alteration as the origin of this material is consistent with the geological interpretation.

The chemical effects of near-surface alteration of crude oil due to influx of meteoric water have been studied in field and laboratory settings, and reviewed by Bailey, et al. (1973), Price (1980), and Curiale (1980). In addition, several environmental geochemistry studies have involved the natural degradation of oil spills at sea (Blumer, et al., 1973). The results of these investigations show that such alteration results from a combination of effects, including biodegradation, water-washing and devolatilization (i.e., evaporation) of the initial material. The chemical effects of such changes in nature are significant

and, in most cases, obvious. 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 have discussed the loss of n-alkanes and isoprenoid isoalkanes from crude oil due to severe biodegradation (Bailey, et al., 1973a; Deroo, et al., 1974). Laboratory simulations have documented gradual loss of these components from oils due to their metabolism by microbes (Jobson, et al., 1972). This depletion of straight-chain and branched-chain alkanes is currently interpreted as resulting from severe biodegradation (Sassen, 1980). On this basis, it appears that the solid bitumens in this study are severely biodegraded crude oil, as shown by the virtual lack of these alkanes in methylene chloride extracts of grahamite (Figure 25). In addition to loss of straight-chain and branched-chain hydrocarbons, aromatic hydrocarbons are also depleted, as indicated by the absence of any prominent aromatic peaks in the chromatograms. This is consistent with results obtained by Gibson (1976), which show that low-molecular weight aromatic compounds can also be metabolized by bacteria. Jobson, et al. (1972) and others have observed a partial depletion of aromatic materials following metabolism of the alkanes. Bailey, et al. (1973a) however, observed metabolism of the aromatic compounds before complete destruction of the n-alkanes.

The work by Bailey, et al. (1973a) also showed that the asphaltene fraction is apparently not metabolized during biodegradation, allowing one to recognize a biodegraded oil by its higher (relative) asphal-

tene 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 methylene chloride-insoluble organic material of the solid bitumens as asphaltenes, and includes the portion of the extract that is also asphaltene material (Tables 9 and 10), then the solid bitumens range from 92.1 to 98.9% in total asphaltene content. In view of the work by Bailey, et al. (1973a), these numbers support an origin due to biodegradation.

The elemental content of the grahamite and impsonite is also consistent with an origin due to biodegradation. Rubinstein, et al. (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 (Figure 63), and increases 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 (Table 5 and 10, respectively). Furthermore, a plot of atomic H/C versus O/C ratios for the oils used by Rubinstein, et al. (1977) shows a very similar trend to that observed for oils and bitumens of the Ouachitas. This is shown by comparison of Figures 59 and 63. It is apparent however, that biodegradation of the Ouachita materials proceeded far beyond the 168 hour limit used by Rubinstein, et al. (1977). These workers simulated naturally-occurring asphaltic material through a series of biodegradation experiments. However, similar results are

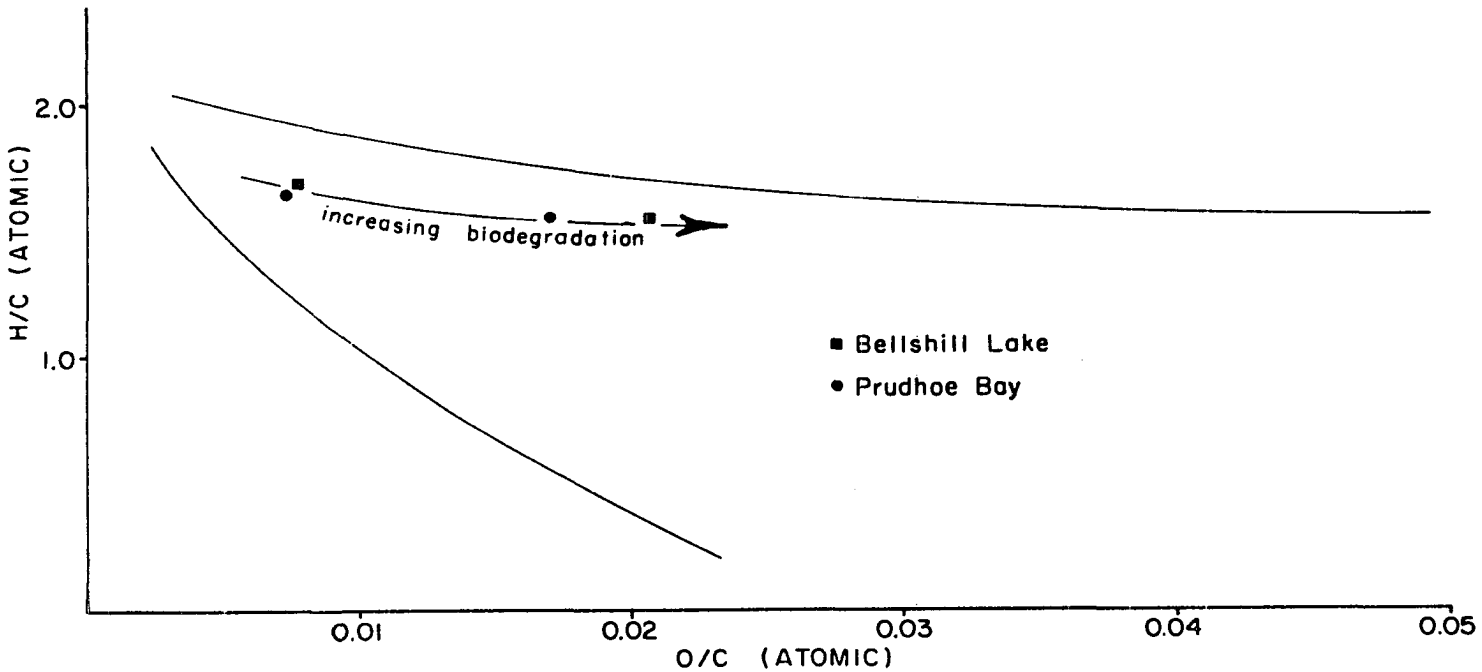


Figure 63. Graph of atomic H/C versus O/C, showing Crude Oil Biodegradation Path. Data from Rubinstein, et al., 1977. Low O/C values are for unaltered oil samples. See text for explanation. Compare with Figure 59.

suggested by Amit and Bein (1979) in their study of real asphalts in the Dead Sea area. They report 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 biodegradation. Several workers have shown that sulfur is generally concentrated in the high-boiling fraction of oils, i.e., the asphaltenes (e.g., Orr, 1978). Therefore, because biodegradation effectively concentrates this fraction, sulfur content increases in a biodegraded oil. This relation is observed in the oils, grahamites, and impsonite of the study area. The sulfur isotope ratio however, does not change significantly during biodegradation (Orr, 1978). This is observed in the present study as well, since the ranges of sulfur isotopes for solid bitumen exhibit a 70+% overlap with those of the oils, as discussed in a previous section. Orr (1978) attributes the increase in sulfur during biodegradation to concentration effects, rather than to addition of non-indigenous sulfur.

In view of the vertical carbon isotope type-curves derived for three of the Ouachita oils (Figure 9), it is also possible to present additional isotopic support for a biodegradation origin of grahamites and impsonite. Microbial utilization of crude oil (as well as water-washing and devolatilization) depletes particular compound types in an oil, namely the n-alkanes, branched-chain alkanes, some aromatic and naphthenic structures, etc. Thus the carbon isotope ratios of the whole oil will only be altered if the metabolized compounds are isotopically different from the non-metabolized compounds. However, as shown in Table 6 and Figure 9, the carbon isotope ratios of various fractions of three of

the Ouachita oils do not differ by more than 1.0 °/oo from each other. For example, removal of all hydrocarbons from oil 11 would result in a residue whose carbon isotope ratio is very similar to that of the original whole oil.

A similar argument can be made for sulfur isotopes. Work by Monster (1972) suggests that the sulfur isotopic ratios of each of the four oil fractions is similar for each of three Saskatchewan oils. If this situation holds for the Ouachita oils, biodegradation would result in little sulfur isotopic fractionation. This suggests that microbial utilization of the Ouachita oils could result in a residue which has an isotopic composition similar to that of other components in the original material.

Comparison of carbon and sulfur isotopic data for oils (Table 5) and solid bitumens (Table 10) therefore, indicates that isotopic evidence is consistent with a biodegraded origin for these materials. This interpretation is consistent with data reported by Orr (1978) who noted little effect on the carbon isotope ratio due to biodegradation of oils from Midway Sunset Field (California).

The results of the vanadium and nickel analyses are also useful as indicators of biodegradation. As mentioned earlier, there appears to be a slight concentration of vanadium in the nonasphaltene materials of the Ouachita oils examined. Thus, biodegradation and devolatilization, which concentrate the asphaltenes, should also result in smaller values for the V/Ni ratio. This has apparently occurred, as shown in Tables 5 and 10. The average V/Ni ratio for the three oils examined is 3.02 (standard deviation = 0.77), while that for the six grahamites is 1.22

(s.d. = 0.87). Thus decreasing V/Ni ratios may represent a novel way of monitoring the progress 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 biodegraded character of these materials. Rubinstein, et al. (1979a, 1979b) have shown that pyrolysis of the asphaltene fraction of undegraded and biodegraded crude oil is useful in elucidating both the structure of the asphaltene and the unaltered-oil origin of the biodegraded crude. These authors show that pyrolyzates of asphaltenes of biodegraded crude oil are very similar in chemical composition to the original undegraded oil. In the case of the present study, pyrolysis of whole grahamite and impsonite approximates pyrolysis of asphaltenes only, since asphaltenes represent 92.1-98.9% of the organic matter.

Results of high-temperature continuous-flow pyrolysis of grahamite and impsonite have been presented earlier. Quasi-n-alkane distributions are shown in Figure 29. Comparison with the n-alkane distributions of the Ouachita oils (Figure 12) suggests many similarities, as discussed earlier. Although these experiments were conducted at very high temperatures (570°C), identical results were reported by Rubinstein, et al. (1979a) for low-temperature (300°C) closed-tube pyrolyzates of asphaltenes isolated from a biodegraded oil. These authors report 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 biodegradation as the origin of the Ouachita material.

In order to minimize the yield of unsaturated hydrocarbon compounds, low-temperature pyrolysis experiments were conducted on selected grahamites and on the impsonite sample. The resultant pyrolyzates were examined for sterane and terpane content. Recent work has shown that the distribution of these materials, particularly the steranes, appears to be significantly altered in cases of severe biodegradation (Reed, 1977; Seifert and Moldowan, 1979). Seifert and Moldowan (1979) have 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 to occur with increasing biodegradation of oil, with regular steranes absent in heavily biodegraded oils. Reed (1977) noted an absence of all steranes in a heavily biodegraded oil. In addition, Seifert and Moldowan (1979) observed several changes in sterane stereochemistry. They also found that excessive biodegradation affects 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, et al., 1977; Wehner and Teschner, 1981). However, in the work of Rubinstein, et al. (1977), the oils in question were artificially biodegraded, for only a period of 168 hours. Consequently, it is possible that either biodegradation did not proceed far enough to alter the steranes, or that the mixed culture used was incapable of doing so.

Oils used in each of the preceding studies were conventional

oils. The Ouachita bitumens however, are solids containing predominantly asphaltene compounds. Consequently, pyrolysis of these materials was necessary to liberate sufficient quantities of steranes and hopanes for GCMS analysis. It has previously been shown (Rubinstein, et al., 1979a) that pyrolysis of asphaltenes of a biodegraded oil yields a pyrolyzate which is chemically comparable to the undegraded oil. Pyrolysis of Ouachita materials reveals definite changes in the sterane distribution between bitumen pyrolyzates and oils, which suggest biodegradation as a mechanism.

Figure 31 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 order oil 11, grahamites 7,5,6,3 and impsonite 44. However, recognizable regular steranes are present even in sample 44. These 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 32. The regular hopanes (17a(H),21b(H)) are present in both oil and pyrolyzates, although the "tricyclic terpanes" concentrations of the pyrolyzates are diminished greatly. Also the relative sizes of peaks 1e and 2 are increased greatly relative 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) report that tricyclic terpanes generally survive biodegradation. Consequently, until further data become available, a full interpretation of the terpane distribution

will not be possible.

In addition to elemental, isotopic and sterane evidence for biodegradation, the metal data are also generally consistent with this mode (biodegradation) of solid bitumen formation. Biodegradation serves to concentrate the non-hydrocarbon compounds in general. Therefore, residual material will be enriched in metal content, as observed for the grahamites depicted in Figure 60.

In summary, there appears to be considerable evidence which indicates that biodegradation was one of the dominant processes that leads to the formation of the Ouachita solid bitumens. However, biodegradation was probably not the sole mechanism because these substances are now solids. Crude oils are know which, in terms of sterane distributions, are biodegraded to a greater extent than these bitumen pyrolyzates, and yet still remain liquids, albeit viscous liquids (Reed, 1977). The proximity of these deposits to the earth's surface suggest that water-washing and devolatilization may have occurred simultaneously, until the bitumens became impermeable to meteoric water. At this point, biodegradation and water-washing would cease, while devolatilization would slowly continue (over a maximum time span of 300 million years) until the material became solid. The implications of such a development to petroleum exploration efforts in the Ouachitas are significant. Solid bitumen in the Ouachita Mountains could serve as a reservoir seal for liquid materials below. This topic will be pursued in more detail later in this report.

The "mature" nature of the terpane and n-alkane distributions of the solid bitumen pyrolyzates indicates that the oils were mature be-

fore the solid material formed. This however, does not preclude a continuation of the maturation process after the solids formed, perhaps analagous to the conversion of bituminous coal to anthracite as a result of 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 Figure 2). Apparently, initially-produced grahamite was thermally-altered here to produce an impsonite. This conclusion is consistent with that of Jacob (1973, 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 CORRELATIONS BETWEEN OIL AND SOURCE ROCKS

Previous Investigations

Attempts to correlate one or more oil families to their respective source rocks have become routine exercises in many oil company and service laboratories. The widespread use of sophisticated analytical techniques in the last twenty years, most notably isotope ratio mass spectrometry, and computer-assisted gas chromatography-mass spectrometry, has resulted in a rapid increase in the number of source rock-oil correlation studies (Barker, 1975). These studies have been reviewed in detail by Fuex (1977, pp. 170-172), Tissot and Welte (1978, pp. 481-485) and Hunt (1979, pp. 503-513). Four of these studies will be briefly summarized below, with an emphasis on the techniques employed.

William's (1974) study of the oils and source rocks of the Williston Basin, USA, was one of the first comprehensive attempts at source rock-oil correlation. The 184 oil samples were grouped into three families, based on similarities in carbon isotope ratio, alkane distribution, C_4-C_7 hydrocarbon type distribution, and optical rotation of the aliphatic fraction. The three oil types could not be uniquely characterized by carbon isotope ratios and optical rotation parameters, and so it was necessary to employ additional techniques. Analysis of both the n-alkanes and the C_4-C_7 components was sufficient to distinguish all three types. Based on the same techniques, correlations to particular source rocks

were subsequently made. Each oil family was found to correlate to specific source rocks in the Basin. Although this investigation represents a pioneering effort in source rock-oil correlation studies, it is noteworthy that each oil family was found to be in stratigraphic proximity to its postulated source. Consequently, the chemical parameters derived from analyses of the oils were not affected significantly by long-distance migration. Furthermore, oil families were restricted to particular strata, being confined to upper and lower evaporite sequences (Dow, 1974). Thus the geologic setting was quite conducive to such an investigation.

Of particular interest to the present study is the oil-rock correlation work of Cardwell (1977). His investigation was directed toward a better understanding of the source of Arbuckle-reservoired oil in the mid-continent region. Based on alkane distributions and various ratios of isoprenoids and n-alkanes, Cardwell suggested that Arbuckle Group carbonates were not hydrocarbon source sequences. On the basis of similarities between Arbuckle (Cambro-Ordovician) oil and oil in Pennsylvanian reservoirs, he concluded that both probably had the same source, namely the Pennsylvanian shales.

The first major source rock-oil correlation study using GCMS techniques was that by Welte, et al. (1975b). Twenty source rock-oil pairs were analyzed for (a) distribution of tetra- and pentacyclic compounds having 27+ carbon atoms, (b) carbon isotope ratio of oils, kerogens and rock extracts, and (c) n-alkane and isoprenoid isoalkane distributions of the oil and rock extracts. These parameters were given weighted values, as effective correlation tools, of 50%, 30% and 20%, respectively. Note the relative value placed on biomarker studies (a) by this

group of workers. Details of this study will be discussed later in this section.

One of the most recent attempts to correlate oils and source rocks is a study by Alexander, et al. (1981). These authors successfully correlated oils produced from the Windalia Sand Member of the Winning Group (Barrow Subbasin) to source rocks of the Winning Group. The major parameters used in the correlation were carbon isotope ratios of paraffinic and aromatic hydrocarbons, and ratios of alkanes and isoprenoid isoalkanes of oils and extracts. The authors considered carbon isotope and pristane/phytane ratios as the most useful correlation tools and weighted these parameters most heavily in their "overall correlation score."

These four investigations indicate the usefulness of current analytical techniques in the correlation of oils and potential source rocks. The most successful techniques appear to be sterane/terpane analysis, isotopic analysis, and distribution and ratios of n-alkanes and isoprenoids. Therefore, these techniques have been relied on most heavily in the present study. In the following discussion, source rock kerogens and source rock extracts of the Ouachita rocks will be compared to Ouachita oils, in an attempt to determine whether Ouachita rocks correlate with these oils.

Oil-Kerogen Correlations

Thermal maturation of kerogen is presumed to result in isotopic fractionation of the organic matter in a source rock, so that expelled oil will be isotopically lighter than its kerogen source (Silverman, 1964). This effect has been corroborated by studies of source rock-oil

pairs (Stahl, 1978; Welte, et al., 1975b). Welte, et al. (1975b) observed an average isotope difference between kerogen and oil of 1.7 °/oo, the kerogen being isotopically heavier. The range between oil-kerogen pairs noted in this particular study was 0.5 to 3.2 °/oo. Stahl (1978) reported this difference to average 1.8 °/oo, with a maximum difference of 2.9 °/oo, based on eight kerogen-oil pairs. Based on the average oil value reported in Table 5 (-29.7 °/oo), the probable source kerogens will be up to 3.2 °/oo heavier than the oil. The most probable kerogen sources will be 1.8 °/oo heavier than the oil. Given a total analytical error of ±0.2 °/oo, the source kerogen for Ouachita oils of the present study should be in the range of -29.7 to -27.7 °/oo. Examination of Table 12 suggests several possible sources on this basis. Note however, that kerogens which have isotopic ratios nearest in value to those of the oils are from the Missouri Mountain, Polk Creek and Womble Formations.

It has been shown that the isotopic ratios of individual oil fractions can be utilized to determine the isotope ratio of the source kerogen for that specific oil (Stahl, 1978, 1980). In order to determine the feasibility of this method in the present study, the type-curve for each oil (Stahl, 1978) is plotted in Figure 9. It is evident that the type-curves for these oils are quite different, even though other parameters indicate a high degree of similarity for the oils. Three of the curves have positive slopes, and suggest a source kerogen from -30.2 to -29.0 °/oo. Again, Missouri Mountain, Polk Creek and Womble samples appear to satisfy this condition (Table 12). The so-called "isotope type-curve" technique also suggests that the oils in question are severely biodegraded (Stahl, 1980). Based on evidence discussed earlier, this

does not appear to be true for oils of the present study. Thus the applicability of source rock-oil matching using isotope type-curves is somewhat questionable for Paleozoic oils.

Oil-Rock Extract Correlation

Correlation between rock extracts and oil based on the molecular distributions of paraffinic hydrocarbons is probably the most common technique in use today. Such methods include correlation of n-alkane distributions (Williams, 1974), isoprenoid ratios (Welte, et al., 1975b; Alexander, et al., 1981) and sterane/hopane distributions (Seifert, et al., 1980). Each of these parameters will be discussed below, for the oils and possible source rocks of the Ouachitas.

N-alkane distributions for oils and source rock extracts are presented in Figure 12 and Figures 38-40, respectively. The oil distributions show a smooth envelope, with decreasing n-alkane content as carbon number increases; exceptions include minor predominances at n-heptadecane and n-nonadecane. The reader should note that oils were not topped (see Appendix I) prior to gas chromatographic analysis. As a result, the major peaks at n-C_{15} to n-C_{17} are not evident. For the source rock extracts, the saturate hydrocarbon fraction was effectively topped prior to analysis. Examination of the n-alkane distributions of the rock extracts (Figures 38-40) shows four samples which have distributions similar to those of the oils. The samples are OGS GCN 30 (Polk Creek Formation), and the three deepest samples from well 28, all Womble Formation samples. Of these four, the Womble Formation samples of well 28 (Figure 40) clearly correlate best with the crude oils. On the basis of n-alkane distributions, it is possible to tentatively ignore the samples of the

Stanley, Arkansas Novaculite and Bigfork stratigraphic intervals as possible sources. Oils examined in this study, although reservoired in Carboniferous rocks, appear to be sourced from Siluro-Ordovician rocks.

Examination of the pristane/phytane ratios of the rock extracts also indicates a Siluro-Ordovician source (Table 14). 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 from the three deepest Womble Formation samples in 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 (compare Tables 6 and 14). If the Womble Formation is the source of these oils, then the n-alkanes appear to have been depleted during or after migration.

In addition to the n-alkane distributions and isoprenoid ratios, the sterane/hopane distributions of the rock extracts also suggest a Siluro-Ordovician source. Comparison of ion chromatograms of Ouachita oils (Figure 20) with those obtained from Stanley (Figure 44), Missouri Mountain (Figure 46), Polk Creek (Figure 47) and Womble (Figure 49) samples shows fairly good agreement. The significance of the Stanley sample however, is questionable because of the probable presence of non-indigenous organic matter in this sample, as discussed in an earlier section. Ion chromatograms shown in Figures 20, 46, 47 and 49 are shown together

in Figure 64. The strong similarity in sterane distribution among the three rock extracts is striking. Consequently, this particular distribution cannot be used to reduce the number of possible source samples below the three shown. Nevertheless, it should be noted that the best match to oil 11 in Figure 64 is sample OGS GCN 30, a Polk Creek sample.

Despite similarities in the distributions of steranes in Figure 64, co-elution of several steranes (see Table 7) could result in an artificial correlation not based on actual compound distributions. Consequently, each extract was analyzed to determine the "true" distribution of steranes, by carbon number. Results of these analyses are shown in Figure 56; the sterane carbon number distributions for the oils are shown in Figure 21. These figures show that, of the three samples exhibiting good sterane matches in Figure 64, 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 56 is also very similar. On this basis, it appears that the Polk Creek Formation is a very probable source for the Ouachita oils.

Figure 65, a comparison of 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 this basis, since it possesses a compound eluting between peaks 1b and 1c which is present in minor quantities in the crude oil. All three extracts under discussion contain some amount of unknown peak B (Figure 23) found in the crude oils. This compound exists in considerably greater concentration in the Polk Creek extract than in either the Missouri Mountain or

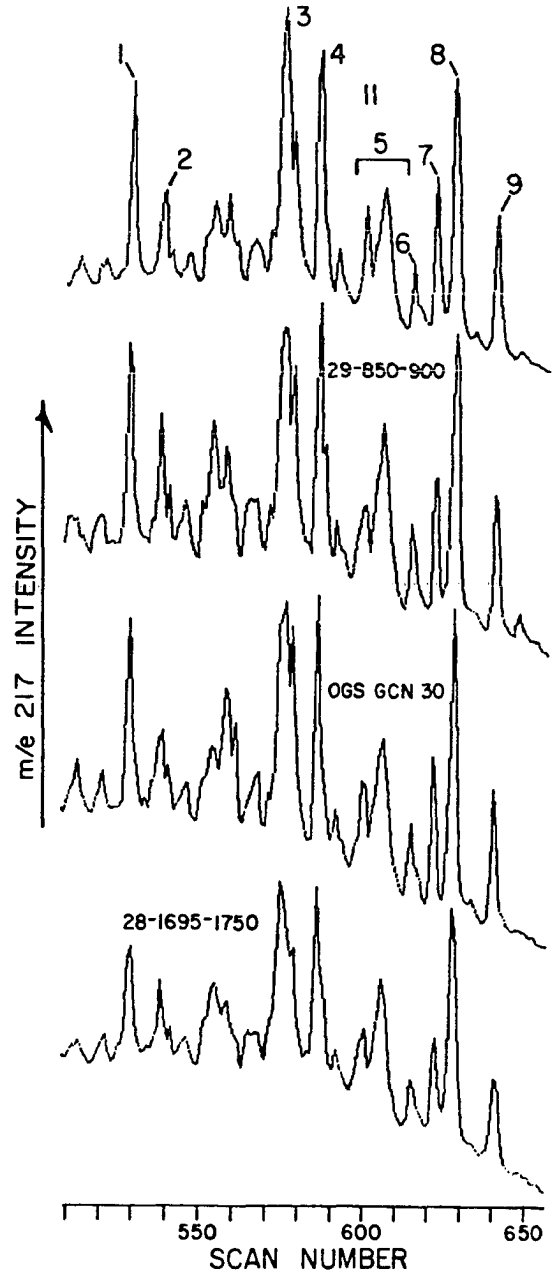


Figure 64. m/e 217 Ion Chromatograms for oil 11 and Probable Source Rocks. See Table 7 for peak identifications.

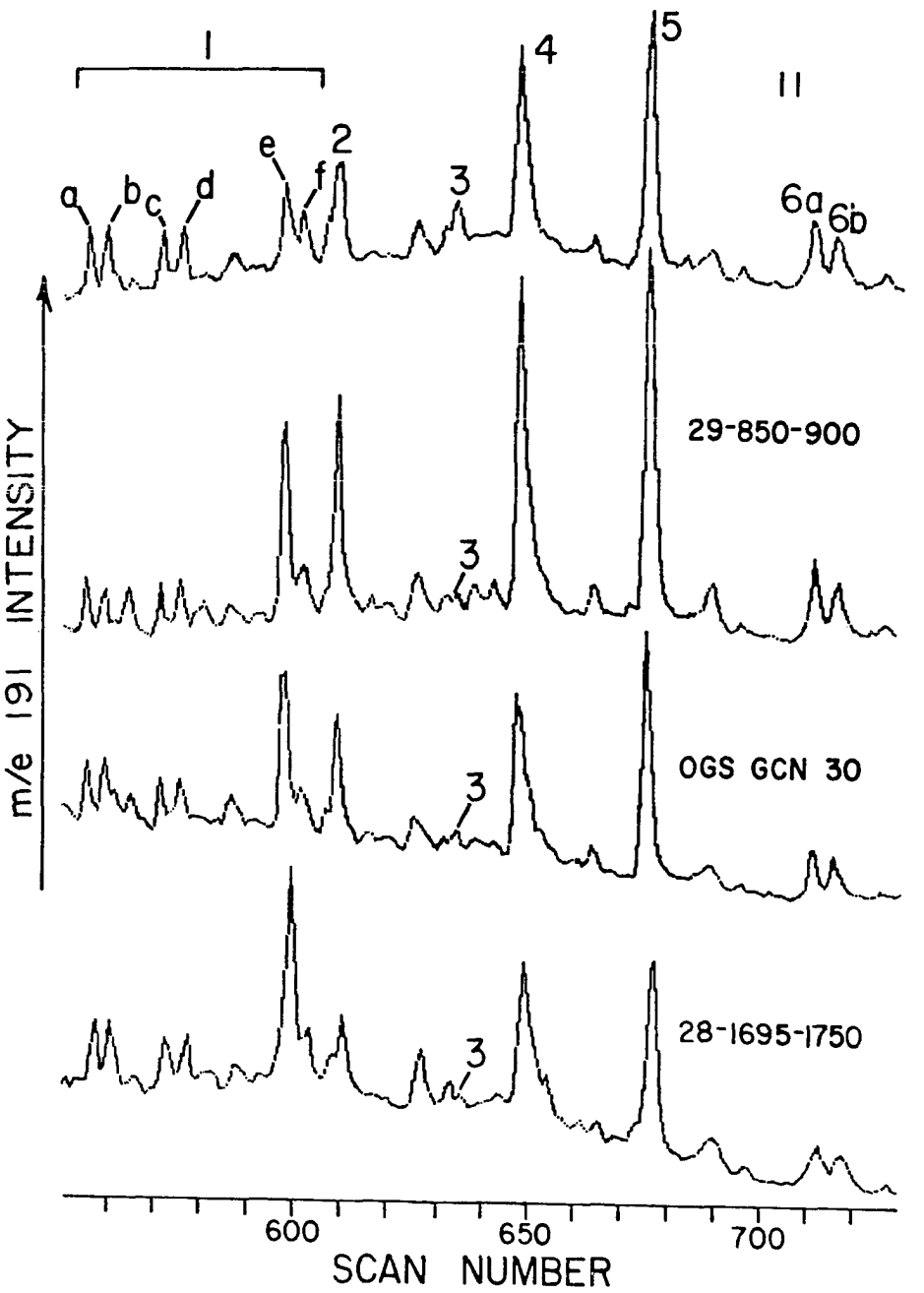


Figure 65. m/e 191 Ion Chromatograms for oil 11 and Probable Source Rocks. See Table 8 for peak identifications.

Womble extracts. The m/e 177 chromatograms for oil 11 and OGS GCN 30 (Figure 66) 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 Formation is a likely source, as was also concluded on the basis of the sterane data.

One of the unusual features of the terpane distributions shown in Figure 65 (and in other m/e 191 ion chromatograms, e.g., Figures 50-55) is the prominence of peaks 1e and 2, relative 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 very obvious in the terpane distributions of the solid bitumen closed-tube pyrolyzates (Figure 32). For example, with the single exception of the terpanes 1a-1d, the pyrolyzate of sample 7 (Figure 32) is almost identical with that of 29-850-900 (Figure 65). Similarly, the pyrolyzate of sample 3 (Figure 32) is almost identical with that of OGS GCN 30 (Figure 65). Some of these correlations are striking, although their meaning is not understood.

Possible Sources for Ouachita Oils

On the basis of isotopic evidence and distribution of n-alkanes, isoprenoid isoalkanes and steranes/hopanes, the oils in the Frontal and Central Ouachitas are sourced from Siluro-Ordovician rocks of the Ouachita Facies. Other data presented 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 Siluro-Ordovician source. As shown in Tables 5 and 10, these ratios range from +14.3 to +20.3 $^{o}/_{oo}$. These ratios are relatively high for petroleum (Coleman, 1977). Data presented by Thode and Monster (1964) and others suggest

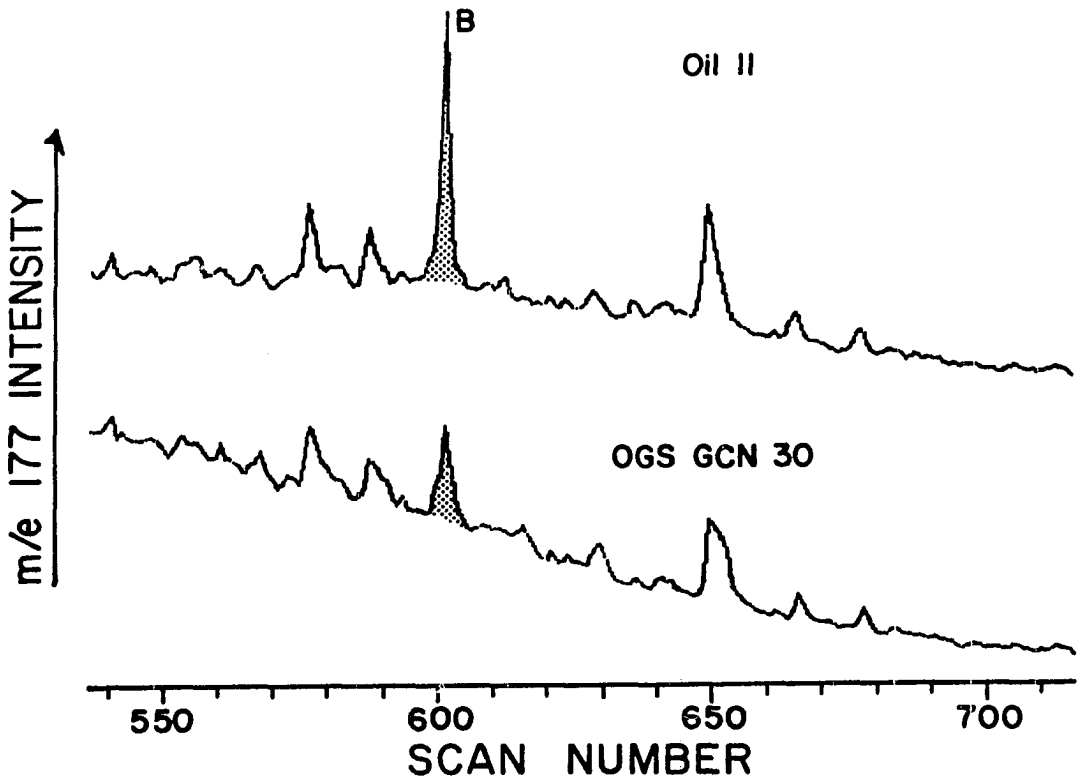


Figure 66. m/e 177 Ion Chromatograms for oil 11 and OGS GCN 30 (Polk Creek). Unknown Peak B is shaded.

that sulfur in sedimentary organic matter (including petroleum) is significantly heavier than sulfur in contemporaneous evaporites. Orr (1978) suggests a difference of 15±5 °/oo. In addition, it has been shown (e.g., Claypool, et al., 1980) that the sulfur isotope ratio of seawater sulfate varied through geologic time, and reached a maximum average value in the Ordovician and Cambrian of +26 to +31 °/oo. Therefore, one might expect the sulfur of an Ordovician oil to be unusually heavy. For example, a 15 °/oo fractionation for sedimented organic matter would yield an oil whose sulfur isotope ratio is +11 to +16 °/oo, which is approximately the range for the oils of the present study. However, the derived curves for changes in isotopic composition of seawater sulfate presuppose open marine conditions (Orr, 1980, personal communication). Such conditions have not been fully documented for Polk Creek or Womble strata. Nevertheless, the heavy sulfur ratios for the oils of this study appear to corroborate a Siluro-Ordovician source conclusion.

Additional corroborating evidence for such a conclusion is the stable carbon isotope ratios for the Ouachita oils. As discussed in an earlier section, although the "light" average ratio encountered (approximately -30 °/oo) suggests a non-marine origin, such ratios are also common in oils from the lower Paleozoic. Silverman (in Welte, 1965, p. 2250) cites a study by Eckelmann, et al. (1962), wherein almost all the oils identified by the latter as being non-marine, based on light carbon isotope ratios, are produced from early Paleozoic reservoirs. Clearly, oils from the early Paleozoic cannot be correctly classified as non-marine (Welte, 1965). The same situation holds in the present study. The geochemical evidence for source rock-oil relationships in the Oua-

chita Mountains indicates a Siluro-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 previously-cited studies.

Other evidence for a Siluro-Ordovician source the V/Ni ratios of the EOM of the Missouri Mountain and Polk Creek samples. The average values for the V/Ni ratios of these formations (Table 13) are 2.9 and 3.7, respectively, while the average ratio of the three oils analyzed is 3.0 (Table 5), suggesting that this ratio may provide a useful parameter of source rock-oil correlation.

Of the three formations under consideration (the Missouri Mountain, Polk Creek and Womble), the Polk Creek and Womble Formations appear to be the most probable sources. Consequently, it might be concluded that only the black shales of the mid-upper Ordovician served as source rocks for the four oils examined in this study. However, due to the absence of the Blaylock Formation in most of the study area (Figure 1), the Missouri Mountain and Polk Creek Formations may be considered a single sequence of shales, spanning the Silurian-Ordovician boundary. Lithologic distinctions between these two formations are therefore somewhat arbitrary. In summary then, the Missouri Mountain-Polk Creek-Womble can be considered as the source sequence for oils of the Frontal and Central Ouachita Mountains of Oklahoma.

POTENTIAL FOR MAJOR OIL ACCUMULATIONS IN THE OUACHITA MOUNTAINS -- A GEOCHEMICAL VIEWPOINT

General Source Potential of the Area

It is clear from the data and discussion presented previously that rocks in the Oklahoma portion of the Ouachita Mountains are capable of sourcing oil, or have sourced oil in the past. Organic matter of suitable type and quantity is present in several formations. In addition, the entire section studied can be considered thermally mature. Consequently, the possible presence of major oil accumulations in the Oklahoma Ouachitas must be considered. The purpose of the present section is to discuss this possibility in light of the data of the present study.

Of the "source-reservoir-trap" requirements which are necessary for an oil accumulation to exist, the first condition appears to be satisfied. While the "reservoir" and "trap" aspects are beyond the scope of this paper, recall that depths in excess of 1000 feet are essentially unexplored throughout most of the Frontal and Central Ouachita Mountains. Consequently, conclusions based on predictions of poor reservoir and trap conditions are pessimistic and premature.

Of the formations studied, shales of the Womble Formation offer the greatest thickness (3500 feet) of hydrocarbon source lithology. Of the fewer than two dozen wells that have penetrated the Stanley Group in the study area (an area containing over 1400 square miles), only one

or two have completely penetrated the Womble Formation. Consequently, nothing is known of the source potential of pre-Womble strata, although several workers have reported the presence of dark shales in the lower Ordovician rocks (Honess, 1923). Consequently, the good source potential observed for upper Ordovician rocks may be supplemented by equal or better quality source sequences of lower Ordovician age.

Implications of a Secondary, Non-Thermal Origin of Grahamite and Impsonite

The reluctance of many operators to implement aggressive exploration programs in the Ouachita Mountains because of the presence of solid bitumens (so-called dead oil) has been discussed. The presence of these materials, and the elevated temperatures of the Arkoma Basin to the north and the Ouachita Core to the south, have resulted in considerable pessimism concerning the hydrocarbon potential of the Frontal and Central Ouachitas. However, the results of this study, particularly those presented on the solid bitumen characteristics, indicate that such pessimism is unwarranted. The conclusions discussed earlier, concerning a secondary, non-thermal origin of both grahamite and impsonite indicate that the presence of these substances does not imply a postmature thermal regime. Most of the Frontal and Central areas are still clearly within the oil window. Consequently, there is no reason to think that oil generated in the past and reservoired in the deep and thus non-biodegraded formations has been thermally-destroyed. These considerations enhance the exploration potential of the deeper sedimentary sequences.

Another implication of a secondary non-thermal origin for these solid bitumens is the notion that these materials may be serving as seals for liquid hydrocarbons reservoired in deeper horizons. This is support-

ed by various statements in the literature, to the effect that the grahamite becomes significantly softer with depth (Ham, 1956). Examination of Figure 2 suggests that, with the exception of the impsonite sample (44), a good empirical correlation exists between oil-producing areas and bitumen localities. This is suggested more clearly in a figure by Fay (1976), which notes that each major oil field in the study area is located within three miles of a grahamite deposit. The possibility of such solid material acting as an updip seal (effectively a stratigraphic trap) is documented clearly by the occurrences of petroleum and asphaltic sandstone in Redden Field. The oil is reservoired in Stanley Group sands dipping to the southeast at about 60 degrees (Fay, 1976), and productive horizons are quite shallow (90-350 feet). The asphaltic sandstone is located approximately 100-200 feet northwest of the productive wells. In all probability, this asphaltic sandstone is the producing sand of the Redden Field, and Redden oil is trapped by asphalt-plugged porosity updip. If this condition prevails, then the solid (impermeable), non-reservoir bitumens described in this study serve as very effective seals for liquid oil, which remains essentially unbiodegraded.

Migration Pathways

In addition to the geographic association of oil and grahamite, Figure 2 clearly shows that both types of hydrocarbons are in proximity to, and are approximately parallel with, the Windingstair Fault. This suggest a migration-trap-seal relation between the fault and the petroleum (including solid bitumen) accumulations. This relation can exist by major and minor faults acting as (1) updip seals, or (2) conduits. However, most of the solid bitumen material is presently found in rocks

of the Stanley Group which, as has been noted, is an improbable source for Ouachita oils. In addition, the grahamite of the region is often encased in shales, which are relatively impermeable to migrating fluids. Consequently, it appears that the faults in question are not acting as seals for hydrocarbons generated down-dip in the same strata. Therefore, the possibility that existing faults may have served as conduits in the past must be considered.

The concept of faults and fractures acting as conduits for the migration of fluids in the subsurface is often invoked in petroleum geology. Price (1976) has reviewed the evidence for migration of fluids, including oil and gas, along faults, while Philippi (1965) has presented one of the best cases for such movement. Philippi concluded that most of the oil in the Los Angeles and Ventura Basins has migrated from depth along deep-seated faults. Concerning fault migration in general, Philippi (1977) says:

> ...vertical migration of petroleum is very common. Based on oil and shale hydrocarbon analyses it was concluded several years ago that during vertical migration petroleum does not move through the bulk of nonsource rock shale bodies, but through faults and fractures (Philippi, 1965). After tectonic movement fault and fracture planes are neither perfectly flat nor smooth. Such planes will not fit any longer, at least temporarily. Thus, intermittently, for shorter or longer periods of time, a channel network may be formed, permitting slow leakage of crude oil and gas from one zone to another, in the direction of the pressure gradient. Surface oil seeps, near fault zones, are present in many oil basins.

Most such evidence is the result of inference. In general, little direct evidence is provided for such migration. In many cases, fault migration is invoked when existing faults constitute a logical path along which an oil may migrate from source to reservoir. Although the evidence presented below suggests faults may serve as conduits, it

must be borne in mind that such conclusions in the Ouachita Mountains area are also inferred, and are not based on direct evidence.

Workers have also investigated fluid movement along faults and fractures in a theoretical framework (Smith, 1966). Much of the work done to determine the sealing and non-sealing nature of faults has concentrated heavily on growth faults. However Lebkuchner, et al. (1972), in a study of the asphaltic deposits of Turkey, note that asphalts are usually located in the hanging wall of reverse faults. These authors suggested that asphalts were essentially squeezed into deep fissures in the rock. In addition, Hanor and Baria (1977) discuss the possibility that, in the Arkansas Ouachitas, barium-rich brines may have moved upward from shallow depths in the subsurface toward bottom sediments. Such movement would have been along fractures and minor faults, and could have occurred during early Stanley time. The presence of grahamite and impsonite near the Windingstair Fault in the Oklahoma Ouachitas suggests migration of oil up along faults and fractures. Given a normal geothermal gradient ($2.7^{o}C/100$ m), in order to remain in the oil window, this oil could have migrated from no deeper than 4500 m (Hunt, 1979, p. 344). The circumstantial evidence for such a suggestion is as follows:

(a) Veins of grahamite and impsonite up to 25 feet in thickness are present near the Windingstair Fault (Fay, 1976). Such thicknesses suggest that a fissure was created, which was subsequently filled with liquid asphalt (Lebkuchner, et al., 1972).

(b) Significant devolatilization must have accompanied biodegradation of the crude oil. Because these volatiles must also have an avenue of escape, this suggests a carrier bed of high permeability. A

fault acting as a "carrier bed" would provide such high "permeability." A shale abutting against a fault would not.

(c) All of the known major oil occurrences, grahamite and impsonite deposits, are located in near-surface Stanley and Jackfork strata, yet the most probable source for this material is the upper Ordovician. This suggests the presence of major vertical conduits in the Frontal and Central Ouachitas, such as would be provided by major faults. Examination of Figure 6, a cross section across this region, shows that the listric faults associated with the Windingstair would provide several avenues of migration for Ordovician-sourced oil.

(d) Detailed studies of the occurrence of grahamite and impsonite in the region indicate that many, if not all, of these deposits occur in anticlines that have been faulted or extensionally fractured from folding (Fay, 1981, personal communication). This strongly suggests vertical migration through fractures and fissures, if only on a local scale.

While each of these points may suggest that faults, fissures and fractures act as oil conduits in the Ouachita, such evidence is not conclusive. Although there is much worldwide evidence for fault zone seepages (Link, 1952), one argument against such fluid movement might be that these faults are dominantly reverse faults which should "seal" potential reservoirs. However, Thompson (1980, personal communication) suggests that these same faults may have become listric normal faults during the Mesozoic, when the Gulf of Mexico opened. If so, fissures may have been created, allowing for an influx of bituminous materials, which subsequently migrated upward. That a portion of a reverse fault

(namely the sole) may become a normal fault has been documented by Royse, et al. (1975), although no known publication suggests complete coincidence of a normal fault with a once-reverse fault. Figure 67-A depicts the case discussed by Royse, et al. (1975), in which the soles of normal and reverse faults coincide. Figure 67-B shows complete coincidence of normal and reverse faults. Central to both Figures 67-A and 67-B is the existence of two different stress fields acting at two different times. Regardless of the nature of the fault at the time of migration, it appears that some migration along faults and fractures did occur.

In summary, it can be noted that oil, grahamite and impsonite appear to be associated with faults which come to the surface. These faults also appear to have served as a migratory conduit for oils sourced much deeper in the Ouachita trough. Consequently, it is concluded that fault migration has played a significant role in the oil and oil-related deposits of the Ouachita Mountain region of Oklahoma.

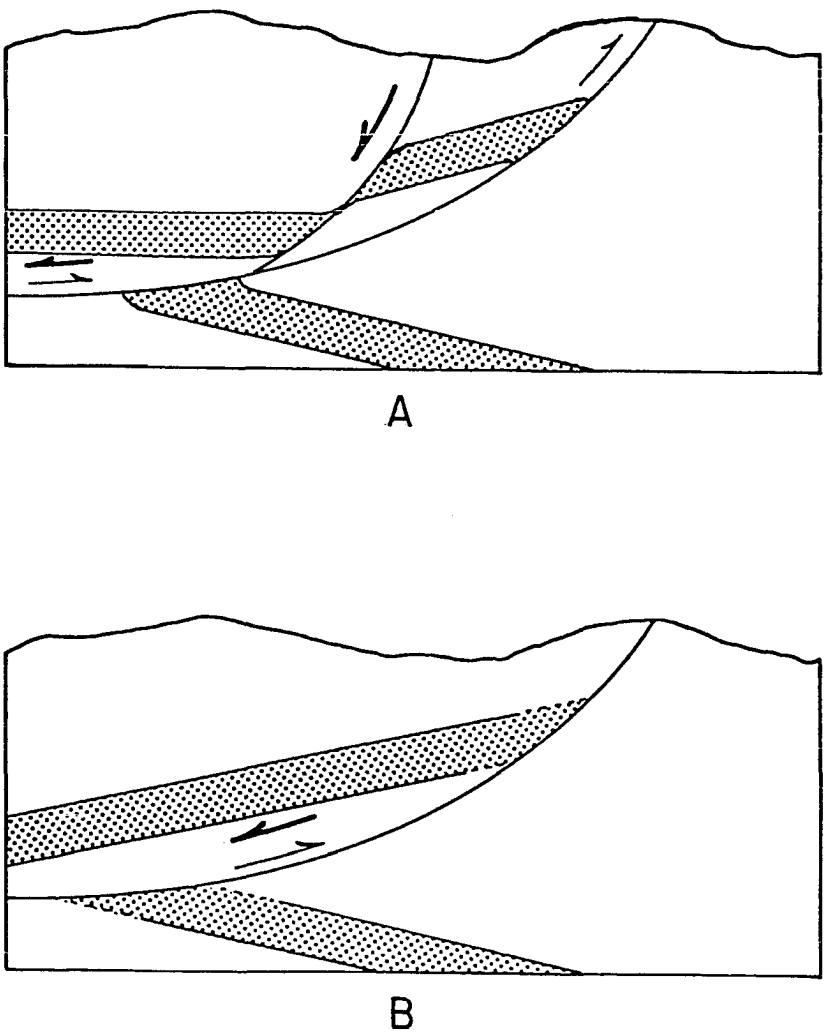


Figure 67. Schematic cross sections showing coincident fault plane surfaces. A: Sole plane of later normal fault is coincident with that of original reverse fault. B: Entire fault plane of original reverse fault is coincident with that of later fault. In both sections, thin arrows indicate direction of initial thrusting, while thick arrows indicate direction of later normal faulting.

CONCLUSIONS

Several general conclusions can be made from the data generated in this study. First and foremost, it is clear that the Stanley-through-Womble section of the Oklahoma Ouachita Mountains contains rocks whose organic matter quantity, quality and maturity level are compatible with the requirements for an oil source rock. It is also clear from thermal maturity data, that these rocks are still within the oil window.

The oils which exist in the Frontal and Central Ouachitas in the study area are paraffinic and generally unaltered. 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 sequences for the studied oils and solid bitumens are Missouri Mountain-Polk Creek-Womble strata, each possessing some characteristics of the oils. The absence of the Blaylock Formation in the study area suggests lithologic continuity from the Missouri Mountain Formation to the Polk Creek Formation.

Several observations suggest large-scale vertical migration.

Among these are (1) oils are reservoired in Pennsylvanian and Mississippian rocks, (2) solid bitumens are found as far downsection as the Bigfork Formation, and (3) the most probable source for these materials is middle to upper Ordovician units. It is proposed here that such migration was facilitated by fractures, and by listric reverse faults, which sole in the Ordovician source beds. Following generation and perhaps limited expulsion from these source beds, creation of the faults allowed migration toward the surface. As oil approached the meteoric water zone, near-surface alteration began. Initially, biodegradation and water-washing were predominant, until such time as permeability was decreased to impede water flow through the degraded oil. At this time, as long ago as 300 million years, biodegradation ceased, and devolatilization continued, and is still occurring at the present time.

Conclusions concerning the oil potential of the Oklahoma portions of the Frontal and Central Ouachita Mountains are possible from the data presented here. This area should definitely be considered by explorationists as 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 rock, is clearly satisfied. The high-temperature history frequently ascribed to the study area has been shown to be unfounded. Furthermore, the oil present is of high quality and low in sulfur. These conclusions, and the relatively large untested areas, suggest that optimism concerning the future of the Ouachita Mountains as an oil province is warranted.

It is appropriate to again quote Honess (1927, p. 31): "...sometime in the future, when gasoline is selling for 50 cents a gallon it

might be worth while to study the Ouachita Mountains." The time to begin seriously exploring for oil in the Ouachita Mountains is now.

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APPENDIX I

DEFINITIONS

Because of their general use throughout the text, the following terms are defined below. Other terms not listed below are defined as they are introduced in the text.

Arbuckle Facies -- "...shelf or platform types of sediments...to the north or west..." of the Ouachita Mountains (Cline, 1960, p. 8).

Bitumen (or Extractable Organic Matter) -- the organic matter present in a rock that can be extracted with organic solvents; in the present study, bitumen is all organic matter in a rock that is extracted with methylene chloride; the term bitumen, as used here, has an entirely different meaning than solid bitumen (see below).

Carbon Ratio -- the ratio of the fixed carbon in a coal to the sum of the fixed carbon and the volatile hydrocarbons present in that coal; usually expressed as a percentage (Gutjahr, 1966).

Dead Oil -- thermally-destroyed, once-liquid petroleum.

Fixed Carbon -- that portion of a coal that is neither moisture, volatile matter, nor ash, as determined by proximate analysis, and expressed as a percentage of the weight of the coal.

Liquid Window (or Oil Window) -- the levels of maturation at which a rock can be capable of the generation of significant amounts of hydrocarbons (Pusey, 1973).

Olefin (or Alkene) -- an unsaturated hydrocarbon, having the general formula C_nH_{2n}, with n being any integer; an alpha-olefin is an olefin having its double bond between the first two carbons of the chain.

Ouachita Facies -- the rocks of the Ouachita Mountains of Oklahoma and Arkansas, and the Marathon Mountains of Texas (Cline, 1960, p. 8), considered to result from continental slope and rise deposition (Wickham, 1978).

Possible Source Rock -- any sedimentary rock that is under consideration as a source rock for oil or gas.

Potential Source Rock -- any sedimentary rock which contains an adequate content of organic matter to serve as a source for oil or gas, but whose thermal maturity is unknown.

Solid Bitumen -- as used in this study, a localized natural substance, non-coaly, rich in carbon (generally over 50% by weight), found in sedimentary rocks.

Source Rock -- a unit of rock that has generated and expelled oil or gas in sufficient quantity to form commercial accumulations (from Dow, 1977).

Topping -- the process of low temperature (less that $60^{\circ}C$), long term (usually 24 hours) heating of an oil to remove the most volatile components.

APPENDIX II

PROCEDURES

Sample Collection and Preparation

Oil

Oil samples 11 and 17 were collected from stock tanks in clean one-gallon bottles, with caps lined with methylene-chloride-washed aluminum foil. Oil 15 was collected from the flowline at the well site. Oil 45 and the gilsonite sample were kindly donated by Chevron USA, Inc.; method of collection is unknown. All four oils were stored at room temperature in sealed bottles until analysis.

Grahamite and Impsonite (Solid Bitumens)

All solid bitumen samples were collected from surface tailings at the site of previously-worked mines, except for samples 5 and 44. Sample 5 was scraped from vein fillings in the Bigfork Formation, collected in the Potato Hills (see Figure 2). Sample 44 was received from Mrs. Walker, Page, Oklahoma, whose son had collected the material from surface tailings at the impsonite mine on Black Fork Mountain.

All solid bitumen samples were washed in de-ionized water, dried and ground (about 60 mesh). In addition, sample 5 was treated with 1.0 N hydrochloric acid to remove calcite associated with the organic matter.

Potential Source Rocks

Subsurface samples were obtained as cuttings from various core and sample libraries in Oklahoma: Ardmore Sample Cut, Shawnee Sample Library, Oklahoma Geological Survey Core and Sample Library. Surface samples were collected by Robert O. Fay and William D. Pitt. Efforts were made to obtain samples from below the weathered zone.

Pre-washed cuttings and surface samples were ground prior to analysis. Most samples were ground to pass 100 mesh prior to extraction. All samples analyzed for total organic carbon and carbon isotope ratio were ground to pass 200 mesh. Following grinding, all samples were stored in glass vials or bottles.

Chemical Procedures

All solvents used in these procedures were re-distilled in all-glass stills from reagent grade commercial solvents, except for 2,2,4-Trimethylpentane (iso-octane), which was glass-distilled as purchased (MCB OmniSolv Reagent). All glassware was conventionally washed with soap and water, and rinsed thoroughly with de-ionized water (purified by reverse osmosis) and dried prior to use. In addition, all glassware was rinsed with organic solvents prior to use; rinsing was done with the most polar solvent that would be used in that glassware. All silica gel, aluminum oxide, glass wool and extraction thimbles were soxhlet-extracted with methylene chloride for at least 20 hours, and dried, prior to use. Finally, all samples, prior to gas chromatographic analysis, were dried under a flow of dry nitrogen gas.

The following gives detailed procedures for each chemical analysis in this study. Refer to Figures 68, 69 and 70 for outlines of the procedures discussed.

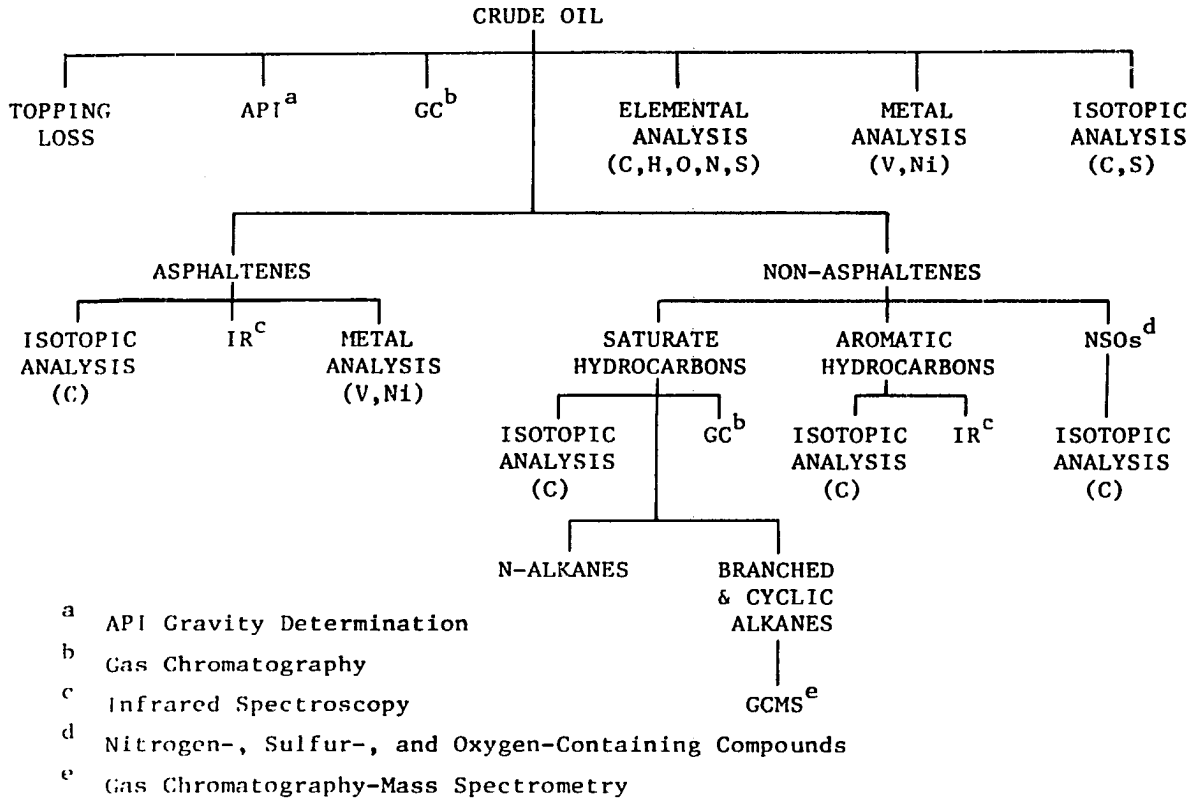
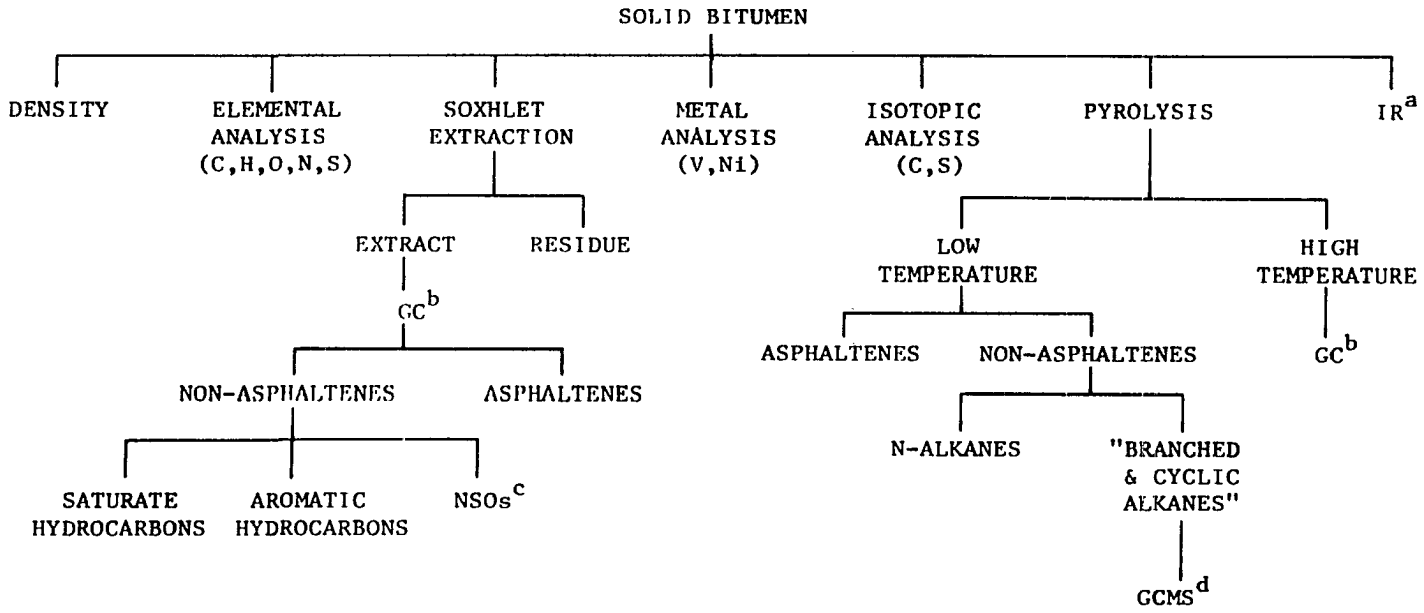


Figure 68. Procedure Flowchart -- Crude Oil.



[a] Infrared Spectroscopy

[b] Gas Chromatography

[c] Nitrogen-, Sulfur-, and Oxygen-Containing Compounds

[d] Gas Chromatography-Mass Spectrometry

Figure 69. Procedure Flowchart -- Solid Bitumens.

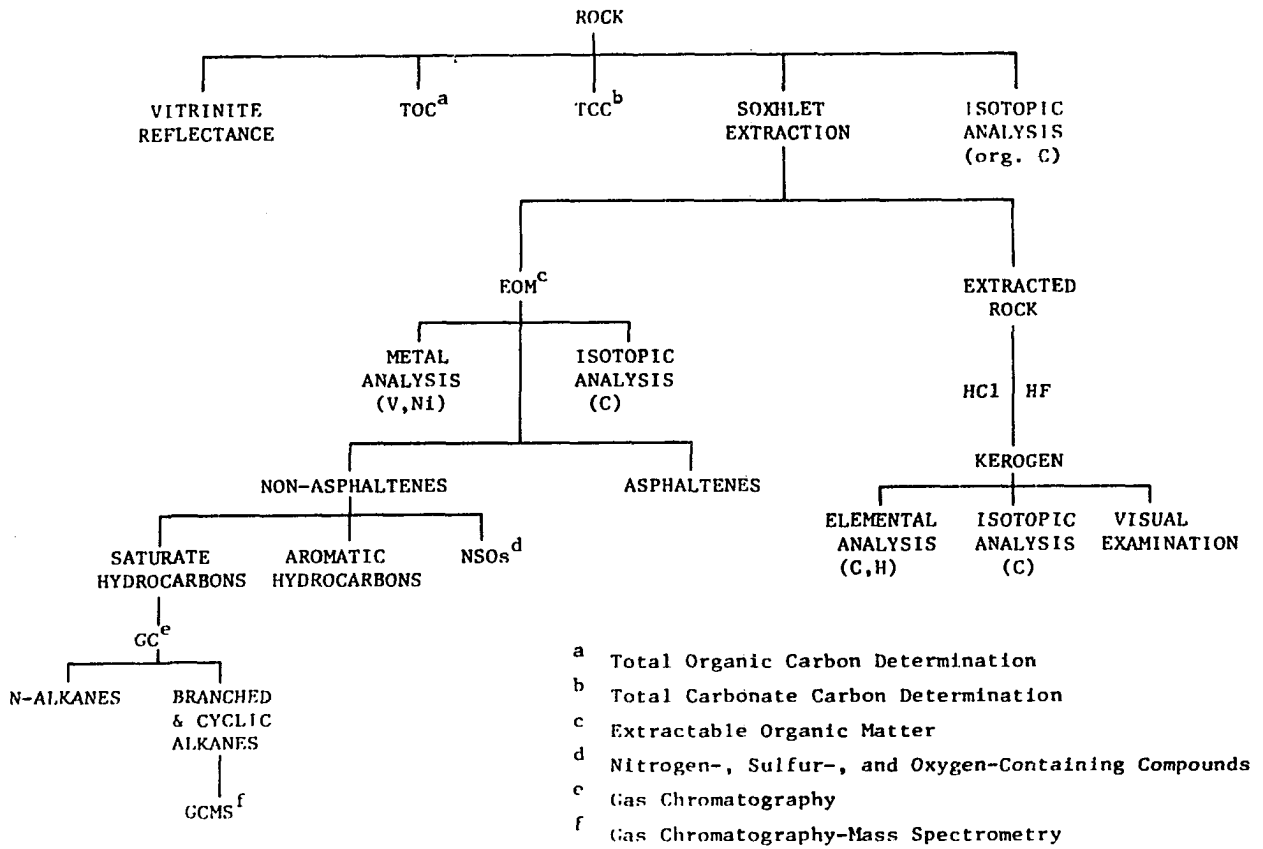


Figure 70. Procedure Flowchart -- Rocks.

Topping

Crude oils were topped for 21 hours at 43°C. Topping loss was determined from initial and final weights of oil (initially approximately 0.5 g were used).

API and Density Determinations

Crude oil API gravity was determined with a Baume heavy liquid hydrometer. The specific gravity determination obtained in this manner was then corrected from room temperature to 60°F (using temperature corrections suggested by Levorson, 1967, p. 196), and converted to API gravity by the conventional formula.

Solid bitumen specific gravity was determined on chunk samples (i.e., not ground), as the ratio of mass to the volume of water displaced.

Vitrinite Reflectance

Whole rock samples, medium to coarsely ground (0.1 to 1.0 mm) were encased in a plastic plug, which was subsequently ground and polished. Sample preparation was done by Michael Lambert of the Oklahoma Geological Survey. Reflectance of the vitrinite macerals was determined using a Vickers Reflectance Microscope, equipped with a Gamma Scientific Digital radiometer (fiber-optic) and photomultiplier tube. A Lambda halogen light source was used, and the reflected light was filtered so that only light of 546 nm wavelength passed to the detector. The detector was calibrated with glass standards. Vitrinite particles were chosen for reflectance measurements without regard to apparent reflectance; reworked material is undoubtably included in the data histograms.

Extraction Procedures

Both rock and solid bitumen samples were extracted in a conventional Soxhlet apparatus (1 liter size), in cellulose thimbles (i.d. = 43 mm; length = 123 mm), with methylene chloride (500 ml) for 20-24 hours. Solid bitumen samples were very "rich" and were extracted a second time with fresh solvent. The extract was separated from methylene chloride by rotary evaporation, using a Buchler Instruments Roto-Vap, to approximately 5 ml liquid volume. The remaining solvent was removed under a stream of dry nitrogen gas. All dried extracts were refrigerated until further analysis.

Deasphalting Procedure

Each oil and extract sample was deasphalted as follows, using a procedure modified after Ebanks, et al. (1977): At least a forty-fold excess of hot n-heptane (about 70°C) was added to about 0.2-0.5 g of sample. The mixture was filtered through a one-half inch pad of Celite 503 (diatomaceous earth, commercially available from J.T. Baker Company), in a 30 ml filter crucible (medium porosity, 10-15 microns). The pad was washed with several aliquots of hot n-heptane. The resultant filtrate (nonasphaltenes) was roto-vapped to about 5 ml, and dried under nitrogen gas. The pad was then washed with methylene chloride, and the filtrate (i.e., the asphaltenes) dried as above. Oil 17 was used to check this analytical procedure for precision, with the following results: Run 1 - Asphaltenes = 2.1%; Run 2 - Asphaltenes = 2.5%.

Column Chromatography

Nonasphaltene materials were fractionated further into para-

ffinic hydrocarbons, aromatic hydrocarbons and nitrogen-, sulfur-, and oxygen containing materials (NSOs) using a procedure modified after Leythaeuser (1973). A glass column (i.d. = 11 mm; length = 650 mm) was plugged at the bottom with glass wool, and filled first with 15.0 g of silica gel (60-200 mesh), then with 5.0 g of aluminum oxide powder. Columns were wet-packed in n-pentane. The fraction elution order is as follows: paraffinic hydrocarbons (n-pentane, total eluent about 40 ml); aromatic hydrocarbons (benzene, total eluent about 30-40 ml); nitrogen-, sulfur-, and oxygen-containing compounds (1:1 methanol:chloroform, total eluent about 30-40 ml, until the column is clean). Following elution with the above solvents, the column was generally clean. This procedure was checked for reproducibility using oil 17. The results are as follows:

	Run 1	Run 2
Paraffinic Hydrocarbons	66.7%	65.7%
Aromatic Hydrocarbons	20.9%	20.7%
NSOs	10.3%	11.1%

In addition, separation efficiency was roughly checked by gas chromatographic analysis of each fraction. N-alkanes were detected in the aromatic fraction in a concentration estimated at no greater than 1% of that fraction. In addition, very minor quantities of n-alkanes were detected in some asphaltene fractions, presumably through occlusion of these molecules in the asphaltene during precipitation. This phenomenon has been observed before (Rubinstein, et al., 1979a) and was not regarded as a major problem.

Molecular Sieving

Selected paraffinic hydrocarbon fractions (and in the case of solid bitumen, nonasphaltene fractions of pyrolyzates) were treated to remove n-alkane material prior to analysis for sterane and hopane content (O'Connor, et al., 1962). The sample was dissolved in iso-octane (0.15 g or less of sample, in 15 ml of solvent). Following 24 hours of heating at 300°C, approximately 8-10 g of 5A molecular sieve was added to the solution, while still hot. This mixture was refluxed for four hours. The remaining solution, and aliquots washed with hot iso-octane from the molecular sieves, was dried under flowing nitrogen gas to remove solvent. The remaining branched and cyclic fraction (or, in the case of the bitumen pyrolyzates, the remaining non-n-alkane fraction) was then topped at 55°C for 24 hours prior to analysis for steranes and terpanes.

Kerogen Concentration

Following extraction of whole rock samples, as described above, selected samples were subjected to treatment designed to concentrate kerogen. Extracted rock material was transferred to Nalgene containers (250 ml Erlenmeyer flasks), and treated with 1.0 N hydrochloric acid repetitively, until carbonate material was removed. This was followed by treatment with 52-55% hydrofluoric acid. Flasks were heated to 40-50°C in a water bath. HF treatment continued for six days, after which time the samples were diluted with deionized water and decanted, repetitively, until the pH of the resultant liquid was greater than 5. The sample/water slurry was then transferred into 50 ml tubes and centrifuged. The water was removed, and the upper "sediment" layers, which contained the

kerogen, were transferred to vials, and brought to dryness under a stream of dry nitrogen gas. The resulting kerogen concentrate was then ground and treated again with 1.0 N HCl. The concentrates were finally sealed in glass ampules under nitrogen until elemental and isotopic analyses were made.

Visual Examination of Kerogen

Prior to sealing the kerogen concentrates under nitrogen, a small amount of each was mounted on a microscope slide, allowed to dry, and examined for pollen and spore coloration. Karen Sullivan of the Oklahoma Geological Survey assisted greatly in this aspect of the work. Color determination were made on a subjective color scale (Wilson, 1971).

Pyrolysis of Solid Bitumens -- High Temperature

All solid bitumens were pyrolyzed in a continuous mode pyrolysis unit. Samples (approximately 30 mg) were pyrolyzed under a continuous flow of helium gas, from 180°C (held for 5 minutes) to 575°C, at a ramp rate of 24.9°C per minute. Evolved volatiles were trapped in a pre-washed quarter-inch stainless steel U-tube, partially immersed in liquid nitrogen. Following pyrolysis, the tube was removed from the system and allowed to come to ambient temperature. The pyrolyzate was then flushed from the tube with methylene chloride, and dried under a flow of dry nitrogen gas.

Pyrolysis of Solid Bitumens -- Low Temperature

Selected solid bitumen samples were also pyrolyzed at relatively low temperatures for a longer period of time. Each sample was placed

in a pre-washed quarter-inch stainless steel tube, in an atmosphere of dry nitrogen gas, capped at each end with Swagelok fittings. The tube was heated in a muffle furnace at 300°C for 23-24 hours. After removal and cooling to room temperature, the tube was opened and flushed with methylene chloride and the solution filtered. The filtrate was then dried of solvent under a flow of dry nitrogen gas.

Total Organic Carbon and Total Carbonate Carbon Analyses

Samples were prepared for total organic carbon analysis by treatment with 1.0 N hydrochloric acid, followed by rinsing with distilled water. This step was repeated until all carbonate carbon was destroyed. Total carbonate carbon was determined as the difference between total carbon and total organic carbon.

A LECO WR-12 Carbon Determinator was used for all carbon analyses. Approximately 1.0 gram each of copper metal and iron chip was used as accelerator; the burn lasted 70 seconds. Optimum sample size was 0.2 grams. 1.0 gram ring standards provided by LECO were used as carbon standards. A dust trap was used downstream from the induction furnace; the "duck cloth" filter was changed frequently. Precision for all analyses was ± 2%.

Carbon Isotope Ratio Analysis

Approximately 0.2-0.4 g of rock or 2-4 mg of oil, solid bitumen or rock extract was combusted to obtain carbon dioxide for mass spectrometric analysis. All samples were combusted in a conventional Craig Line (Craig, 1953, 1957), at 950°C, scrubbed of water by cycling through a dry ice-methanol trap, and treated to reduce the oxides of nitrogen. Carbon dioxide was analysed immediately after preparation.

Isotopic analyses for carbon were conducted on a Vacuum Generators Micromass 602C isotope ratio mass spectrometer. All analyses were made relative to petroleum standard NBS 22, conventionally taken to have a value of -29.4 °/oo, relative to the Chicago PDB standard (0.0 °/oo). Results are reported relative to PDB, following the usual corrections, including that specified by Craig (1957) to compensate for the isotope ratio of the working standard (in this case, NBS 22).

It should be noted that there apparently exists a controversy concerning the isotope ratio of NBS 22 relative to PDB. It has been recently suggested that NBS 22 has a value of -29.8 to -29.7 °/oo, rather than the usually-assumed -29.4 °/oo (Fuex, 1981, personal communication). Yeh and Epstein (1981), in 23 replicate analyses, obtained a value of -29.9 °/oo for this standard. In any case, for comparison purposes, as used in this study, this change is not a major concern. All values presented can be corrected to the "true" isotope value by subtracting approximately 0.4 °/oo from all reported values.

Metal Analysis

Crude oils, asphaltenes, rock extracts and solid bitumens were analyzed for vanadium (V) and nickel (Ni) by flameless atomic absorption. All samples except solid bitumens were run in xylene solution (isomeric mixture unknown). All solid bitumens were run as solutions of carbon disulfide. Particulate matter was filtered before analysis, when necessary.

Crude oils were analyzed for vanadium and nickel content on a Perkin-Elmer Atomic Absorption Spectrophotometer, Model 305B, equipped with a Perkin-Elmer Graphite Furnace, Model HGA-2200. Deuterium arc

background correction was used for both elements (although it was necessary to reduce the amperage to the vanadium lamp from 40 ma to 27 ma, in order to allow usage of the background corrector). Vanadium was analyzed at the 318.4 nm absorption line, on a single-element hollow cathode lamp; nickel was analyzed at the 232.0 nm absorption line, on a multi-element lamp (Co, Cr, Cu, Ni and Mn). The lamps were manufactured by Perkin-Elmer. Temperature-controlled maximum power heating was used for both elements. Argon was the purge gas for the graphite assembly, while air was used as a purge for the deuterium arc assembly, to prevent ozone buildup on the optical system. The purge of argon was reduced for 3 seconds during the initiation of atomization, in order to increase atomic lifetime in the graphite tube.

Cycling temperatures and times for vanadium and nickel were:

	V	Ni
Drying temperature	200°C	200°C
Drying time	40 s	50 s
Charring temperature	1300°C	1000°C
Charring time	100 s	30 s
Atomization temperature	2800°C	2700°C
Atomization time	15 s	15 s
Slit setting	0.7 nm	0.2 nm
Source amperage	27 ma	30 ma

In all runs, a drying peak of about 0.015 absorption units was noted during vanadium analysis. Conostan organometallic standards were used to construct working curves for each element in specific solvents (i.e., xylene or carbon disulfide). These curves had correlation coefficients (r^2) of 0.99+ (xylene) and 0.98+ (carbon disulfide).

Samples of 10 microliters were injected into the graphite tube,

using an Eppendorf pipette and Curtin Matheson Scientific, Inc. Disposable Pipet Tips (orange). These Pipet Tips were found to "bleed" nickel when in contact with xylene for more than two injections. Consequently, only one injection was made per Pipet Tip, which was then discarded. No such bleeding was evident for vanadium, or for carbon disulfide solutions.

Infrared Spectrometry

A Beckman 4210 Infrared Spectophotometer was used for all IR work. The unit has resolution of 1.5 cm^{-1} at 2400 cm^{-1}, and 0.5 cm^{-1} at 1000 cm^{-1}. Abscissa expansion (0.4X) was used throughout, and all scans were made at 300 cm^{-1} per minute. Aromatic and asphaltene fractions were run as solid films, from evaporation of n-pentane and methylene chloride, respectively, on sodium chloride plates. All scans are linear in wavenumber, with a change of scale at 2000 cm^{-1}.

Gas Chromatography

All gas chromatographic analyses conducted in this study were done on either a Hewlett-Packard 5830A or 5840A instrument. All analyses were made on a 25 meter fused silica SP 2100 capillary column. Injection was in the split mode (approximately 77:1 split was used for all correlation exercises). No attempt was made to correct for split discrimination. Column flow was about 1.25 cc/minute, helium. Standards for co-injection were obtained through various commercial service companies. Oven temperature and other zone temperature conditions are given in the captions to the relevant figures.

Gas Chromatography-Mass Spectrometry

Samples were run in solution of n-pentane, on a 30 meter X 0.25 mm (i.d.) fused silica capillary column, coated with J & W Durabond DB-5 (SE-54 equivalent) phase. GC conditions: 40°C (isothermal for 1 minute), ramped at 12°C per minute to 150°C (held 0 minutes), ramped at 8°C per minute to 310°C (held until the homohopanes eluted). Column flow rate (linear) = 24 cm/second, helium. Zone temperatures: Injector (purged-splitless) = 250°C; interface oven = 250°C; manifold = 84°C.

The instrument used was a Finnigan 4000 GCMS, linked to an INCOS 2400 (Nova 3) data system. The end of the analytical column was directly connected to the ion source, which was at a temperature of approximately 250°C. Ionization voltage was 70 eV; scans were taken from 35 to 450 amu every 2 seconds. Spectra were acquired at an electron emission of 300 micro-amps, at a preamp sensitivity of 10^{-7} amp/volt, using an electron multiplier voltage of -1900 volts. A total of 750 scans were acquired, and stored on disc. All information was eventually transferred to tape for permanent storage.

Elemental Analysis, Sulfur Isotope Analysis, and Sulfur Determinations

All carbon, hydrogen, oxygen and nitrogen, and some sulfur analyses were done by Micro-Analysis, Inc., Wilmington, Delaware. Most sulfur determinations and all sulfur isotope analyses were conducted by the Mobil Field Research Laboratory, at the direction of Dr. Wilson Orr. The author is indebted to Dr. Orr for these analyses.

Appendix III

List of Sample Locations and Types

Table 16. 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	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	Atoka	T1N-R15E Sec. 8	Stanley Group	Received from Chevron USA, Inc. From Frank Sellmeyer #1 Loman well.

Appendix III

List of Sample Locations and Types

Table 17. 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[a]	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[a]	Arkansas Novaculite (6500-9200 ft); Bigfork (9900-11100 ft)	Oklahoma Geological Survey, Norman, OK

[a] See Appendix IV.

Appendix III

List of Sample Locations and Types

Table 18. Rock Samples (Outcrop)[a]

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)	---

[a] Collected in November, 1977, by Robert O. Fay and William D. Pitt.

APPENDIX IV

DENTON PERRIN FORMATION TOPS

Samples from the Denton Perrin Well (Sample Numbers 31 and 40) were used in this study. This well, located in Pushmataha County, Oklahoma, at T2S R15E Section 9 (SE SW), was completed first in 1957 by Southwest Exploration Company, as a D & A (dry and abandoned) hole with a TD (total depth) of 11,328 feet. The well was logged to 11,135 feet. In 1978, this well was worked over (OWWO) and completed as a gas well, producing from the Arkansas Novaculite and Bigfork Formations. Originally, formation tops were published by Chenoweth (1959) based on electric logs. The report filed with the Corporation Commission of the State of Oklahoma is consistent with the tops called by Chenoweth (1959). However, the formation tops as called by those who reworked the well in 1978 are significantly different from those reported by Chenoweth (1959), as noted by Morrison (1980a). The new "scout ticket" for the 1978 OWWO lists these "new" formation tops. The discrepancies are noted below:

Stratigraphic Interval	Chenoweth (1959) tops (feet)	Morrison (1980a) tops (feet)
Stanley	surface	surface
Arkansas Novaculite	6,400	6,458
Missouri Mountain	9,200	6,955
Polk Creek	9,550	7,155
Bigfork	9,820	7,456

Stratigraphic Interval	Chenoweth (1959) tops (feet)	Morrison (1980a) tops (feet)
Fault	10,780	--
Bigfork	10,780	--
Womble	--	9,015
Fault	--	9,020
Stanley	--	9,020
mid-Simpson	--	9,963
Arkansas Novaculite	--	10,972
TD	11,328	11,328

Several samples from this well were used in this study (Table 8). These are either from the Arkansas Novaculite, Missouri Mountain, Polk Creek and Bigfork Formations (according to Chenoweth, 1959), or from the Stanley, Polk Creek, Bigfork and Simpson Formations (according to Morrison, 1980a, and the scout ticket for the reworked well). The discrepancy between these two sources is shown diagramatically in Figure 71, and results from variation in the thickness of the Arkansas Novaculite Formation. The Chenoweth (1959) interpretation has been used throughout this study, for the following reasons: (1) The Chenoweth (1959) interpretation was derived only two years after the well was drilled, while that from the scout ticket source was derived over twenty years after drilling was completed. (2) The Arkansas Novaculite is anomalously thin in the scout ticket interpretation (see Figure 71 and Table 1). Chenoweth (1959) reports that very steep dips are encountered in this area (up to 75 degrees). This suggests that the thin Arkansas Novaculite section as noted in the scout ticket is in error. (3) The new interpretation places a Simpson wedge between the Stanley on top and the Arkansas Novaculite below (see above). However, no fault boundary is noted above or below the Simpson. Further, such an interpretation is somewhat unlikely, given that the Simpson is Ordo-

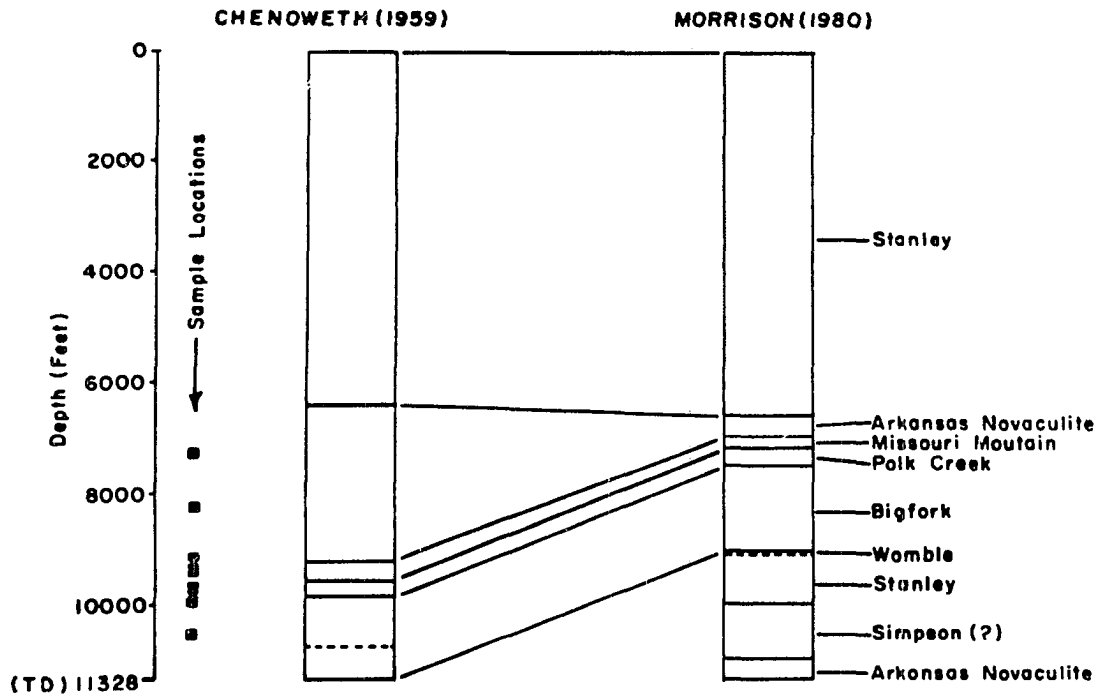


Figure 71. Denton Perrin Well Formation Tops. Discrepancies between two authors are as noted, and discussed in text.

vician and the Stanley is Mississippian. (4) The Corporation Commission report for this well is more consistent with the Chenoweth (1959) interpretation than with the OWWO data. Finally, formation tops as used in this study are subject to the usual errors associated with rotary samples. It remains for the reader to determine whether the geochemical data fit one interpretation better than another.

Appendix V

Miscellaneous Data Tables

Table 19. Oil N-Alkane and Isoprenoid Data

N-Alkane Number	Percentage of C_{15} to C_{33} Range			
	11 (S. Bald)	15 (Bald)	17 (Redden)	45 (N. Daisy)[a]
15	14.0	12.4	13.4	14.3
16	11.8	11.2	11.0	11.7
17	11.4	10.3	11.2	11.3
18	8.8	9.1	8.6	9.3
19	8.9	8.1	8.9	8.6
20	7.0	6.9	7.0	7.6
21	6.1	5.8	6.3	7.1
22	5.3	5.3	5.5	6.4
23	4.7	4.9	5.0	5.6
24	4.1	4.4	4.2	4.5
25	3.4	4.0	3.5	4.1
26	3.0	3.6	3.2	3.0
27	2.6	3.1	2.0	2.2
28	2.4	2.7	2.5	1.7
29	2.0	2.1	2.1	1.2
30	1.3	1.6	1.5	0.7
31	1.5	1.7	1.5	0.5
32	1.0	1.4	1.0	0.3
33	0.6	1.3	0.6	0.2
Isoprenoid Number	Percentage of C_{15} to C_{20} Range			
15	16.5	16.1	16.9	14.3
16	26.9	23.4	25.3	26.5
18	19.2	19.2	19.6	22.6
19	21.7	24.4	22.7	21.3
20	15.7	16.9	15.6	15.3

[a] Peak heights for n-alkanes and isoprenoid isoalkanes of oil 45 were measured; otherwise, figures given are for integrated areas. The depression of the high-carbon-number portion of the n-alkane distribution for oil 45 (Figure 11) results from peak height reduction due to peak broadening at high temperatures.

Appendix V

Miscellaneous Data Tables

Table 20. High-Temperature Pyrolyzate (Quasi-)N-Alkane Data

Carbon Number[a]	Sample Number (%)							
	3	5	6	7	8	21	44	Gilsonite
15	8.6	10.1	12.3	6.6	12.1	11.3	8.3	6.7
16	14.6	15.9	14.9	10.8	15.6	12.4	11.5	10.6
17	13.0	12.3	13.4	10.8	14.0	10.8	10.5	11.8
18	9.6	8.8	10.1	10.8	10.1	9.4	9.1	6.7
19	8.6	6.2	8.6	11.2	8.6	8.7	8.0	7.3
20	7.5	6.1	7.0	9.0	7.7	7.6	13.0	7.7
21	7.0	5.3	6.4	8.6	7.3	6.3	6.9	4.8
22	5.6	5.3	5.2	7.2	5.2	6.1	6.5	5.2
23	4.9	5.2	4.3	5.3	4.5	5.6	5.3	4.9
24	4.7	4.3	4.2	4.4	3.2	4.5	4.3	8.7
25	5.6	4.5	3.5	4.0	2.7	5.5	4.3	8.1
26	3.9	3.7	2.6	3.4	2.4	3.2	4.0	6.4
27	2.4	3.3	2.4	1.9	1.8	2.6	2.6	3.9
28	1.5	2.8	1.7	1.9	1.5	2.0	2.4	2.9
29	1.2	2.7	1.5	1.7	1.5	1.6	1.2	1.8
30	0.9	1.8	1.1	1.2	1.0	1.5	1.0	1.2
31	0.7	1.5	0.9	1.0	0.9	1.0	0.7	1.3

[a] Each number is the sum of the integrated area for the alpha-olefin and n-alkane for that carbon number. See text for details.

Appendix V

Miscellaneous Data Tables

Table 21. Extractable Organic Matter N-Alkane and Isoprenoid Data

Sample Number	N-Alkanes[a]																			Isoprenoids[b]	
	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	19	20
24-3600-3700	5.9	8.0	9.1	6.5	6.2	5.4	5.3	6.0	7.0	6.9	6.2	6.0	5.0	4.2	3.8	3.1	2.6	1.7	1.2	59.2	40.8
24-4140-4320	6.8	7.2	7.8	6.1	5.8	9.2	24.0	4.5	4.2	3.8	4.6	2.8	2.2	4.9	1.9	1.5	1.2	0.9	0.6	56.2	43.8
25-3390-3445	3.3	5.4	8.7	8.5	9.7	8.1	11.1	6.4	6.1	5.5	5.0	4.7	4.0	3.4	3.1	2.7	1.9	1.4	1.0	50.8	49.2
25-4000-4050	2.9	5.9	10.3	10.4	11.7	10.3	9.1	8.2	7.0	5.6	5.3	4.0	2.8	2.3	1.9	0.8	1.0	-	-	51.9	48.1
26-510-600	2.5	3.9	4.5	3.0	2.7	2.7	3.7	5.8	7.7	8.5	9.1	8.5	8.0	7.4	7.2	5.8	4.5	2.7	1.6	58.9	41.1
26-801-843	0.8	1.4	3.1	3.8	6.1	6.3	7.6	9.8	10.4	9.8	9.9	7.0	5.7	4.7	4.5	3.2	2.7	1.9	1.4	40.3	59.7
OCS GCN 25	1.2	1.6	2.3	1.7	1.8	1.9	2.9	5.0	6.9	8.9	9.8	9.7	9.8	9.2	8.9	7.3	5.4	3.4	2.2	56.5	43.5
OCS GCN 31	-	-	-	-	-	0.7	2.0	4.3	6.8	8.5	11.0	10.3	10.8	10.7	10.8	10.0	7.1	4.3	2.9	--	--
40-7200-7300	6.1	9.6	13.0	10.3	9.9	8.8	11.8	12.4	8.0	3.8	2.6	1.4	1.0	0.8	0.6	-	-	-	-	58.5	41.5
40-8200-8300	1.9	4.1	7.9	8.8	10.3	10.6	13.8	14.8	9.9	5.5	4.3	2.8	1.8	1.5	1.4	1.2	0.9	0.4	-	46.7	53.3
40-9100-9200	6.0	9.0	11.3	7.0	5.4	4.3	8.4	16.1	12.6	6.3	3.3	2.4	2.0	1.8	1.7	1.4	0.9	-	-	59.3	40.7
29-850-900	5.3	8.0	12.1	8.8	8.6	7.4	7.5	7.9	6.5	5.1	4.4	3.8	3.6	3.1	3.2	2.3	2.2	1.6	1.2	53.5	46.5
31-9240-9295	10.5	15.9	22.8	11.6	8.7	5.0	3.9	4.1	4.0	3.6	3.3	2.5	1.9	1.4	0.8	-	-	-	-	63.7	36.3
31-9415-9465	2.8	7.7	15.6	13.1	11.4	7.7	6.3	6.5	6.4	5.8	6.5	4.2	2.7	1.8	1.0	0.3	-	-	-	52.4	47.6
31-9615-9665	4.2	7.1	12.0	10.2	10.0	7.6	6.5	7.0	6.7	5.5	7.8	4.4	3.7	2.9	2.4	1.4	0.8	-	-	51.7	48.3
31-9715-9765	2.4	4.3	7.4	5.4	4.7	3.8	4.5	6.1	7.4	7.4	8.2	7.5	6.9	6.3	5.9	4.6	3.6	2.3	1.2	56.0	44.0
OCS GCN 30	13.9	11.7	11.9	8.9	7.3	6.0	4.9	4.5	4.5	4.3	4.2	3.6	3.4	3.0	2.7	1.0	1.8	1.0	0.6	55.9	44.1
40-9900-10000	5.6	8.4	11.2	8.6	8.3	5.7	9.2	16.7	12.4	6.3	2.9	1.5	1.0	0.8	0.7	0.4	0.2	-	-	56.7	43.3
40-10500-10600	2.7	5.9	10.0	8.8	8.2	6.2	12.0	20.0	13.6	6.0	2.3	1.2	0.9	0.6	0.6	0.3	-	-	-	55.3	44.7
OCS GCN 22	1.0	1.4	2.3	2.0	1.7	1.8	2.4	4.3	6.0	8.6	9.5	9.0	9.1	9.2	9.7	8.2	6.7	4.6	2.8	53.2	46.8
25-9900-10000	7.9	9.6	11.9	8.4	7.4	4.3	3.4	3.9	4.5	5.1	5.3	4.6	4.5	4.2	4.3	3.6	3.1	2.3	1.7	62.8	37.2
25-10400-10500	12.7	15.3	12.9	13.1	10.6	7.0	4.7	4.0	4.0	3.1	4.4	2.1	1.7	1.4	1.3	0.9	0.7	-	-	60.4	39.6
28-1640-1695	7.8	8.6	9.9	7.8	7.2	6.4	5.7	5.6	5.8	5.4	5.3	4.4	4.2	4.0	3.5	2.7	2.5	1.8	1.3	61.3	38.7
28-1695-1750	9.7	10.8	12.0	9.6	9.3	7.5	6.4	5.6	5.1	4.5	4.0	3.2	3.0	2.6	2.1	1.5	1.4	1.1	0.8	57.1	42.9
28-1750-1800	8.4	11.2	12.7	9.7	9.1	7.4	6.4	5.7	5.1	4.2	4.4	3.1	2.7	2.4	2.1	2.0	1.5	1.2	0.9	58.8	41.2
28-1800-1860	7.7	9.4	10.8	9.0	8.5	7.5	6.7	5.9	5.2	4.8	4.3	3.7	3.2	3.4	2.8	2.1	2.0	1.5	1.4	58.0	42.0

[a] Each n-alkane as a percentage of all n-alkanes from C_{15} to C_n.

[b] Each isoprenoid as a percentage of the isoprenoids i-C_{19} + i-C_{20} (i.e., pristane and phytane).

Appendix V

Miscellaneous Data Tables

Table 22. Distribution of Steranes by Carbon Number (Data)

Sample Type	Sample Number	Carbon Number of Sterane (%)[a]		
		27 (m/e 372)	28 (m/e 386)	29 (m/e 400)
OILS	11	36.4	16.0	47.6
	15	40.9	11.8	47.3
	17	34.2	14.2	51.7
	45	36.2	22.8	41.0
PYROLYZATES	3	39.5	9.1	51.4
	5	51.7	12.7	35.6
	6	38.0	3.9	58.2
	7	51.7	14.2	34.1
	44	38.4	17.8	43.8
ROCK EXTRACTS	24-4140-4320	59.8	9.1	31.1
	25-3390-3445	44.9	13.9	41.2
	40-7200-7300	56.7	15.7	27.5
	40-8200-8300	46.6	10.7	42.7
	29-850-900	55.7	13.0	31.3
	31-9415-9465	66.8	11.5	21.6
	31-9615-1665	31.7	15.8	52.5
	OGS GCN 30	34.9	18.5	46.6
	40-9900-10000	56.8	17.3	25.9
	40-10500-10600	49.1	12.0	39.0
	28-1695-1750	43.8	17.2	39.0
	28-1750-1800	54.7	16.6	28.7

[a] Calculated by integration of particular m/e ion chromatograms over the region of sterane elution.

APPENDIX VI.

Depiction of Northward-Thrusting of Ouachita Rocks

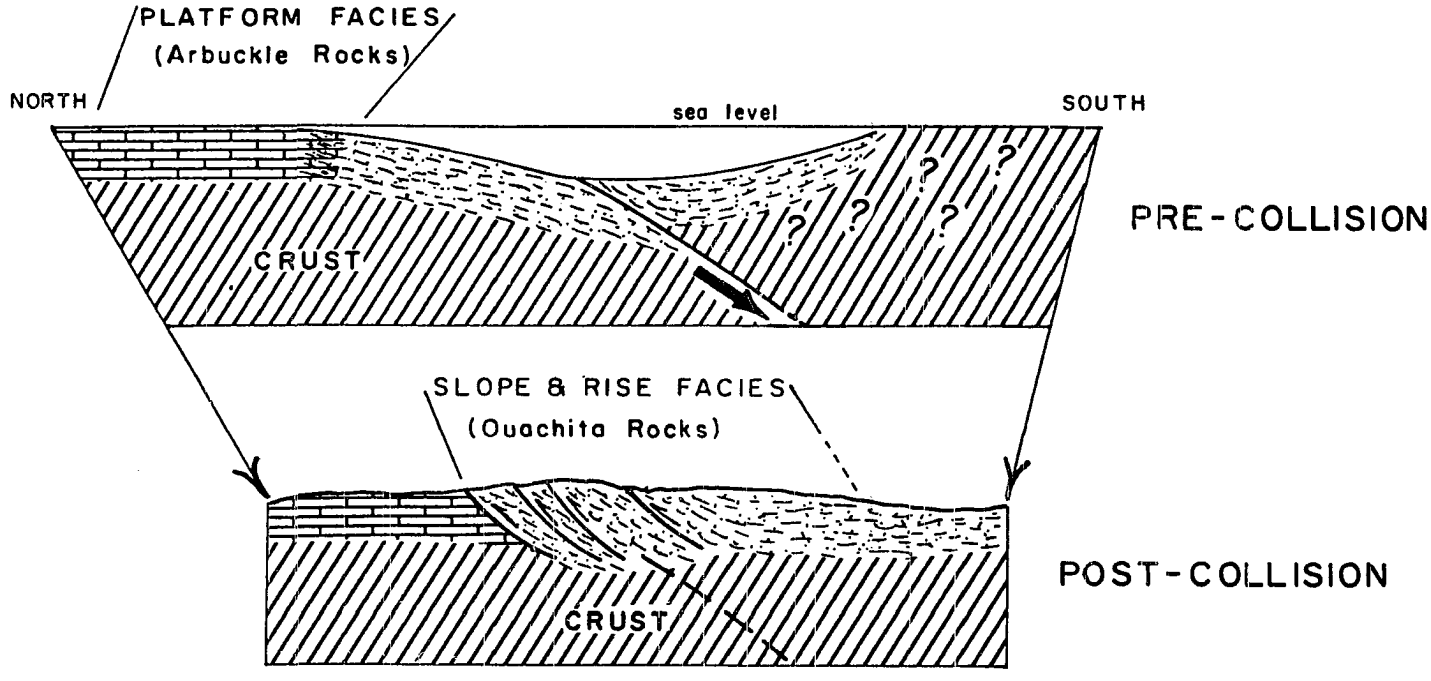


Figure 72. Diagram depicting Thrusting of Ouachita Rocks (slope/rise) over Arbuckle Rocks (platform). After Wickham, et al. (1976).