

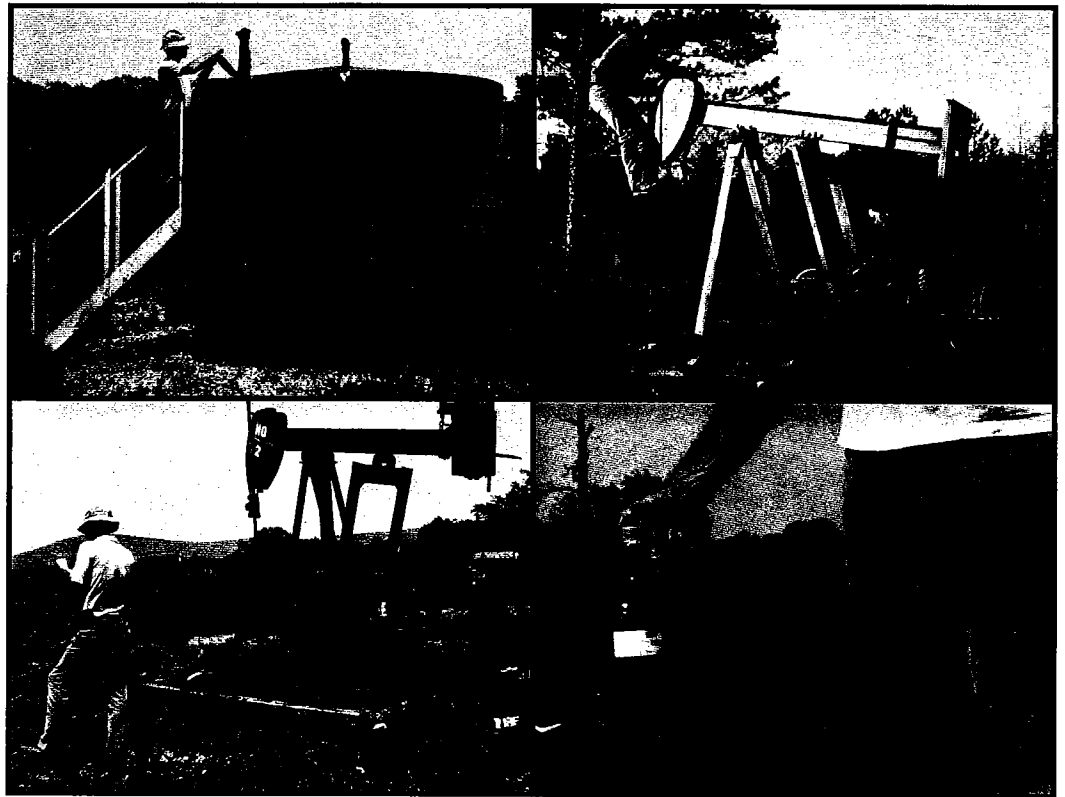


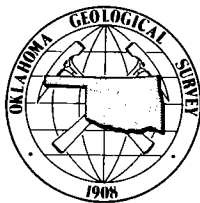
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A Geochemical Study of Crude Oils and Possible Source Rocks in the Ouachita Tectonic Province and Nearby Areas, Southeast Oklahoma

Jane L. Weber





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Southeast Oklahoma**

Jane L. Weber

Oklahoma Geological Survey

Charles J. Mankin, *Director*

The University of Oklahoma

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SPECIAL PUBLICATION SERIES

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Front Cover

Collecting oils in the Ouachita Mountains was a memorable experience. These four photographs capture some of the activities involved. *Upper left:* Anything in there? Jock Campbell (OGS geologist) checks out a stock tank near the Rowland Bledsoe 1 well in Bald S field. *Upper right:* Pump motor not working? No need to worry. A "two-manpower engine" (OGS geologist Neil Suneson on the rod and Jock Campbell at the wheel) operates the pumpjack at the Warren 1 well in eastern Latimer County. *Lower left:* Don't forget the paper work. Standing next to the pumpjack at Four North 1 in Bald S field, Jock Campbell records location notes. *Lower right:* Mission accomplished! The hand of Neil Suneson holds a properly labeled bottle of oil just taken from the Harvey Harmon 2 stock tank in Idabel W field.

Photos by Jane Weber

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CONTENTS

ABSTRACT	1
INTRODUCTION	1
SAMPLE COLLECTION	3
Oils	3
Rocks	5
ANALYTICAL PROCEDURES	5
Whole-Rock Treatment	5
Fractionation of Oils and Extracts	7
Gas Chromatography	7
Gas Chromatography–Mass Spectrometry	7
Other Procedures	7
ORGANIC GEOCHEMISTRY	8
Crude Oils	8
Source Rocks	15
DISCUSSION	20
Oils	20
Rocks	23
Correlations	26
CONCLUSIONS	29
ACKNOWLEDGMENTS	30
REFERENCES CITED	30

ILLUSTRATIONS

Figures

1. Study area of Ouachita tectonic belt	2
2. Generalized stratigraphic column of the Ouachita Mountains	6
3. Representative gas chromatograms of saturate fraction of Ouachita-area oils	10
4. Distribution of isoprenoids in Ouachita-area oils	14
5. Representative <i>m/z</i> 191 mass chromatograms for Ouachita-area oils	16
6. Normalized percent of tricyclic terpanes in Ouachita-area oils	17
7. Mass chromatograms showing similarity of sterane distributions in Ouachita-area oils	19
8. Typical distributions of monoaromatic steranes in Ouachita-area oils	21
9. Typical distributions of triaromatic steranes in Ouachita-area oils	22
10. Example gas chromatograms of saturate fraction from Ouachita rock extracts	22
11. Mass chromatograms showing terpane distributions in Ouachita rock extracts	23
12. Representative <i>m/z</i> 217 mass chromatograms for Ouachita rock extracts	24
13. Selected <i>m/z</i> 253 mass chromatograms for Ouachita rock extracts	24
14. Crossplots of geochemical data showing relations among oils	27

Tables

1. Identification and location of crude oil samples	4
2. Location of rock samples and gross chemical data for rocks and extracts	5
3. Bulk properties of oils	9
4. Geochemical data for oils	12
5. Geochemical data for rock extracts	18
6. Identification of terpanes and steranes	20
7. Chemical characteristics of Ouachita tectonic belt oils	28

A Geochemical Study of Crude Oils and Possible Source Rocks in the Ouachita Tectonic Province and Nearby Areas, Southeast Oklahoma

Jane L. Weber

ABSTRACT.—Thirty oils from the Oklahoma part of the Ouachita tectonic belt plus 15 oils from adjacent areas were characterized to determine their genetic relations. All tectonic belt oils in Oklahoma, including those from Isom Springs, belong to one major family; an oil from north of the trace of the Ti Valley fault belongs to a subtype. The oils are predominantly marine and moderately mature to mature; their source rock was deposited in a mildly reducing environment. Geochemical features of these oils are: *n*-alkane maximum at C₁₅ or C₁₇; moderate amount of isoprenoids; pristane/phytane ratio close to 1.5; an odd-even carbon-number preference close to unity; abundant C₂₇ and C₂₉ steranes and diasteranes; C₃₀ greater than C₂₉ hopane; moderately abundant homohopanes; prominent tricyclic terpanes; carbon-isotope (saturate) values around -30‰; sulfur content averaging 0.4%; and the presence of 28,30-bisnorhopanes (tentative identification).

Oils found in Cretaceous strata immediately south of the Ouachita Mountains are mildly biodegraded and exhibit characteristics associated with a carbonate-evaporite origin. They are chemically similar to Talco, Texas, oil and are probably additional examples of Sassen's (1989) Type I migrated (Jurassic) Smackover oil.

Some Ardmore basin oils adjacent to the buried Ouachita tectonic belt are geochemically similar to the tectonic belt oils. The significance of this finding warrants a new, interdisciplinary attempt to explain the petroleum system(s) of the Ouachita tectonic belt.

Twenty-five shale samples and one tar sand from outcrops in the Ouachita Mountains were also examined. Of eight stratigraphic intervals tested, the Caney, Woodford, Arkansas Novaculite, and Polk Creek show evidence of having good hydrocarbon-source potential. Maturity levels range from immature to mature, following no discernible geographic, stratigraphic, or structural pattern; none of the rocks with good potential is mature enough to have served as a source for Ouachita oils. However, biomarker distributions of some of the rocks resemble those of the oils, suggesting that where more deeply buried, those formations—representing both foreland and Ouachita facies—merit consideration as possible sources for Ouachita oils. Insufficient data were generated to conclude whether a Stanley tar-sand bitumen correlates with oils from nearby wells.

INTRODUCTION

The Ouachita tectonic province extends from Alabama to northern Mexico. Although mostly buried, it has two surface exposures—the Ouachita Mountains in west-central Arkansas and southeastern Oklahoma and the Marathon Mountains in West Texas. This study deals only with that part of the province located in Oklahoma. Throughout this paper the terms “Ouachita tectonic belt,” “Ouachita Mountains,” and “Ouachitas” are limited in reference to that part of each entity located in southeastern Oklahoma.

In the Ouachita Mountains, oil is found mostly in small, shallow pools in the “central oil belt” (Suneson and

Campbell, 1990), which closely follows the trace of the Windingstair fault (Fig. 1). At some locations, gas is also produced from deeper traps. Most oil production is from the Mississippian Stanley Group. Farther to the southwest, near the edge of the Cretaceous overlap, hydrocarbons have been produced from the Devonian Arkansas Novaculite (oil and gas), Ordovician Bigfork Chert (oil and gas), and Pennsylvanian Wapanucka Limestone (gas). The Wapanucka also produces gas north and northeast of the shallow oil pools. South of the Broken Bow uplift, oil is found at shallow depths in Cretaceous strata. At the extreme southwest end of the buried part of the Ouachita tectonic belt, near the Isom

Springs field, most oil is produced from the Arkansas Novaculite at a depth of several thousand feet. Some oil, however, is in sandstone reservoirs above the novaculite (e.g., Mississippian [Stanley] and Cretaceous).

Ordovician to Lower Pennsylvanian (pre-Atoka Formation) strata exposed in and beneath the Ouachita Mountains comprise two groups. “Foreland facies” strata are characterized by fossiliferous shales, sandstones, and limestones deposited on the shallow-water shelf of the southern margin of the North American plate. The upper part of this sequence is locally exposed at the base of thrust sheets along the northern margin of the Ouachita tectonic belt;

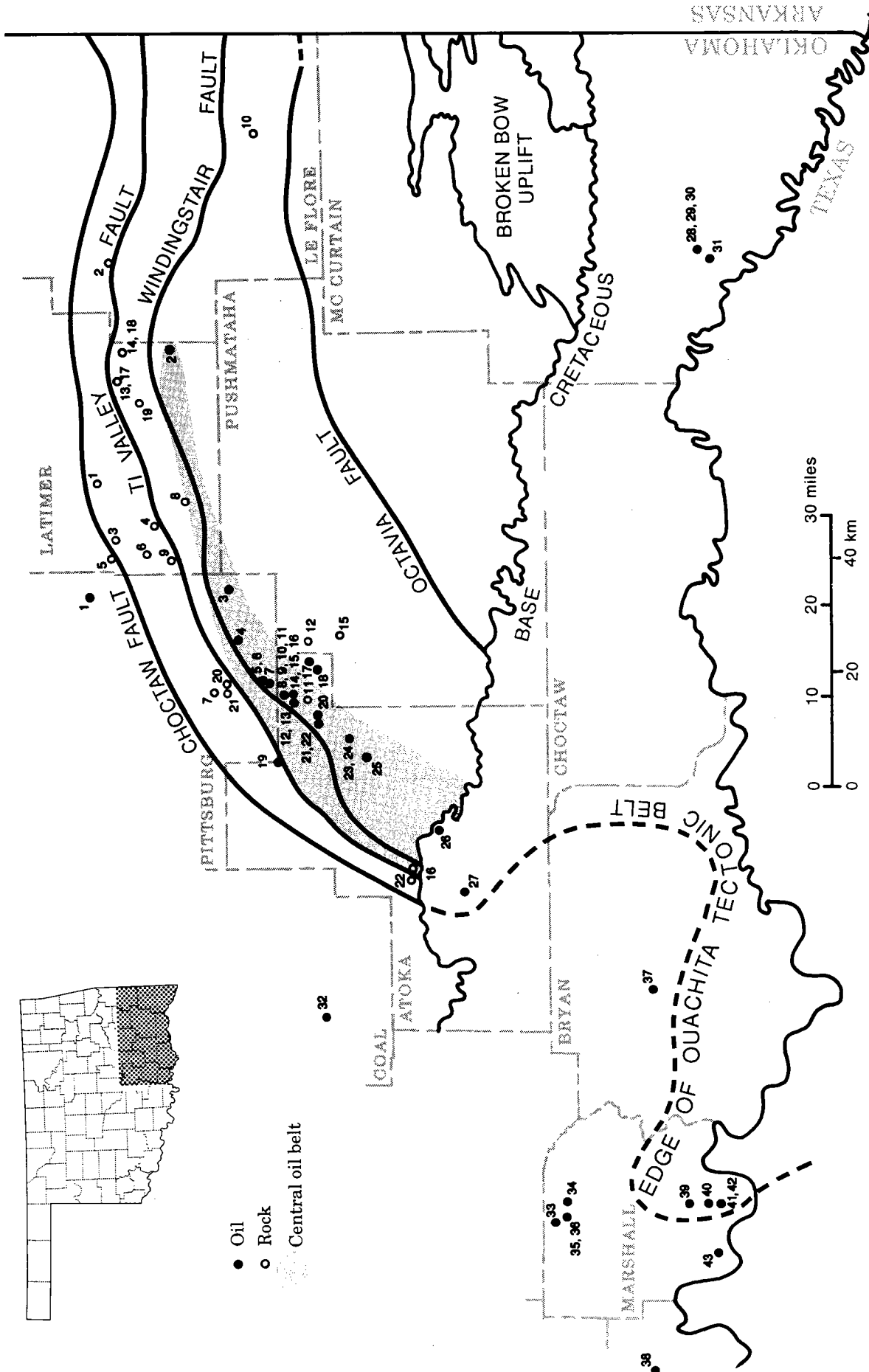


Figure 1. Study area of Ouachita tectonic belt in southeastern Oklahoma showing geographic distribution of crude oil and outcrop samples (see Tables 1 and 2 for location and identification). Location of buried thrust front is from Hardie (1990); central oil belt is from Suneson and Campbell (1990). Texas oil samples 44 and 45 not shown.

the sequence also underlies most, if not all, of the exposed part of the Ouachitas (Leander and Legg, 1988; Suneson and Campbell, 1990). The implication of such a structural arrangement is that potential foreland-facies source rocks extend beneath the Ouachitas. "Ouachita facies" strata represent the deep-water equivalent (mostly shale) deposited south of the continental margin. The Middle Pennsylvanian Ouachita orogeny juxtaposed the dissimilar facies along a series of north-directed thrust faults and a basal subhorizontal décollement. The autochthonous, sub-thrust location of the facies transition is unknown. Historically, the allochthonous position has been considered to be the Ti Valley fault (Hendricks, 1959).

Several workers have attempted to explain the origin and accumulation of oils in the Ouachita tectonic belt. In general, geologists have tended to approach the problem by mentally synthesizing regional geologic relations, whereas geochemists have tended to develop and utilize site-specific data on oils and rocks to arrive at their interpretations. Both approaches contribute to an understanding of the problem.

For example, Morrison (1980) suggested that the Arkansas Novaculite is its own source rock where it is productive in the Isom Springs field. He indicated that the fracturing commonly associated with overthrust belts created the necessary permeability for this rock to release its hydrocarbons. Zemmels and others (1985), who studied the geochemistry of both Devonian novaculite and Isom Springs oils, supported a Devonian source for these oils. On the basis of the geochemistry of four oils, 11 outcrop samples, and cuttings from 10 wells between the Octavia and Windingstair faults in the central part of the Ouachita Mountains, Curiale (1983) concluded that the most probable source for oils and solid bitumens in that region is Ordovician to Silurian. He identified the Missouri Mountain, Polk Creek, and Womble Shales as possessing characteristics that are the same as or similar to those of the oils. In contrast, Chenoweth (1985, 1989) favored foreland-facies strata in the southern Oklahoma aulacogen as a

source for Ouachita oil. He based his hypothesis on the observation that hydrocarbon distribution along the entire length of the tectonic belt is uneven, with high concentrations localized near aulacogens in southern Oklahoma and West Texas. Curiale (1983, 1992) and Chenoweth (1989) also briefly mentioned that (autochthonous) foreland-facies strata beneath exposed Ouachita-facies rocks are a possible but speculative source for Ouachita oils. Finally, because Stanley Group sandstones typically serve as regional reservoirs, Stanley Group shales may be viewed as possible Ouachita oil source rocks. However, these rocks are thought to contain mostly gas-generating type III kerogen (Curiale, 1983; Houseknecht and Matthews, 1985).

In 1986, the Oklahoma Geological Survey began a long-term review of the geology and resources of a region encompassing the northern Ouachita Mountains, including a systematic examination of oils and possible petroleum source rocks. As sample evaluation progressed, oils from the same structural trend farther to the southwest in Marshall County were added to the study, as were oils from several areas adjacent to either the exposed or buried Ouachita tectonic belt. The rationale was that if oils collected within the tectonic belt are similar to one another but different from oils outside the belt, such knowledge would advance the understanding of the Ouachita tectonic province. Of particular interest was whether oils south of the Broken Bow uplift have the same (or similar) source as Ouachita oils.

The primary objective of this study was to determine the genetic relations among oils within the Ouachita tectonic belt and the relations between those oils and some oils adjacent to the belt, especially the oils south of the Broken Bow uplift. A secondary objective was to determine whether possible source rocks collected in the Ouachitas (or their more deeply buried equivalents) are the source for the oils. Finally, bitumen from a tar sand was investigated to evaluate whether it matches nearby oils. Comparison of the oils with one another and with the rock extracts has been achieved by examining distributions of their

biomarker compounds: *n*-alkanes and isoprenoids obtained from gas chromatography (GC) and steranes and terpanes obtained from coupled gas chromatography-mass spectrometry (GC-MS). Other chemical data that helped to characterize the oils and extracts are also presented and discussed.

SAMPLE COLLECTION

The geographic distribution of oil and rock samples is shown in Figure 1 and described in Tables 1 and 2.

Oils

I sampled seven of nine oil fields recognized by the Nomenclature Committee of the Mid-Continent Oil and Gas Association (Burchfield, 1985) as being in the Ouachita Mountains. One field not sampled (Potapo Creek) has been under the waters of McGee Creek Reservoir since 1985; the other unsampled field (Limestone Gap) is abandoned. Oils were also collected from four unnamed pools and one well located in a gas field at the southwestern edge of the Ouachita Mountains, giving a total of 26 crude oils collected from the Ouachitas. These oils plus four more from the Isom Springs field comprise the Ouachita tectonic belt (OTB) sample set. In addition, 15 other oils, primarily from areas to the west and south of the Ouachita Mountains, were included. The complete sample set includes two pairs of duplicates: oils 28 and 29 collected two years apart from the Harvey Harmon 2 well in Idabel W field and oils 41 and 42 collected nine months apart from the Victor 1 well at Isom Springs.

Most oil wells in the Ouachitas are stripper wells (≤ 10 bbl/day) that are pumped intermittently. In recent years, the unprofitability of this type operation has led to many of the sampled wells being abandoned as producers. Consequently, samples were obtained from a variety of sources in whatever way proved feasible: supplied by operator, pumper, or well owner; taken from stock tank, flowline, or wellhead; baled from open-pipe hole; or, in one case (East Texas field), purchased from a museum. In at least two instances in Bald S field, sampled stock tanks contain oil commingled from two wells.

TABLE 1. — IDENTIFICATION AND LOCATION OF CRUDE OIL SAMPLES

Sample number	Well	Field	Location	Producing unit	Production depth (ft)
1	Webber A-1 ^a	Wilburton ^a	5N-17E-18	Spiro	9,468–9,514
				Wapanucka	9,552–9,694
2	Warren 1	"Talihina"	3N-21E-2	Stanley	156–164
3	Jim 1	"Star"	2N-17E-5	Stanley	1,044–1,054
4	Wilkins 1	"Oil Well Hol"	2N-16E-8	—	260
5	Dallas James 1	Bald	2N-15E-28	Stanley	—
6	Dallas James 2	Bald	2N-15E-28	Stanley	—
7	J. M. Smith 2	—	2N-15E-33	Stanley	~136
8	"S Bald"	Bald S	1N-15E-5	Jackfork	188–236
9	Crockett D	Bald S	1N-15E-5	Jackfork	450–680
10	Crockett 2	Bald S	1N-15E-5	Jackfork	185–225
11	Smith 1 ^a	Bald S	1N-15E-5	Upper Stanley	650–850
12	Rowland Bledsoe 1	Bald S	1N-15E-7	Stanley	452–916
13	Foster B-2	Bald S	1N-15E-7	Stanley	555–603
14	Foster 1	Bald S	1N-15E-8	Stanley	1,260–1,320
15	Four North 1-1 and 1-2 ^b	Bald S	1N-15E-8	Stanley	2,042–2,107
					722–826
16	Fraser 1 and Loman 1 ^b	Bald S	1N-15E-8	Upper Stanley	650–1,250
17	Isom 4	Daisy SE	1N-15E-24	Upper Stanley	1,330–1,352
18	Williams 1-26 ^a	Daisy SE	1N-15E-26	Stanley	7,430–7,700
19	Lambert 2W	Wesley E	1N-14E-6	Misener ^c	1,649–1,682
20	Gamble 1-25 ^a	Daisy W	1N-14E-25	Stanley	(TD = 7,502)
21	School Land 2	Daisy W	1N-14E-26	Stanley	(TD = 487)
22	Wyrick 2-26	Daisy W	1N-14E-26	Arkansas Novaculite	8,534–8,566
23	"Redden"	Redden	1S-14E-9	Upper Stanley	30–600
24	E. Miller 2	Redden	1S-14E-9	Middle Stanley	192
25	Lee Cole 1	"Minnett"	1S-14E-19	Atoka	125
26	Anson 1	Atoka Townsite SE	2S-12E-35	Arkansas Novaculite	7,101–7,119
27	Taylor ^a	Atoka Townsite S ^a	3S-11E-15	Big Fork	2,840–3,060
28	Harvey Harmon 2 ('88)	Idabel W	7S-23E-33	Goodland Ls.	280
29	Harvey Harmon 2 ('86)	Idabel W	7S-23E-33	Goodland Ls.	280
30	"Harvey Harmon?"	Idabel W	7S-23E-33	—	—
31	Smith	Idabel W	8S-23E-5	—	315–345
32	Daniel 1	Oconee	1N-9E-32	Wapanucka	3,658–3,864
33	Jacks-Stout 1	Madill	5S-5E-9	Woodford	4,911
34	Sycamore Unit G	Madill	5S-5E-14	Sycamore	4,813
35	Bessie Sterling 1	Madill	5S-5E-15	Viola	5,100
36	NMBSU M-8	Madill	5S-5E-15	Bromide	6,432
37	Lee "B" 2	Durant E ^a	6S-9E-35	Oil Creek	7,594–7,740
38	Bedo 2	Enville SW	6S-2E-35	Birdseye	4,577–5,774
39	Neff 2	Isom Springs	7S-5E-23	(Cretaceous)	412
40	Bruce 1	Isom Springs	7S-5E-35	Arkansas Novaculite	4,750
41	Victor 1 (I)	Isom Springs	8S-5E-2	Arkansas Novaculite	4,550
42	Victor 1 (II)	Isom Springs	8S-5E-2	Woodford Chert	2,262–4,540
43	Northcutt A-1	Powell S	8S-4E-1	Desmoinesian	4,862–4,890
44	Talco I.S.D. 1	Talco	NW Titus County, TX	Paluxy	4,300
45	Daisy Bradford 3	East Texas	Smith County, TX	—	—

^aListed as gas well/gas field.^bCommingled oil from two wells.^cAs listed on Oklahoma Corporation Commission 1002A, Well Completion Report.

" " = Name assigned for this study.

TD = Total depth.

TABLE 2. — LOCATION OF ROCK SAMPLES AND GROSS CHEMICAL DATA FOR ROCKS AND EXTRACTS

Sample number	Formation	Location	Vitrinite reflectance (%)	EOM (ppm)	Carbon-ate ^a (%)	TOC (%)	GI ^b (%)	RPP ^c	T _{max} (°C)	Saturate (%)	Aromatic (%)	NSO (%)	Asphal-tene (%)
1	Atoka	5N-19E-29	—	160	8.6	0.9	—	—	—	—	—	—	—
2	Atoka	4N-23E-4	—	1,210	7.1	1.8	30	15	505	68	12	6	13
3	Atoka	4N-18E-5	—	134	4.4	0.5	—	—	—	37	9	17	37
4A	Atoka	4N-18E-28	—	157	17.2	1.1	—	—	—	17	6	37	40
4B	Atoka	4N-18E-28	—	136	21.0	1.2	—	—	—	12	5	37	45
5A	Atoka	4N-17E-2	—	151	4.3	1.0	—	—	—	17	14	29	40
5B	Atoka	4N-17E-2	—	80	4.0	1.1	4	7	501	—	—	—	—
6	Atoka	4N-17E-24	—	168	7.6	1.5	10	6	470	13	4	33	49
7	Atoka	3N-15E-32	0.70	167	6.7	1.0	14	7	474	42	12	16	30
8	Johns Valley	3N-18E-12	—	573	4.7	2.4	9	47	468	34	9	37	21
9	Johns Valley	3N-17E-2	—	356	10.2	3.0	6	12	473	18	7	41	33
10	Stanley Group	2N-25E-26	1.12	170	4.8	0.9	22	5	505	46	13	15	26
11	Jackfork	1N-15E-19	0.65	310	7.6	2.0	19	30	489	43	21	18	18
12	Stanley (tar sand)	1N-16E-19	—	17,500	—	—	—	—	—	25	27	12	35
13	Caney	4N-21E-6	—	2,820	16.2	4.4	7	232	480	37	15	34	14
14	Caney	4N-21E-11	—	6,290	23.0	4.6	15	496	485	—	—	—	—
15	Caney	1S-16E-4	0.57	1,570	9.0	5.4	6	340	468	44	18	33	5
16	Arkansas Novaculite	2S-11E-13	0.47	3,300	12.2	12.5	3	1,410	468	14	19	21	46
17	Woodford	4N-21E-6	—	3,340	6.1	8.5	4	623	484	30	21	33	16
18	Woodford	4N-21E-11	—	2,440	33.0	3.6	9	262	490	—	—	—	—
19	Woodford	4N-20E-15	—	514	15.0	2.0	—	—	—	39	15	29	17
20A	Woodford	2N-15E-4	—	2,460	27.6	5.9	6	1,430	470	28	33	24	15
20B	Woodford	2N-15E-4	—	2,040	30.5	4.6	—	—	—	37	27	22	14
21A	Woodford	2N-15E-5	—	1,370	21.8	2.0	—	—	—	56	18	16	11
21B	Woodford	2N-15E-5	0.52	936	17.2	4.6	4	472	470	44	20	25	11
22	Polk Creek	2S-11E-14	0.66 ^d	980	4.4	6.1	4	537	470	24	27	29	20

^aDetermined as HCl-soluble material.

^bGeneration index from Pyrocell data: $[P_1 / (P_1 + P_2)] \times 100$.

^cRelative petroleum potential from Pyrocell data: $(P_1 + P_2)$ per gram of rock.

^dGraptolite reflectance—roughly equivalent to vitrinite reflectance (Bustin and others, 1989).

Rocks

Initially, I investigated as potential source rocks 61 shales collected from 50 outcrops throughout the Ouachitas. Weber (1992) listed sample locations and results. Measurements of total organic carbon (TOC) and extractable organic matter (EOM) were used as a screen to determine which rocks had the capacity for producing significant quantities of hydrocarbons. Thirty-six shales (29 outcrops), including the three samples collected from the Collier Shale and Springer Formation (Fig. 2), contained less than the generally accepted minima of 0.5% total organic

carbon and ~100 ppm extractable hydrocarbons required to generate and expel hydrocarbons from clastic rocks (see, for example, Tissot and Welte, 1984; Bayliss, 1985; Perrodon, 1988) and were not studied further. The remaining 25 shales (21 outcrops), plus a tar sand (bitumen-impregnated sandstone), are discussed in this paper.

The rocks represent eight formations and include four sets of two samples from the same outcrop. These double samples are not duplicates; they serve to illustrate the scatter in analytical data to be expected from small-scale organic facies variations within a rock unit. Samples col-

lected only centimeters apart, even in a visually homogeneous lithology, can differ in organic content because of varying depositional conditions (Miranda and Walters, 1992).

ANALYTICAL PROCEDURES

Whole-Rock Treatment

Rocks were washed, dried, and then finely ground in a moving-plate pulverizer.

For TOC determinations, 0.1–0.6 g portions of 200-mesh samples were treated with warm 2N followed by 4N hydrochloric acid in filtering crucibles to remove carbonates and then analyzed on a Leco WR-12 Car-

PENN.	SERIES	OUACHITA MOUNTAINS, OKLAHOMA	
		FRONTAL BELT	CENTRAL & SOUTHERN
PENN.	Atokan	● 1 Atoka Fm.	○ 9 (15)
	Morrowan	Wapanucka Ls.	Johns Valley Shale ○ 2 (5)
		Springer Fm. ○ (2)	● 3 Jackfork Group ○ 1 (4)
MISSISSIPPIAN	Chesterian	"Caney" Sh.	Stanley Shale
	Meramecian		
	Osagean		● 17 ○ 1 (9)
	Kinderhookian		○ 3
DEVONIAN	Upper	Woodford Sh.	Arkansas Novaculite
	Lower		● 2 Pinetop Chert ○ 1
SILURIAN	Upper	Missouri Mountain Shale	
	Lower	Blaylock Sandstone	
ORDOVICIAN	Upper	Polk Creek Shale ○ 1	
		Bigfork Chert	
	Middle	● 1	
		Womble Shale	
		Blakely Sandstone	
	Lower	Mazarn Shale	
		Crystal Mountain Ss.	
		Collier Shale	
CAMBRIAN	Upper	? — ? — ○ (1)	

Figure 2. Generalized stratigraphic column for the Ouachita Mountains, Oklahoma (after Ferguson and Suneson, 1988; Suneson, 1988), showing formations from which samples were taken. ● = number of oil samples; ○ = number of rock samples included in this paper; () = number previously rejected as potential source rocks.

bon Determinator. TOC values reported are the average of duplicate determinations, with an average relative percent standard deviation of 0.7%.

To determine EOM, 30–100 g of ground sample were extracted in a Soxhlet apparatus with dichloromethane (24 hr). A strip of shiny copper metal was placed in each extraction flask to remove elemental sulfur. Solvent was removed with a rotary evaporator, and the extract was air-dried and weighed.

Pyrolysis data were obtained in the Geochemistry Laboratory of the University of Oklahoma School of Geology and Geophysics by heating ≤ 80 mg of whole rock in a Ruska Pyrocell. Following an initial hold of 2 min, samples were heated from 30°C to 320°C at 60°C/min, cooled to 290°C at 50°C/min to enable baseline separation of the two major peaks, held isothermally for 1 min, heated at 30°C/min to 600°C, and held isothermally for 4 min. Peak areas were used for calculations.

Fractionation of Oils and Extracts

Volatile components (C_{15-}) were removed from oils by heating at 43°C for 18 hr. Results of this topping process are reported as loss on evaporation.

Asphaltenes were precipitated by adding a 50-fold excess of *n*-pentane or *n*-hexane to topped oils and *n*-heptane to extracts. After sitting overnight, asphaltenes were filtered through dual, stacked polyethylene frits (20 μ m) in preweighed disposable cartridges. The cartridges were air-dried and reweighed to determine asphaltene content. For oil samples, values for asphaltene and nitrogen-sulfur-oxygen-containing (NSO) fractions were combined and reported as nonhydrocarbons.

Deasphalted oils and extracts were separated on mini-chromatographic columns (5-mL serological pipets) of activated high-purity silica gel (60–200 mesh atop 100–200 mesh) overlain with alumina. Stepwise elution with *n*-pentane or *n*-hexane, benzene, and 1:1 chloroform/methanol for oils and *n*-heptane, benzene, and 1:1 benzene/methanol for extracts yielded satu-

rate, aromatic, and NSO fractions, respectively. Solvents were evaporated by air-drying. Fraction weights were not obtained for residues weighing less than 5 mg.

Gas Chromatography (GC)

Whole oils and saturate fractions of both oils and rock extracts were analyzed on a Hewlett Packard 5840 gas chromatograph equipped with a split injection system, a flame-ionization detector, and a 30 m \times 0.25 mm Supelco SPB-1 capillary column (0.25- μ m film thickness). The carrier gas was helium; injector and detector temperatures were 300°C and 310°C, respectively. Following an initial hold of 0.1 min, the oven temperature was programmed from 60°C to 290°C at 8°C/min. The final temperature hold varied from 5 to 15 min, depending on the nature of the sample. Peak-height measurements were used for all calculations. Identifications were based on comparisons with an in-house standard containing C_9 through C_{26} *n*-alkanes, pristane, phytane, and even-numbered *n*-alkanes from C_{28} through C_{34} .

Gas Chromatography-Mass Spectrometry (GC-MS)

Whole Oil

Z. A. Wilk of the analytical department at Unocal Science & Technology Division (Brea, California) generated data for selected whole oils on a VG 70-250SE high-resolution mass spectrometer coupled to a Hewlett Packard gas chromatograph fitted with a 30-m DB-5 capillary column. Data were acquired at 5000 mass resolution by multiple-ion monitoring at mass to charge ratios (m/z) of 191.18 (terpanes), 217.20 (steranes), 231.12 (triaromatic steroid hydrocarbons), and 253.20 (monoaromatic steroid hydrocarbons).

Branched and Cyclic Alkanes in Rock Extracts

A branched and cyclic alkane fraction was prepared by removing *n*-alkanes from the saturate fractions of extracts with 5A molecular sieves. A mixture of ≤ 25 mg of saturates, 5 g of activated molecular sieves (Union Carbide S-115), and GC-grade *iso*-octane was allowed to sit overnight

at room temperature with occasional swirling. Solvent was decanted and allowed to evaporate. The resulting branched and cyclic alkane residues were analyzed in the Geochemistry Laboratory of the University of Oklahoma School of Geology and Geophysics by using a Varian 3400 GC interfaced with a Finnigan Triple Stage Quadrapole (TSQ 70). Chromatography was carried out on a 25 m \times 0.22 mm SGE HT-5 aluminum-clad column containing a siloxane carborane stationary phase (0.10- μ m film thickness). The conditions were: injector, 300°C; oven, 40°–120°C at 10°C/min, 120°–300°C at 1.8°C/min, isothermal for 18 min; transfer line, 300°C; and ion source, 200°C. Operation was in the multiple-ion detection mode, monitoring the m/z 191 (terpanes), m/z 217 (steranes), and m/z 253 (monoaromatic steroid hydrocarbons) ions at 70 eV. Data were acquired by using Finnigan's Interactive Chemical Information System aided by a DEC RSX-11M Plus Operating System.

For both methods, peak identifications were made by comparison with published chromatograms (Brooks and others, 1988; Horstad and others, 1990; Jones and Philp, 1990; Waples and Machihara, 1990); biomarker ratios were calculated from peak-height measurements.

Different GC-MS analytical systems and procedures can result in significantly different biomarker ratio values (Fowler and Brooks, 1990). It is with this caveat that oil and extract data are evaluated and compared in this study.

Other Procedures

API gravities were measured with a hydrometer at room temperature and then corrected to 60°F. Vitrinite reflectance (R_o) measurements, provided by Brian J. Cardott of the Oklahoma Geological Survey, were made by determining the percentage of white light (546 nm) reflected from polished kerogen pellets immersed in oil. Dispersed organic matter was isolated from the rock mineral matrix by successive treatment with hydrochloric acid, hydrofluoric acid, hydrochloric acid again, and, finally, water rinses. Sulfur was determined at Unocal by x-ray fluorescence.

Nickel and vanadium were determined at Unocal by either atomic absorption or inductively-coupled-plasma methods. Stable carbon-isotope ratios (provided by Unocal) are expressed in per mil deviation relative to the PDB standard.

ORGANIC GEOCHEMISTRY

Crude Oils

An earlier paper (Weber, 1990) on 25 of the oils discussed here dealt only with information obtained from whole-oil and bulk analyses. That investigation emphasized gross chemical composition of either the entire sample or large parts thereof. This paper presents additional whole-oil data (Table 3), but focuses on the molecular level.

For ease of discussion, the oils have been grouped into three categories—Ouachita tectonic belt (OTB), Cretaceous, and Nearby oils—according to their location in or near the Ouachita tectonic belt.

1. Ouachita tectonic belt (OTB) oils were collected south of the trace of the Choctaw fault and the leading edge of the buried tectonic belt extending to the southwest. Thirty oils from "Talihina," "Star," "Oil Well Hol," Bald, Bald S, Wesley E, Daisy SE, Daisy W, Redden, "Minnett," Atoka Townsite SE, Atoka Townsite, and Isom Springs fields are in this group.

2. Cretaceous oils were collected south of the Broken Bow uplift (Idabel W field) and from the Talco (Texas) field, about 45 mi farther to the southwest. Five oils are in this group.

3. Nearby oils include one oil from Wilburton gas field in the southern Arkoma basin, one oil from Oconee field in the western Arkoma basin, seven oils from the Ardmore basin (Madill, Durant E, Enville SW, and Powell S fields) northwest of the subsurface expression of the Ouachita tectonic belt, and one oil from East Texas field.

Gas Chromatography

Figure 3 presents a representative total saturate profile from every oil or gas field (or pool). Several of these profiles show effects of alteration processes. Two oils, 31 and 39, are devoid of *n*-alkanes owing to bio-

degradation. There is wide agreement (for example, Connan, 1984; Alexander and others, 1983; Spiro and others, 1983) that biodegradation is a sequential process characterized by preferential removal of *n*-alkanes—beginning with the lower homologs, followed by isoprenoids and other branched alkanes, and finally by cyclic alkanes and some aromatics. Evidence of biodegradation in these two samples is not surprising. Oil 31 was taken from beneath a tar mat in a stock tank at an abandoned producer; oil 39 is from a very shallow (412 ft) reservoir. Several other oils, including the remaining members of the Cretaceous group, show the effects of more limited biodegradation than that seen in the two oils just discussed. In oil 4, the relatively higher amounts of isoprenoids indicate only partial destruction of its *n*-alkanes; this oil also exhibits a second feature commonly attributed to the effects of bacterial action—a "hump" of unresolved compounds along the baseline. Oil 7 shows partial destruction of lower-molecular-weight *n*-alkanes, resulting in an apparent maximum at C₂₀. In oils 17, 19, 32, and to a lesser extent 27, decreased *n*-alkane content is evidenced by relatively high Pr/C₁₇ and Ph/C₁₈ ratios (Table 4). Oil 27 shows other effects of biodegradation as well. Table 3 lists much higher concentrations of sulfur, nickel, and vanadium for oil 27 than for other OTB oils (Waples, 1981) and a (relatively) low loss on evaporation (9.1%). Cretaceous oils 28 and 44 are both characterized by reduced amounts of *n*-alkanes; oil 28 also has a baseline hump. An example of a profile affected by maturity is oil 1. This oil, produced in association with gas, is highly mature.

With the exceptions noted, saturate profiles of OTB oils (Fig. 3A) are strikingly similar. Features common to most oils throughout this group are a maximum at C₁₅ or C₁₇; gradually decreasing amounts of higher-numbered *n*-alkanes; a slight predominance of odd-numbered carbon atoms as calculated by the odd-even preference (OEP), especially in the C₁₅–C₁₉ region; moderate amounts of isoprenoids, with pristane exceeding phytane; and similar

small-peak groupings between dominant *n*-alkane peaks. These features describe moderately mature, algal-based, predominantly marine oils generated in clastic source rocks under mildly reducing conditions (Kinghorn, 1983; Tissot and Welte, 1984; Philp, 1985).

Compared to other OTB oils, Daisy SE oils (17 and 18) have higher Pr/Ph ratios (Table 4). Because non-forced ambient air was the means for removing solvent from all fraction residues, differential solvent blow-down is an unlikely cause of this variation. Nonexperimental factors that can result in higher Pr/Ph values are (1) greater contribution from land-derived organic matter (Jørgensen and others, 1990); (2) greater degree of oxidation during deposition of organic matter (Jørgensen and others, 1990); (3) sources of pristane in addition to chlorophyll (Kvenvolden and others, 1987; Philp and Lewis, 1987); and (4) maturation effects. In a study of Smackover oils, Sofer (1988) noted a tendency for pristane/phytane to be higher in more mature oils, particularly condensates. Oil 18 qualifies as a near condensate (API gravity 48°). Produced as associated oil from a depth of about 7,500 ft in a gas well, it lacks significant *n*-alkanes above C₂₄. Almost half its compounds (46.0%) are easily evaporated (Table 3). However, oil 17, though sampled from a wellhead under high gas pressure, is not a highly mature oil. It has a full range of *n*-alkanes, an API gravity of 39°, and an only moderate loss on evaporation (27%) (Table 3). The relatively higher Pr/Ph ratio in Daisy SE oils appears to be a primary condition, i.e., related to the oil's source and/or environment rather than to secondary alteration.

Considering the extent to which GC profiles of crude oils can vary, the Cretaceous and Nearby oils (Fig. 3B, C) are more similar than dissimilar to OTB oils. However, there are noteworthy differences, some of which are source related. The Cretaceous oils, with their dominance of phytane over pristane, probably originated from rocks deposited in an anoxic or saline environment. Other apparent differences—including the baseline hump on oils 28 and 31, depletion of *n*-alkanes (particularly

TABLE 3. — BULK PROPERTIES OF OILS

Sample number	°API gravity	$\delta^{13}\text{C}$ saturate (‰)	$\delta^{13}\text{C}$ aromatic (‰)	Sulfur (ppm)	Nickel (ppm)	Vanadium (ppm)	Loss on evaporation (%)	Saturates (%)	Aromatics (%)	Nonhydrocarbons (%)	OEP ^a ($\text{C}_{16}\text{--}\text{C}_{20}$)
1	35	-30.6	-29.1	2,660	3.0	3.2	8.4	74	12	13	1.1
2	37	-30.2	-29.4	2,080	1.7	1.7	16.0	73	20	7	1.2
3	33	-30.3	-29.7	4,200	6.2	5.7	17.0	61	26	13	1.2
4	32	—	—	—	—	—	16.0(2)	61(2)	20(2)	19(2)	1.2
5	34	—	—	—	—	—	18.0	60	28	12	1.1
6	34	-30.4	-29.2	4,930	6.8	13.0	17.0	60	27	13	1.1
7	22	-30.5	-29.4	6,010	6.6	5.7	6.1	47	37	15	1.1
8	36	—	—	—	—	—	16.0	69	20	10	1.1
9	38	-30.2	-29.3	2,630	2.3	2.6	20.0	71	21	8	1.1
10	37	—	—	—	—	—	18.0	71	22	7	1.1
11	40	—	—	—	—	—	22.0	70	21	9	1.1
12	36	-30.1	-29.5	2,820	3.0	4.3	15.0	70	22	8	1.1
13	32	—	—	—	—	—	10.0	62	25	13	1.1
14	36	—	—	—	—	—	18.0	69	21	10	1.1
15	37	-30.2	-29.5	3,610	3.3	6.7	18.0	71	21	8	1.2
16	39	—	—	—	—	—	22.0	69	23	8	1.1
17	39	-30.3	-29.1	1,140	2.1	0.9	27.0	73	20	7	1.1
18	48	—	—	—	—	—	46.0	—	—	—	1.2
19	39	-29.5	-28.3	983	2.6	<0.1	23.0	74	16	11	1.1
20	38	-30.4	-29.1	3,340	2.7	3.8	25.0	65	22	13	1.2
21	35	-29.9	-29.2	1,950	2.9	1.9	7.8	74	19	7	1.1
22	47	—	—	—	—	—	26.0	—	—	—	1.1
23	34	—	—	—	—	—	13.0	72	19	9	1.1
24	41	-29.7	-28.8	1,390	3.9	1.9	26.0	78	16	6	1.1
25	34	-30.2	-29.2	6,300	16.0	48.0	19.0	58	25	17	1.2
26	—	-30.1	-29.3	1,430	9.7	1.4	12.0	68	15	16	1.1
27	21	-30.4	-30.2	16,800	40.0	167.0	9.1	39	25	36	1.1
28	21	-25.5	-25.0	27,600	4.8	5.1	3.7	49	29	22	1.0
29	23	—	—	—	—	—	13.0	51	34	15	—
30	23	-25.5	-25.2	26,900	4.4	5.0	6.9	48	35	17	1.1
31	20	-25.2	-24.9	28,100	3.6	4.8	—	51	32	16	—
32	37	-31.2	-30.4	1,180	4.4	1.4	28.0	65	13	23	1.0
33	33	—	—	—	—	—	21.0	63	28	9	1.0
34	37	-30.7	-29.6	5,840	14.0	28.0	26.0	55	26	19	1.0
35	38	—	—	—	—	—	27.0	63	28	10	1.2
36	38	—	—	—	—	—	26.0	67	25	9	1.2
37	—	-30.4	-29.5	3,960	8.1	5.1	3.3	68	14	18	1.1
38	31	—	—	—	—	—	13.0	58	19	23	1.6
39	31	—	—	—	—	—	11.0	69	22	8	—
40	41	-30.4	-29.6	2,930	7.7	17.0	27.0	77	18	4	1.0
41	40	—	—	—	—	—	22.0	76	16	8	1.1
42	—	—	—	—	—	—	19.0	64	14	21	1.1
43	34	—	—	—	—	—	24.0	57	19	24	1.1
44	19	-25.9	-25.4	37,500	22.0	24.0	9.6	36	27	37	1.0
45	—	-28.5	-24.9	3,920	8.2	<0.1	3.7	70	21	9	1.1

^aOEP = $[(C_i + 6 C_{i+2} + C_{i+4}) / (4 C_{i+1} + 4 C_{i+3})]^{(-1)^{i+1}}$; using peak-height data from GC of whole oil.

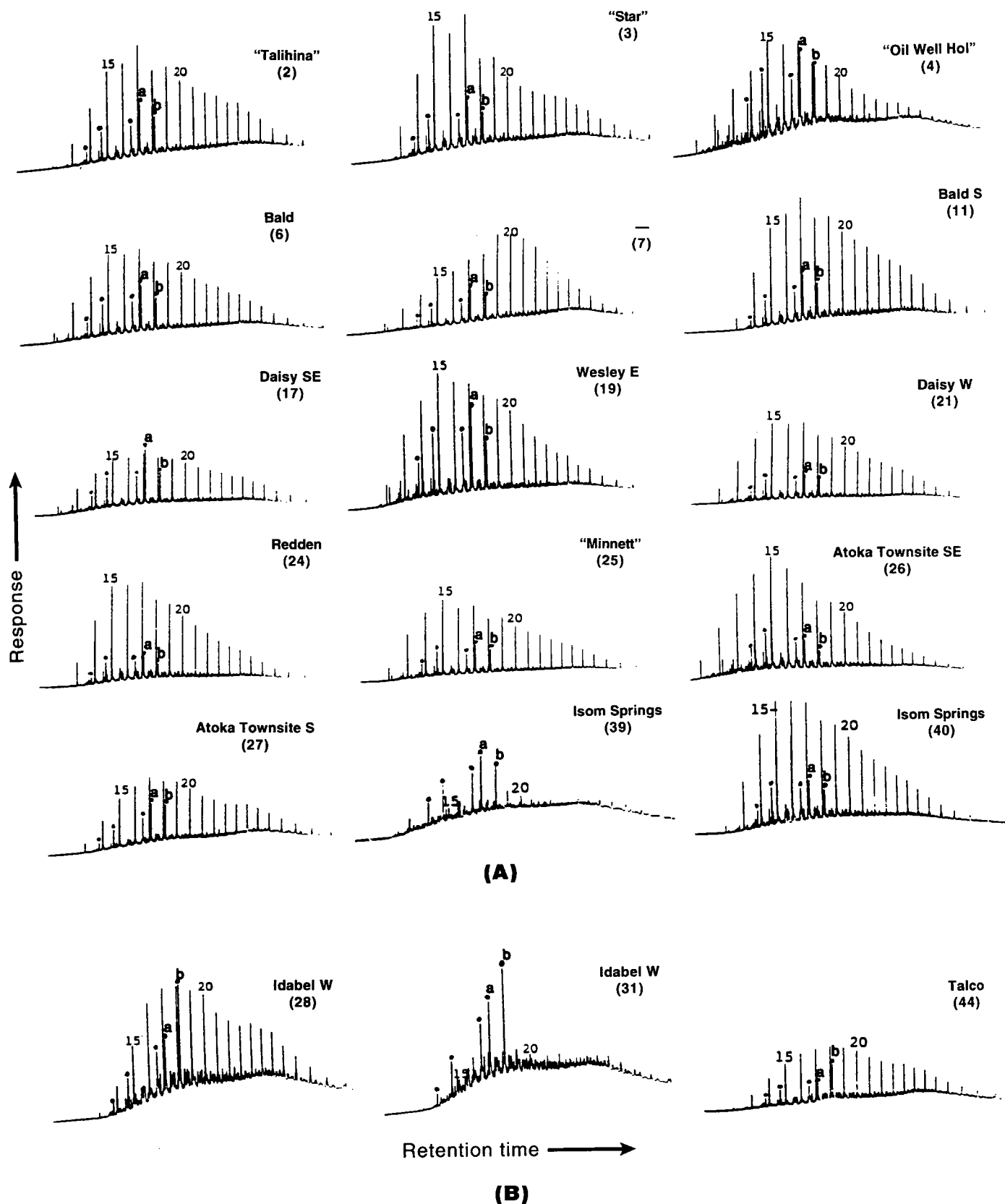


Figure 3 (above and opposite page). Representative gas chromatograms of saturate fraction of Ouachita-area oils: (A) Ouachita tectonic belt (OTB) oils, (B) Cretaceous oils, (C) Nearby oils. Numbers are n -alkane carbon numbers; (●) isoprenoid, (a) pristane, (b) phytane. Peak heights are not comparable between samples because of varying signal attenuations used.

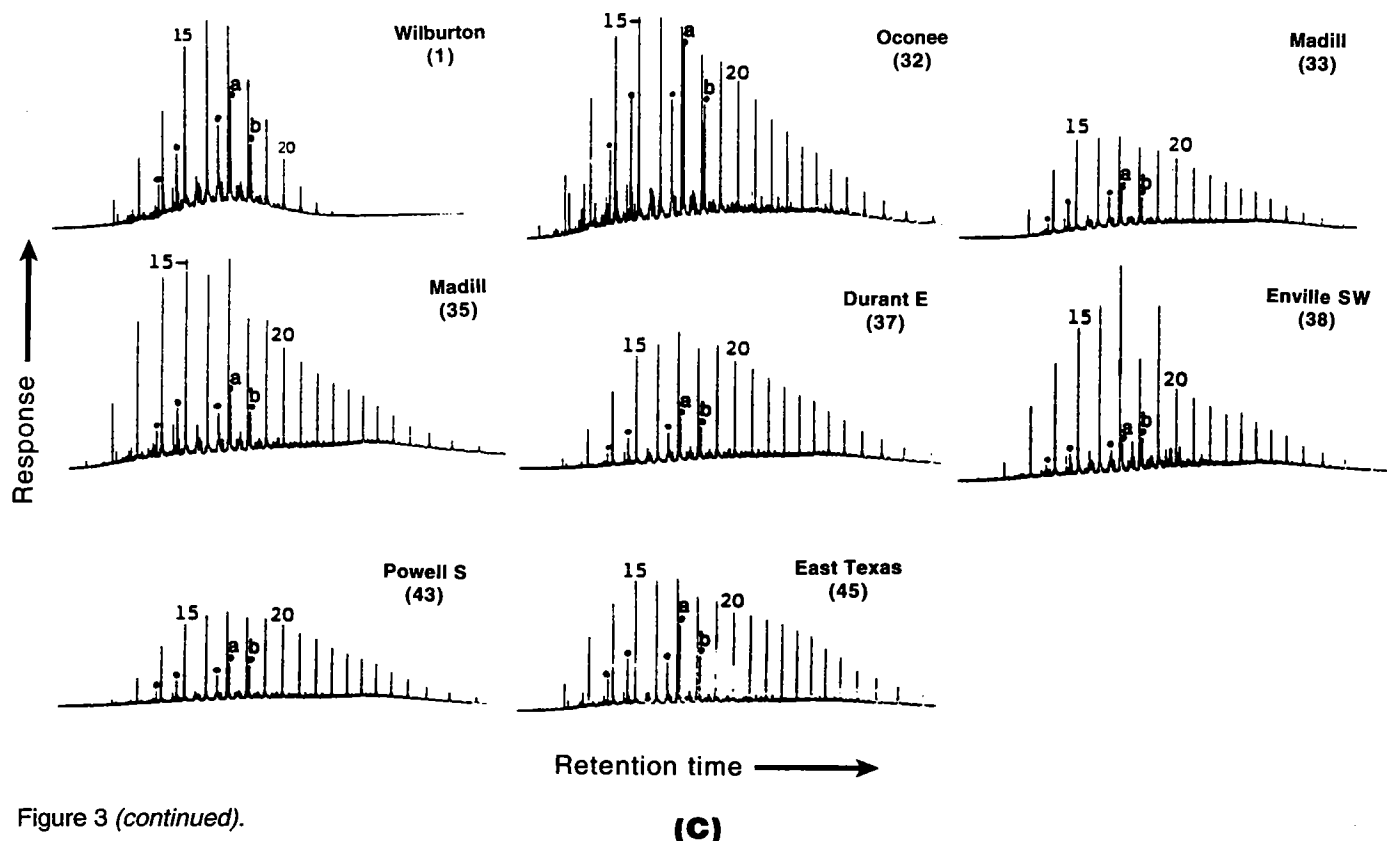


Figure 3 (continued).

(C)

noticeable on whole-oil chromatograms), and high concentration of isoprenoids relative to *n*-alkanes—are attributed to biodegradation. Oil 38, a Nearby oil, has characteristics associated with both an Ordovician source—low concentration of isoprenoids, pronounced OEP at C_{17} and C_{19} (Reed and others, 1986; Longman and Palmer, 1987)—and a carbonate source—pristane/phytane <1 (Moldowan and others, 1985; Clark and Philp, 1989). Since this oil is produced from an Ordovician limestone, the reservoir rock may be serving also as a (partial) source. Maturity effects dominate the GC profile of oil 1, a Nearby oil from the Wilburton gas field in the southern Arkoma basin. The absence of significant *n*-alkanes above C_{22} reflects the extent to which this oil has undergone thermal cracking of its heavier-molecular-weight compounds.

Isoprenoid-distribution plots (Fig. 4) can provide corroborating evidence in oil-oil correlation studies. Allowing for normal analytical variation, the plots shown in Figure 4A are essentially the same. They represent

22 of 30 OTB oils and 7 of 10 Nearby oils. Distributions for the remaining OTB and Nearby oils are plotted separately (Fig. 4B,C) to highlight their different shapes, some of which can be attributed to alteration effects. The decrease in relative concentration of lower-molecular-weight isoprenoids seen in Figure 4B is sometimes due to biodegradation. Three oils already mentioned as being biodegraded (7, 17, and 39) appear in this group. It has been postulated that as maturation progresses, phytane and pristane are thermally cracked to yield shorter-chain homologs (Kvenvolden and others, 1987; Thompson and Kennicutt, 1992). At high maturity levels, then, the “M” shape of a distribution plot will tilt downward to the right, as seen in Figure 4C. On the basis of their high API gravities and whole-oil GC profiles, two of these oils (18 and 22) are highly mature. However, there are no data to support a similar conclusion for the other two (4 and 26).

The plot for the Cretaceous oils (Fig. 4D) is dominated by high relative concentrations of *i*- C_{20} (phytane). Such a distribution typically

signifies a strongly reducing or saline (either carbonate or evaporite) depositional environment and, in this case, suggests a true source difference from other oils in the study. The skew toward higher-molecular-weight isoprenoids in oil 31 of this group is due to its loss of low-molecular-weight compounds through volatilization and biodegradation.

Although oils beyond the Ouachita tectonic belt were not the main target of this investigation, the pattern of GC profiles obtained for samples from the Madill field in Marshall County deserves special comment. Oils 33 (Fig. 3C) and 34 (not shown), from reservoirs in the Woodford Shale and Sycamore Limestone, respectively, have profiles that appear to be exact overlays of one another. Profiles of oils 35 (Fig. 3C) and 36 (not shown), from reservoirs in Ordovician rocks, are seemingly identical to one another but different from the Woodford-Sycamore set. The oils from Ordovician reservoirs have a definite odd-preference in the C_{15} – C_{19} region and a steeper slope of successive *n*-alkane peak tops, giving them a distinctive “Ordovician ap-

TABLE 4. — GEOCHEMICAL DATA FOR OILS

Sample number	Pr ^a Ph	Pr ^b C ₁₇	Ph ^c C ₁₈	20S ^d		$\beta\beta^e$		C ₂₀ ^f		C ₂₄ tet ^g		C ₂₃ tri ^h		Tri ⁱ H	BNH ^j		C ₂₉ H ^k		M ^l		22S ^m	
				20S+20R		$\beta\beta+\alpha\alpha$		C ₂₀ +C ₂₈		C ₂₆ tri		C ₃₀ H			BNH+C ₃₀ H		C ₃₀ H		M+H		22S+22R	
1	1.8	0.58	0.49	0.49		0.63		—		—		24.0		—	—		0.74		—		—	
2	1.4	0.48	0.46	0.56		0.65		0.56		1.0		0.57		0.87	0.23		0.50		0.09		0.59	
3	1.5	0.37	0.41	0.53		0.57		0.52		0.97		0.91		0.57	0.25		0.65		0.09		0.60	
4	1.3	0.87	1.0	—		—		—		—		—		—	—		—		—		—	
5	1.5	0.57	0.50	—		—		—		—		—		—	—		—		—		—	
6	1.4	0.56	0.48	0.52		0.55		0.27		1.0		0.38		0.36	0.16		0.65		0.10		0.59	
7	1.3	0.54	0.41	0.51		0.58		—		1.3		0.78		0.68	0.18		0.70		0.10		0.59	
8	1.4	0.36	0.33	—		—		—		—		—		—	—		—		—		—	
9	1.4	0.37	0.34	0.53		0.60		0.30		0.96		0.43		0.40	0.17		0.60		0.10		0.59	
10	1.4	0.35	0.32	—		—		—		—		—		—	—		—		—		—	
11	1.3	0.37	0.35	—		—		—		—		—		—	—		—		—		—	
12	1.5	0.28	0.24	0.52		0.61		0.43		0.93		0.59		0.44	0.14		0.62		0.10		0.57	
13	1.6	0.48	0.39	—		—		—		—		—		—	—		—		—		—	
14	1.4	0.34	0.32	—		—		—		—		—		—	—		—		—		—	
15	1.4	0.38	0.40	0.52		0.61		0.29		0.99		0.39		0.40	0.20		0.59		0.10		0.59	
16	1.4	0.37	0.34	—		—		—		—		—		—	—		—		—		—	
17	2.0	1.2	0.73	0.53		0.58		0.36		1.1		0.35		0.36	0.12		0.45		0.09		0.57	
18	2.0	0.51	0.46	—		—		—		—		—		—	—		—		—		—	
19	1.7	0.84	0.58	0.52		0.54		0.22		1.1		0.29		0.45	0.09		0.48		0.10		0.61	
20	1.3	0.38	0.45	0.55		0.61		0.46		0.97		0.41		0.38	0.22		0.60		0.08		0.61	
21	1.4	0.31	0.30	0.54		0.60		0.47		1.1		0.32		0.42	0.14		0.53		0.09		0.58	
22	1.9	0.29	0.26	—		—		—		—		—		—	—		—		—		—	
23	1.5	0.32	0.28	—		—		—		—		—		—	—		—		—		—	
24	1.5	0.24	0.21	0.51		0.58		0.38		0.97		0.31		0.29	0.13		0.61		0.10		0.58	
25	1.3	0.41	0.46	0.52		0.60		0.25		1.0		0.38		0.41	0.21		0.71		0.10		0.60	
26	1.8	0.34	0.26	0.53		0.58		—		1.1		0.53		0.52	0.17		0.65		0.10		0.60	

27	1.2	0.58	0.61	0.55	0.60	0.23	1.0	0.38	0.30	0.13	0.78	0.08	0.60
28	0.5	0.55	1.2	0.50	0.61	0.48	5.6	0.31	0.12	0.03	1.1	0.07	0.58
29	0.6	0.53	1.1	—	—	—	—	—	—	—	—	—	—
30	0.6	0.71	1.4	0.55	0.58	0.50	5.5	0.34	0.14	0.02	1.2	0.06	0.60
31	0.6	3.2	8.5	0.54	0.59	0.55	5.9	0.36	0.15	0.03	1.1	0.06	0.60
32	1.6	0.87	0.66	0.56	0.61	0.54	0.97	0.45	0.80	0.14	0.41	0.09	0.60
33	1.3	0.43	0.38	—	—	—	—	—	—	—	—	—	—
34	1.3	0.41	0.37	0.53	0.57	0.31	1.0	0.50	0.45	0.10	0.58	0.08	0.60
35	1.5	0.31	0.32	—	—	—	—	—	—	—	—	—	—
36	1.6	0.42	0.37	—	—	—	—	—	—	—	—	—	—
37	1.3	0.38	0.33	0.54	0.62	0.72	0.88	1.1	0.90	0.21	0.63	0.06	0.63
38	0.9	0.14	0.28	—	—	—	—	—	—	—	—	—	—
39	1.4	4.9	6.0	—	—	—	—	—	—	—	—	—	—
40	1.4	0.33	0.29	0.52	0.58	0.40	0.98	0.92	0.59	0.17	0.65	0.08	0.61
41	1.6	0.28	0.22	—	—	—	—	—	—	—	—	—	—
42	1.4	0.30	0.26	—	—	—	—	—	—	—	—	—	—
43	1.2	0.43	0.43	—	—	—	—	—	—	—	—	—	—
44	0.6	0.33	0.68	0.54	0.58	0.46	5.2	0.29	0.10	0.02	1.2	0.06	0.60
45	1.7	0.64	0.47	0.55	0.58	0.62	1.0	0.17	0.27	0.06	0.38	0.10	0.59

^a Pristane/phytane (GC of whole oil).^b Pristane/*n*-heptadecane (GC of whole oil).^c Phytane/*n*-octadecane (GC of whole oil).^d C₂₅ 14 α (H), 17 α (H) steranes (*m/z* 217).^e C₂₃ 14 β (H), 17 β (H) and 14 α (H), 17 α (H) steranes (*m/z* 217).^f C₂₀ and C₂₈ (20R) triaromatic steroids (*m/z* 231).^g C₂₄ tetracyclic/C₂₆ tricyclic ((S+R)/2) terpanes (*m/z* 191).^h C₂₃ tricyclic terpane/C₃₀ 17 α (H) hopane (*m/z* 191).ⁱ C₂₈-C₂₉ (S+R) tricyclics/C₂₉-C₃₀ 17 α (H) hopanes (*m/z* 191).^j 17 α (H), 21 β (H) and 17 β (H), 21 α (H)-28,30-bisnorhopanes (?) and C₃₀ 17 α (H) hopane (*m/z* 191).^k C₂₉/C₃₀ 17 α (H) hopanes (*m/z* 191).^l C₃₀ 17 β (H), 21 α (H) moretane and 17 α (H), 21 β (H) hopane (*m/z* 191).^m C₃₂ 17 α (H), 21 β (H) bishomohopanes (*m/z* 191).

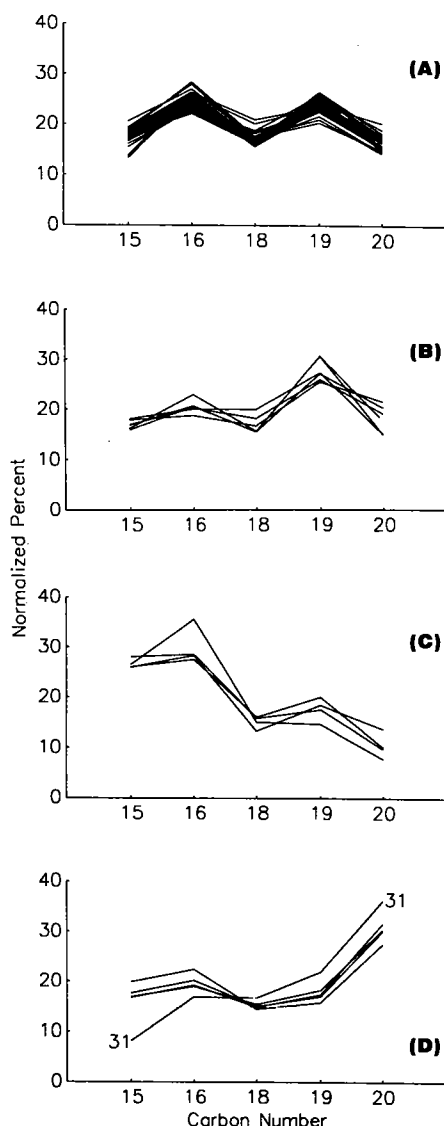


Figure 4. Distribution of isoprenoids in Otachita-area oils. Note: i -C₁₇ usually is not present in crude oils. (A) Most Otachita tectonic belt (OTB) and Nearby oils, (B) and (C) see text for groupings, (D) Cretaceous oils.

pearance" and suggesting an Ordovician source. However, they lack one Ordovician characteristic, relatively low isoprenoid concentrations. Oils 33 and 34, on the other hand, display no Ordovician-type characteristics. This difference raises a series of questions. Do the two sets of oils come from different source rocks? Is either set a mixture of oil types? Or do the differences observed in the Madill samples merely reflect a microfacies change within the same source unit, perhaps one more (or

less) favorable to specific algal growth? It is known that the main contribution of certain marine plankton to organic matter is C₁₄–C₂₀ n -alkanes with an OEP and a maximum at C₁₅ or C₁₇ (Kvenvolden and others, 1987). While it is recognized that the differences noted here may be more a matter of degree than kind, the Madill samples invite further study.

Gas Chromatography–Mass Spectrometry

Terpanes.—The m/z 191 mass chromatograms shown in Figure 5 were selected to illustrate the diversity of terpene profiles obtained for oils in this study. But at the same time, and more important, they reveal features common to all except the Cretaceous oils: hopanes equal to or greater than the tricyclics; C₂₄ tetracyclic equivalent in peak height to each C₂₆ tricyclic isomer; C₃₀ > C₂₉ hopane; homohopanes (C₃₁–C₃₅ doublets) decreasing in peak height with increasing carbon number; and a moderately sized unknown peak tentatively identified as 28,30-bisnorhopanes (BNH) on the basis of its relative retention order (Brooks and others, 1988). What was previously thought to be 17 α (H),21 β (H)-28,30-bisnorhopane is actually co-eluting stereoisomers, the 17 α ,21 β form and the 17 β ,21 α form, and therefore is more appropriately referred to as 28,30 bisnorhopanes (Moldowan and others, 1984; Brooks and others, 1988). Waples and Machihara (1991) noted that the limited worldwide occurrence of this compound is associated with anoxic depositional conditions.

The greatest variation in terpene distributions occurs in the region between the C₂₉ tricyclic doublet and C₂₉ hopane. It appears from close inspection that co-elution is a serious problem on this part of the chromatogram. That is why the two C₂₇ hopanes commonly referred to as T_s and T_m have not been identified (except in the Cretaceous oils) and used as a source or maturity parameter in this study. The width (seen more easily on a full-scale chromatogram) of what might ordinarily be labeled the T_m peak suggests it is not a single-compound peak. From the height of the C₂₈ and C₂₉ tricyclic ter-

pane doublets, it is likely that the C₃₀ doublet is also present and contributing to peak areas in this region. Other possible elutants in this region are a trisnorhopane related to and commonly found with the bisnorhopanes discussed previously. Further GC–MS measurements, such as those provided by metastable-ion monitoring, are needed to help decipher this group of peaks.

In their distribution of terpanes, the Cretaceous oils (Fig. 5B) differ significantly from all other oils in this study. T_s and T_m are readily identified, mostly because there is less small-peak clutter. Hopanes greatly dominate the tricyclic terpanes; the unknown (BNH?) peak is absent; the concentration of C₂₈–C₂₉ tricyclic doublets is diminished; the C₂₄ tetracyclic/C₂₆ tricyclic ratio is roughly 5; C₂₉ > C₃₀ hopane; C₃₁–C₃₅ homohopanes are abundant; and the C₃₅/C₃₄ homohopane ratio is close to 1. All but the first two features have been associated with oils originating from carbonate rocks (Aquino Neto and others, 1983; Clark and Philp, 1989; Riediger and others, 1990; Waples and Machihara, 1991). Peters and Moldowan (1991) found that high C₃₅ homohopane indices coupled with low Pr/Ph ratios, as is found in this group of oils, may indicate reducing, but not necessarily hypersaline, depositional conditions.

Normalized percentage distributions of the tricyclic terpene series (plotted vs. carbon number in Fig. 6) are useful for comparing and contrasting the different groups of oils. All oils show a maximum at C₂₃. Figure 6A reveals little variation in the overall shape of the distribution plots for OTB and Nearby oils. Two exceptions, OTB oil 19 and Nearby oil 32, are shown in Figure 6B. These oils have lower concentrations of C₁₉–C₂₁ members of the series and higher concentrations of the C₂₈–C₂₉ doublets, with C₂₉ noticeably less abundant than C₂₈. Other similarities between these two oils will be discussed later. The unimodal profile of the Cretaceous oils (Fig. 6C) is decidedly different from all others. Distribution patterns for this family of compounds are not yet fully understood in terms of source, environment of deposition, and maturation

effects (see, for example, Šaban and others, 1988; Waples and Machihara, 1991), although recent work by Aquino Neto and others (1992) suggests *tasmanites* as a possible source.

Steranes.—Typical sterane distributions obtained by monitoring the m/z 217 ion are shown in Figure 7. The major peaks are C_{27} and/or C_{29} regular steranes and diasteranes, with C_{29} compounds dominating in all but the East Texas oil (45). It is also the only oil that contains prominent C_{28} steroid compounds. The abundance of diasteranes in all the oils would seem to imply a clay-rich source (Sieskind and others, 1979) although Longman and Palmer (1987) found significant diasteranes in oils derived from clay-free sediments. The presence of diasteranes does not preclude a carbonate source for the Cretaceous oils. Clark and Philp (1989, and references therein) documented a number of recent studies in which diasteranes have been found in oils and extracts from carbonate-evaporite sequences. Where clay minerals are absent or present in low amounts, such as in carbonates, diasteranes may form via mechanisms dependent on a highly reducing depositional setting (Philp and Lewis, 1987).

What are thought to be C_{30} sterane isomers are also present in all samples. Amounts vary from traces and undifferentiated small peaks in most of the oils to distinct peaks in the Cretaceous oils. In addition, the Cretaceous group peaks appear to have slightly different retention times from those in the other groups. Whether the peaks in question are regular C_{30} desmethyl steranes or ring-A methylated C_{29} steranes has not been established.

Aromatic Steroid Hydrocarbons.—Regular steranes in which one or more of three six-membered rings becomes benzene-like through loss of hydrogen atoms are referred to as aromatic or aromatized steroid hydrocarbons. Monoaromatic steroids (MAS) are readily detected by monitoring their mass spectral base peak at m/z 253. Triaromatic steroids (TAS) are generally thought to result from further aromatization of monoaromatic steroids, but may also have a

source independent of MAS (Seifert and others, 1984; Curiale and Odermatt, 1989). Their base peak is at m/z 231.

Typical distributions for both MAS and TAS are presented in Figures 8 and 9, respectively. Because certain data that would assist in the interpretation of the chromatograms were not available, ratio parameters involving individual compounds have not been calculated. However, normalized distribution plots of the largest peaks can be very useful for comparing the oils. Seven peaks in the C_{27} – C_{29} range were selected for comparing monoaromatic steroids (Fig. 8 insets) whereas five peaks in the C_{26} – C_{28} region were chosen to compare the triaromatic steroids (Fig. 9 insets).

The match-ups observed for both the MAS and TAS distributions are similar to those found for the tricyclic terpanes in that (1) all OTB oils except 19 plot with oils from the Ardmore basin area; (2) oils 19 and 32, though somewhat similar to the main group of oils, plot as a separate pair; and (3) Cretaceous oils have distinct distributional patterns. Plots for Nearby oils 45 (East Texas) and 1 (adjacent foreland basin) are also shown separately. (C_{26} – C_{28} TAS peaks for oil 1 were too small to measure.) While the plots display a minor resemblance between East Texas oil and the Cretaceous oils, no other parameters in this study support a compositional relation between these oils.

Source Rocks

The likelihood that a sedimentary rock will generate hydrocarbons depends on the amount and type of organic matter it contains and its level of thermal maturity. Since the rocks selected for this study were known to contain sufficient organic material, only the type and maturity level of that material remained to be determined. GC and GC–MS analyses provided information on the nature and depositional environment of organic matter in the rocks. These two methods, as well as pyrolysis and vitrinite reflectance, provided information on thermal history.

Table 2 summarizes bulk-analysis

data for the rock samples, and Table 5 presents molecular data for the rock extracts.

Pyrolysis

Seventeen shales were chosen for Pyrocell pyrolysis. For purposes of this paper, pyrolysis can be explained as temperature-programmed rapid heating of whole-rock samples in an inert atmosphere to volatilize and release hydrocarbons, which are then detected and measured. At lower temperatures, free hydrocarbons (those already present in the rock pores) are thermally extracted (P_1). With increasing temperature, kerogen thermally degrades to produce a second group of hydrocarbons (P_2). The temperature corresponding to the maximum detector response during the P_2 interval depends on both the heating rate and the maturity of the sample. This temperature is designated T_{max} . Although this pyrolysis technique is similar to the well-known Rock-Eval method, none of the values or parameters reported in Table 2 may be equated directly with those derived from a Rock-Eval analysis. The different heating rates employed here not only shift absolute temperature ranges for the two major peaks but also produce different pyrogram profiles.

Even though the pyrolysis data presented in Table 2 are not directly comparable with similar data generated elsewhere, they are extremely useful for evaluating the rocks of this study on a relative basis. The generation index (GI) calculates free (already generated) hydrocarbons as a percentage of total (initially available) hydrocarbon content. If all hydrocarbons are indigenous to a sample and none has yet migrated, the index serves as a measure of how much kerogen has been converted to petroleum. That is, it functions as a maturity parameter. T_{max} values are also helpful in estimating relative maturity levels; the higher the temperature, the greater the thermal maturity of the rock. The ratio of the combined areas of P_1 and P_2 (actual area measurements in this case since the Pyrocell was not calibrated against a hydrocarbon standard) to the weight of rock used to produce

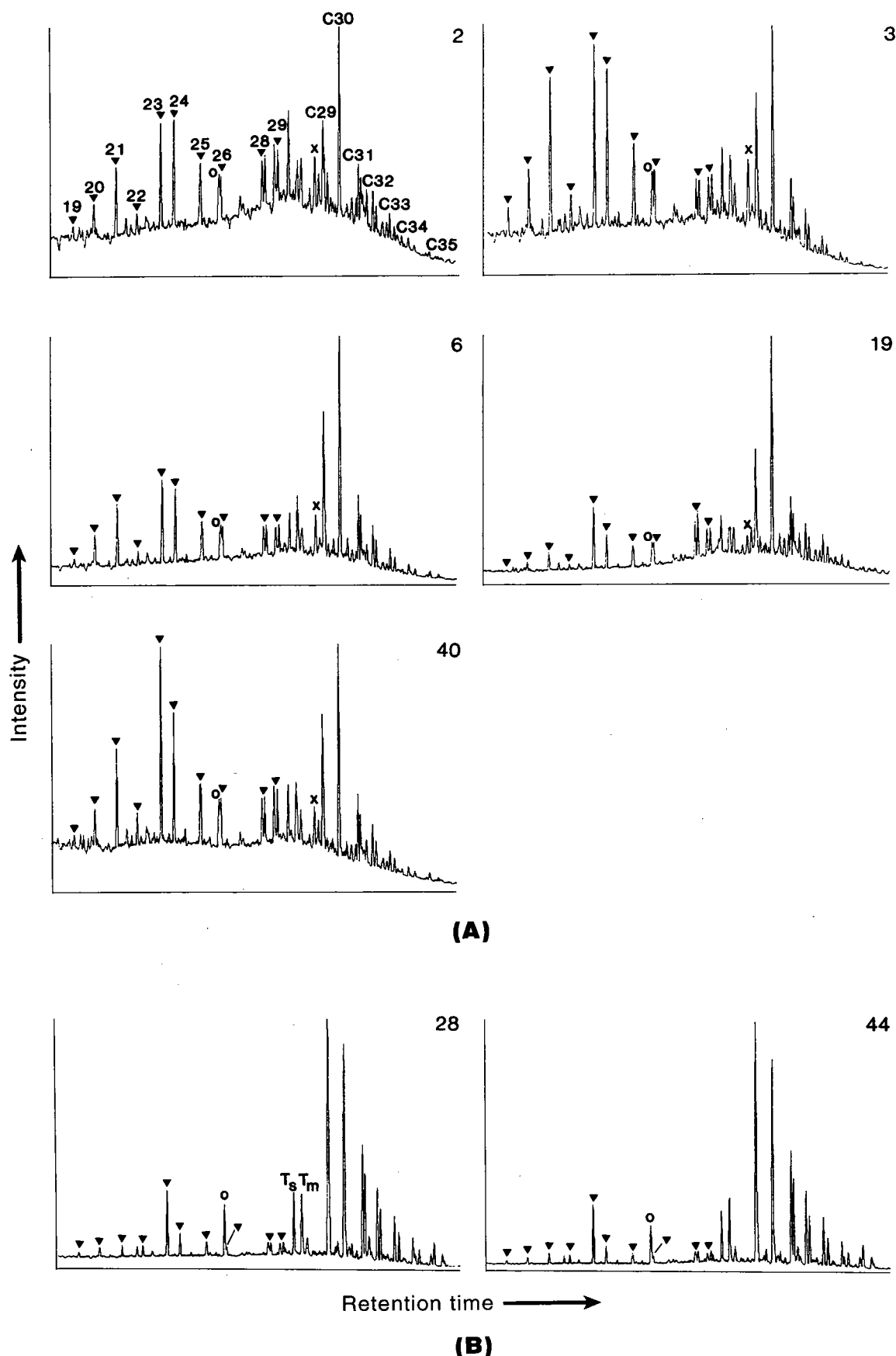


Figure 5 (above and opposite page). Representative m/z 191 mass chromatograms showing distribution of terpanes in Ouachita-area oils: (A) Ouachita tectonic belt (OTB) oils, (B) Cretaceous oils, (C) Nearby oils. ▼ = tricyclic terpane; ○ = tetracyclic terpane; ✕ = tentatively identified as 28,30-bisnorhopanes. Peak identifications are given in Table 6.

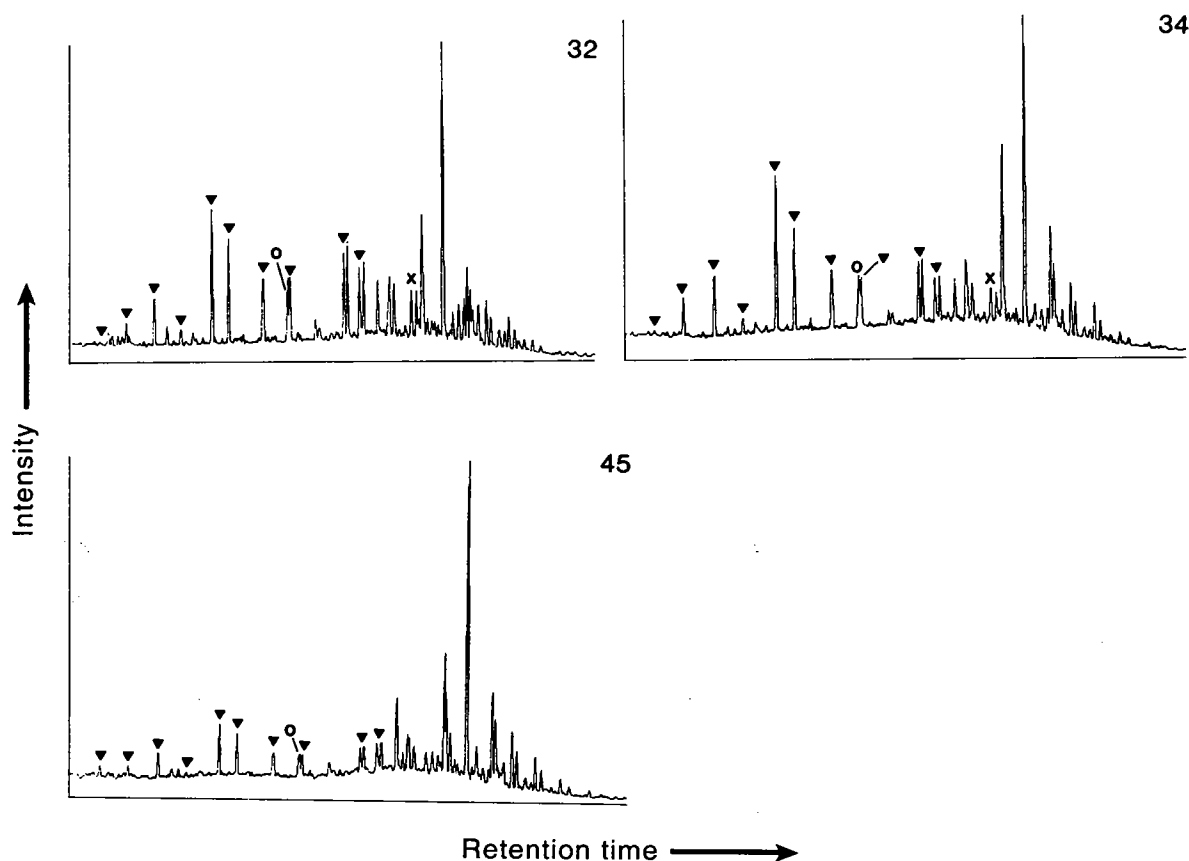


Figure 5 (continued).

(C)

the P_1 and P_2 hydrocarbons provides a rough approximation on a relative scale of the petroleum potential (RPP) of each rock. From the data presented in Table 2, the Atoka, Johns Valley, Jackfork, and Stanley shales have the least potential for generating significant amounts of hydrocarbons; their RPP ratios are in the 5–50 range. On the other hand, all of the Caney, Woodford, Arkansas Novaculite, and Polk Creek samples have significantly greater potential. Their RPP ratios are orders of magnitude higher, ranging from 200 to 1400.

Gas Chromatography

Total saturate fractions of the rock extracts were analyzed by GC. Example chromatograms are shown in Figure 10. The extracts have a slight odd-carbon preference and a maximum in the C_{15} – C_{21} region, with decreasing n -alkane peaks thereafter. Most samples exhibit relatively moderate to significant quantities of sterane and hopane biomarkers and relatively high amounts of isopre-

noids, particularly pristane and phytane. About half the samples display a “hump” of unresolved compounds. Several of the features just described are commonly associated with immaturity in extracts.

The Pr/Ph ratio for non-Atoka samples averages 1.5 and ranges from 1.0 to 2.0 (Table 5). This is the same average ratio calculated for OTB oils, which have a Pr/Ph range of 1.2–2.0.

The tar-sand chromatogram (not shown) depicts a degraded bitumen, with only traces of n -alkanes and isoprenoids visible atop a broad hump of unresolved compounds.

Gas Chromatography–Mass Spectrometry

Representative extract GC–MS chromatograms (Fig. 11) show that the same distribution of terpenoid

Figure 6 (right). Normalized percent of tricyclic terpanes in Ouachita-area oils. Mean value used for C_{28} and C_{29} isomers. (A) Most Ouachita tectonic belt (OTB) and Nearby oils, (B) oil 19 (OTB) and oil 32 (Nearby), (C) Cretaceous oils.

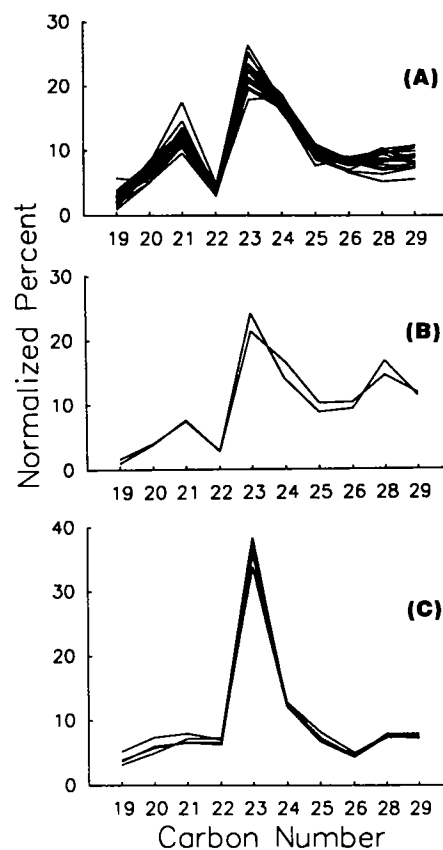


TABLE 5. — GEOCHEMICAL DATA FOR ROCK EXTRACTS

Sample number	Pr ^a Ph	Pr ^b C ₁₇	Ph ^c C ₁₈	20S ^d 20S + 20R	ββ ^e ββ + αα	C ₂₄ tet ^f C ₂₆ tri	Tri ^g H	C ₂₉ H ^h C ₃₀ H	M ⁱ M + H	22S ^j 22S + 22R
1	1.3	1.5	0.77	—	—	—	—	—	—	—
2	2.4	0.44	0.20	—	—	—	—	—	—	—
3	0.8	0.85	0.76	—	—	—	—	—	—	—
4A	0.7	1.1	1.0	0.29	0.20	0.21	0.24	1.2	0.15	0.59
4B	0.7	1.2	1.1	—	—	—	—	—	—	—
5A	3.4	1.1	0.39	—	—	—	—	—	—	—
5B	3.8	1.2	0.32	—	—	—	—	—	—	—
6	1.8	1.1	0.48	—	—	—	—	—	—	—
7	1.8	0.76	0.69	—	—	—	—	—	—	—
8	1.5	1.6	1.5	0.36	0.23	0.77	0.13	0.96	0.17	0.58
9	1.4	1.2	0.94	—	—	—	—	—	—	—
10	2.0	0.37	0.32	—	—	—	—	—	—	—
11	1.9	0.83	0.66	0.40	0.57	1.2	0.26	0.79	0.20	0.58
12	—	—	—	—	—	1.2	—	0.84	0.08	0.59
13	1.5	1.0	0.77	—	—	—	—	—	—	—
14	1.1	0.54	0.44	0.43	0.58	1.4	0.34	0.55	0.17	0.57
15	1.3	1.5	1.4	0.25	0.18	0.61	0.12	0.83	0.16	0.56
16	1.2	0.63	0.46	0.24	0.26	1.2	0.20	0.82	0.18	0.49
17	1.3	0.23	0.19	0.42	0.57	1.7	0.22	0.78	0.13	0.56
18	1.1	1.4	1.0	—	—	—	—	—	—	—
19	1.7	0.51	0.37	—	—	—	—	—	—	—
20A	1.3	0.85	0.71	—	—	—	—	—	—	—
20B	2.0	2.1	0.98	0.44	0.44	2.4	0.05	0.98	0.11	0.57
21A	1.6	2.1	1.5	—	—	—	—	—	—	—
21B	1.6	0.68	0.65	—	—	—	—	—	—	—
22	1.0	0.41	0.36	—	—	—	—	—	—	—

^aPristane/phytane (GC of saturate fraction).^bPristane/*n*-heptadecane (GC of saturate fraction).^cPhytane/*n*-octadecane (GC of saturate fraction).^dC₂₉ 14α(H), 17α(H) steranes (*m/z* 217).^eC₂₉ 14β(H), 17β(H) and 14α(H), 17α(H) steranes (*m/z* 217).^fC₂₄ tetracyclic/C₂₆ tricyclic ((S + R)/2) terpanes (*m/z* 191).^gC₂₈–C₂₉ (S + R) tricyclics/C₂₉–C₃₀ 17α(H) hopanes (*m/z* 191).^hC₂₉/C₃₀ 17α(H) hopanes (*m/z* 191).ⁱC₃₀ 17β(H), 21α(H) moretane and 17α(H), 21β(H) hopane (*m/z* 191).^jC₃₂ 17α(H), 21β(H) bishomohopanes (*m/z* 191).

compounds present in the oils is found in the rock extracts. However, extract concentrations of tricyclic terpanes relative to the hopanes and C₂₄ tetracyclic relative to the C₂₆ tricyclics more closely resemble concentrations found in the OTB and Nearby oils than in the Cretaceous oils. Of particular interest are relative amounts of C₂₈ and C₂₉ tricyclics. C₂₈ exceeds C₂₉ except in the Jackfork extract, where their concentrations roughly parallel each other. In the oils, C₂₈ exceeds C₂₉ in OTB oils 7, 19, and 26 and Nearby oils 32 and 34. Whereas a simultaneous increase of all tricyclic terpanes C₂₈ and above

may signal increased migration distance (Seifert and Moldowan, 1981), the significance of a change or reversal in the ratio of C₂₈ to C₂₉ is not known. Other differences between the extracts and oils on *m/z* 191 mass chromatograms exist primarily in concentrations of compounds affected by maturity: T_s, T_m, moretanes (C₂₉ and C₃₀), and relative amounts of R and S homohopane isomers.

It is difficult to compare sterane assemblages in the rock extracts with those in the oils because of overshadowing maturity effects. Nevertheless, it can be seen in Figure 12 that the rocks, like the oils, contain

mostly C₂₇ and C₂₉ steranes and diasteranes, with detectable C₃₀ isomers.

Selected MAS mass chromatograms (Fig. 13) also reveal resemblances between rock-extract profiles and some whole-oil profiles (Fig. 8). However, it is not possible to make a detailed comparison of monoaromatic steroid hydrocarbons in the rock extracts and oils, since individual compounds have not been identified on either set of chromatograms.

Single-ion mass chromatograms obtained for the tar sand are undecipherable owing to excessive "noise," but a reconstruction of its total ion

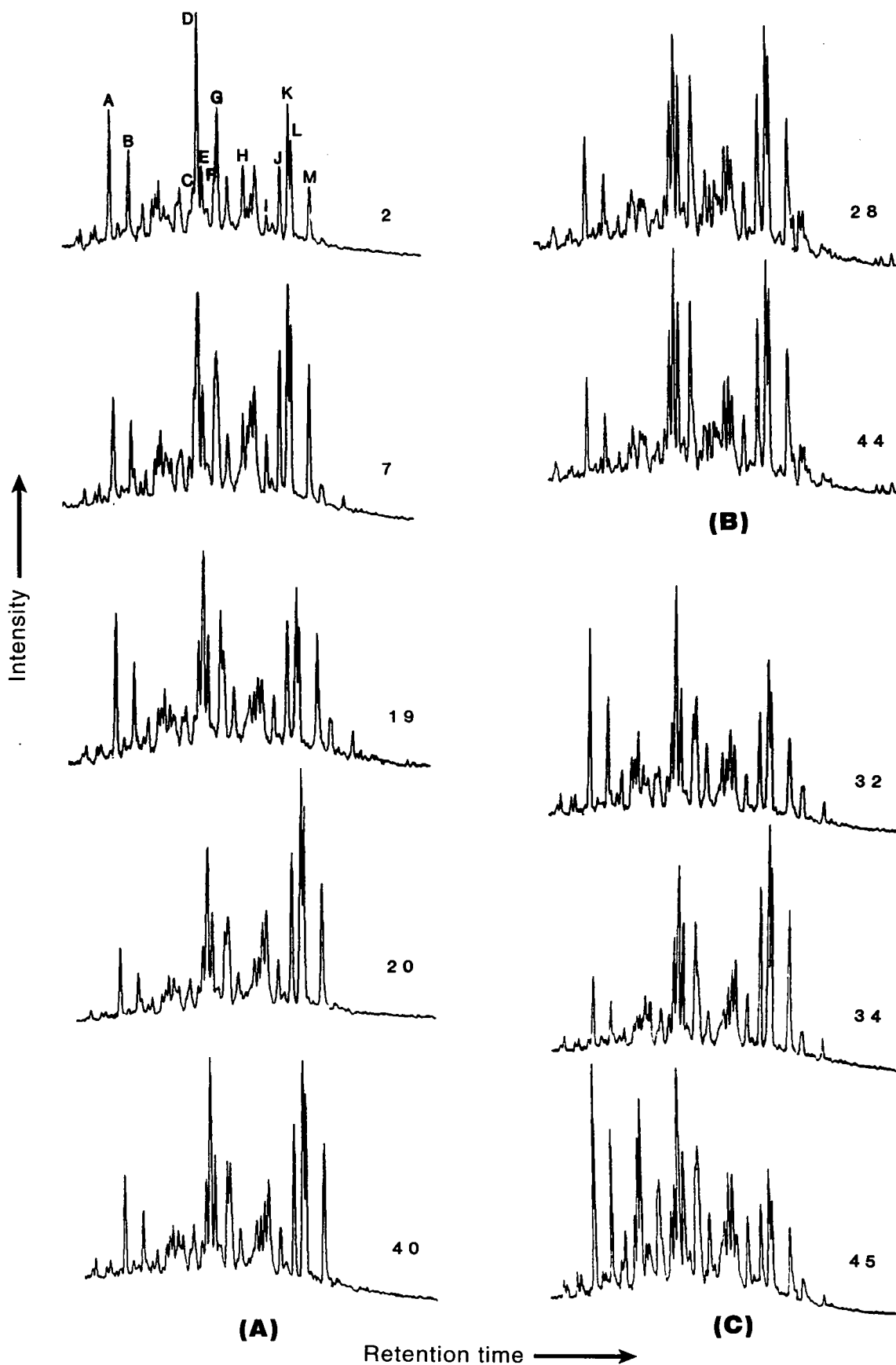


Figure 7. Mass chromatograms (m/z 217) showing similarity of sterane distributions in Ouachita-area oils: (A) Ouachita tectonic belt (OTB) oils, (B) Cretaceous oils, (C) Nearby oils. Peak identifications are given in Table 6.

current (Fig. 11) displays a distribution of hopanes and homohopanes not unlike that found in OTB and most Nearby oils.

DISCUSSION

Oils

Table 4 lists several parameters derived from the extent of various sterane and hopane temperature-induced isomerization (transformation) reactions. Because of their working ranges, these maturity parameters normally have limited use for oils; they are more suitable for rock extracts. However, for shallow oils not likely to have suffered extensive in-reservoir maturation (such as many in this study), these ratios of isomer abundance are an expression of the thermal maturity of the parent source rock at the time the oils migrated. Consequently, they provide information about both the oil and its source rock.

Numerous authors (for example, Zumberge, 1987; Jørgensen and others, 1990; Waples and Machihara, 1991) have pointed out that biomarker maturity parameters are unlikely to agree perfectly with one another and that expecting even general agreement between them and other types of maturity indicators, such as vitrinite reflectance or pyrolysis data, may be optimistic. Such admonitions emphasize the need to consider all available information when assessing maturity levels.

The $C_{29} \alpha\alpha\alpha$ 20S/(20S + 20R) sterane ratio is considered by many to be the most important and reliable biomarker maturity parameter (for example, Fowler and Brooks, 1990; Waples and Machihara, 1991). C_{29} isomers are thought to provide the most accurate data, since they are the least susceptible to peak overlap in mass chromatograms. The ratio stabilizes when the proportion of 20S reaches 50–56% (Jørgensen and others, 1990). This event usually occurs within the oil-generation window, often at about 0.9–1.0% R_o (Sofer and others, 1986), when the main phase of oil expulsion is thought to occur. All oil samples but one have ratios in the equilibrium range (Table 4), indicating that their source rocks were most likely in their main expulsion phase at the time these oils migrated.

TABLE 6. — IDENTIFICATION OF TERPANES AND STERANES

Terpanes (<i>m/z</i> 191)		
19	Tricyclic terpane	C_{19}
20	Tricyclic terpane	C_{20}
21	Tricyclic terpane	C_{21}
22	Tricyclic terpane	C_{22}
23	Tricyclic terpane	C_{23}
24	Tricyclic terpane	C_{24}
25	Tricyclic terpanes (22S + 22R)	C_{25}
o	Tetracyclic terpane	C_{24}
26	Tricyclic terpanes (22S + 22R)	C_{26}
28	Tricyclic terpanes (22S + 22R)	C_{28}
29	Tricyclic terpanes (22S + 22R)	C_{29}
T_s	18 α -22,29,30-trisnorhopane	C_{27}
T_m	17 α -22,29,30-trisnorhopane	C_{27}
x	(17 α ,21 β and/or 17b,21 α)-28,30-bisnorhopanes ?	C_{28}
C_{29}	17 α ,21 β -30-norhopane	C_{29}
y	17 β ,21 α -30-normoretane	C_{29}
C_{30}	17 α ,21 β -hopane	C_{30}
z	17 β ,21 α -moretane	C_{30}
C_{31}	17 α ,21 β -30-homohopanes (22S + 22R)	C_{31}
C_{32}	17 α ,21 β -30,31-bishomohopanes (22S + 22R)	C_{32}
C_{33}	17 α ,21 β -30,31,32-trishomohopanes (22S + 22R)	C_{33}
C_{34}	17 α ,21 β -30,31,32,33-tetrahomohopanes (22S + 22R)	C_{34}
C_{35}	17 α ,21 β -30,31,32,33,34-pentahomohopanes (22S + 22R)	C_{35}
Steranes (<i>m/z</i> 217)		
A	13 β ,17 α -diasterane (20S)	C_{27}
B	13 β ,17 α -diasterane (20R)	C_{27}
C	14 α ,17 α -sterane (20S)	C_{27}
D	13 β ,17 α -diasterane + 14 β ,17 β -sterane (20R)	$C_{29} + C_{27}$
E	14 β ,17 β -sterane (20S)	C_{27}
F	14 α ,17 α -sterane (20R)	C_{27}
G	13 β ,17 α -diasterane (20R)	C_{29}
H	14 α ,17 α -sterane (20S)	C_{28}
I	14 α ,17 α -sterane (20R)	C_{28}
J	14 α ,17 α -sterane (20S)	C_{29}
K	14 β ,17 β -sterane (20R)	C_{29}
L	14 β ,17 β -sterane (20S)	C_{29}
M	14 α ,17 α -sterane (20R)	C_{29}

Oil 1 is the exception. It is not uncommon for highly mature oils and condensates to have anomalous biomarker ratios, an occurrence due frequently to their low absolute biomarker content (Waples and Machihara, 1991).

Isomerization at C_{22} in the 17 α (H),21 β (H) homohopanes is represented in this paper by the C_{32} 22S/(22S + 22R) ratio. Equilibrium values of 55–60% conversion are attained at the beginning of or before the oil-

generation window, corresponding to a vitrinite reflectance of 0.5–0.7% (Zumberge, 1987; Sundararaman and others, 1988; Jørgensen and others, 1990; Waples and Machihara, 1991). Table 4 shows expected equilibrium values (0.57–0.63) for all oil samples.

At a still lower maturity level, about 0.5% R_o , the decrease in concentration of ($\beta\alpha$ -configuration) moretanes relative to their ($\alpha\beta$ -configuration) hopane isomers is essentially com-

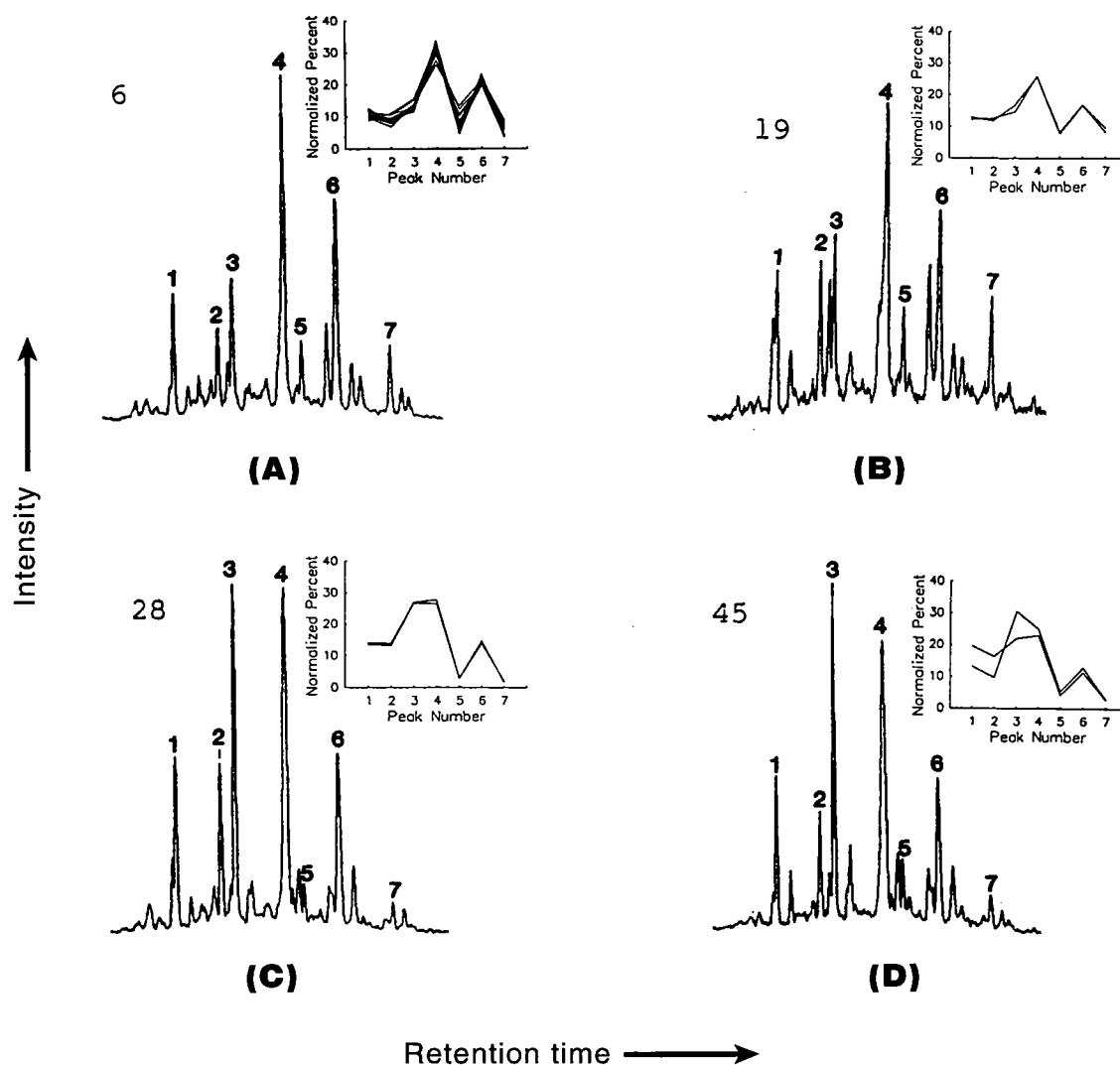


Figure 8. Typical distributions of monoaromatic steranes (m/z 253) in Ouachita-area oils. Numbered peaks refer to those normalized for inset plots. (A) Ouachita tectonic belt (OTB) and Ardmore basin (Nearby) oils, (B) oil 19 (OTB) and oil 32 (Nearby), (C) Cretaceous oils, (D) oils 1 and 45 (Nearby).

plete (Sofer and others, 1986). Typical moretane/hopane ratios for oils are between 0.05 and 0.10 (Zumberge, 1987; Waples and Machihara, 1991). Ratios calculated from the oils in this study (0.06–0.10) fall within this range (Table 4).

Three oils (1, 18, and 22) exhibit several characteristics normally associated with a highly mature oil: API >45°; diminished amounts of n -alkanes above C_{20} ; preponderance of C_{20} – C_{22} over C_{26} – C_{29} aromatic steroids; and large amounts of tricyclic terpanes (especially in the C_{19} – C_{21} range) compared to the higher-molecular-weight hopanes (van Graas, 1990). All three oils are produced from moderately deep (7,500–

9,500 ft) reservoirs. Oil 1 is Spiro-Wapanucka production from a gas field in the foreland basin adjacent to the Ouachita tectonic belt. Oil 18, produced from the Stanley, and oil 22, produced from the Arkansas Novaculite, are both from wells that coproduce gas. The high maturity of these samples is attributed to the degree of thermal evolution of their source rock, not to in-reservoir maturation. At regional geothermal gradients (see Cheung, 1978), burial at 9,500 ft is insufficient to cause the changes observed here.

An attempt to rank the remaining oils by maturity level was unsuccessful owing to the narrow range of thermal maturities involved. While

some differences were noted in the parameters applied, no clear and consistent trend emerged. Among the oils of the Ouachitas, a case could be made that, on the basis of the relative amounts of tricyclic terpanes to hopanes and lower-molecular-weight vs. higher-molecular-weight triaromatic steroids (Table 4), the two easternmost oils, 2 and 3, are the most mature and oil 27, the westernmost sample, is the least mature. Oil 27 also contains the lowest percentage of saturated hydrocarbons (39%) (Table 3) and has the lowest C_{19}/C_{23} tricyclic ratio (0.04) (two other parameters sometimes used to assess maturity; Šaban and others, 1988; Lu Songnian and others, 1990).

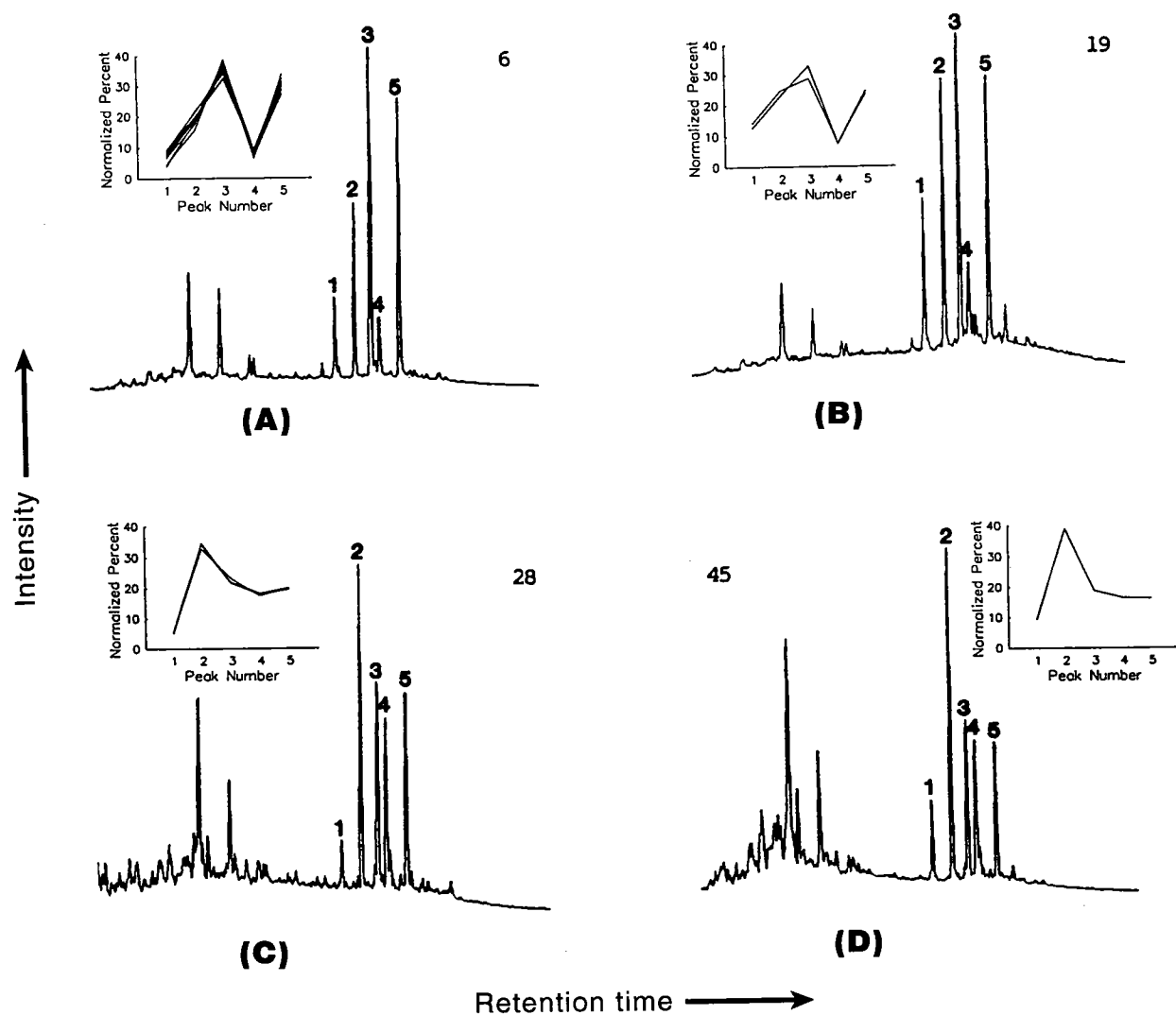


Figure 9. Typical distributions of triaromatic steranes (m/z 231) in Ouachita-area oils. Numbered peaks refer to those normalized for inset plots. (A) Ouachita tectonic belt (OTB) and Ardmore basin (Nearby) oils, (B) oil 19 (OTB) and oil 32 (Nearby), (C) Cretaceous oils, (D) oil 45 (Nearby).

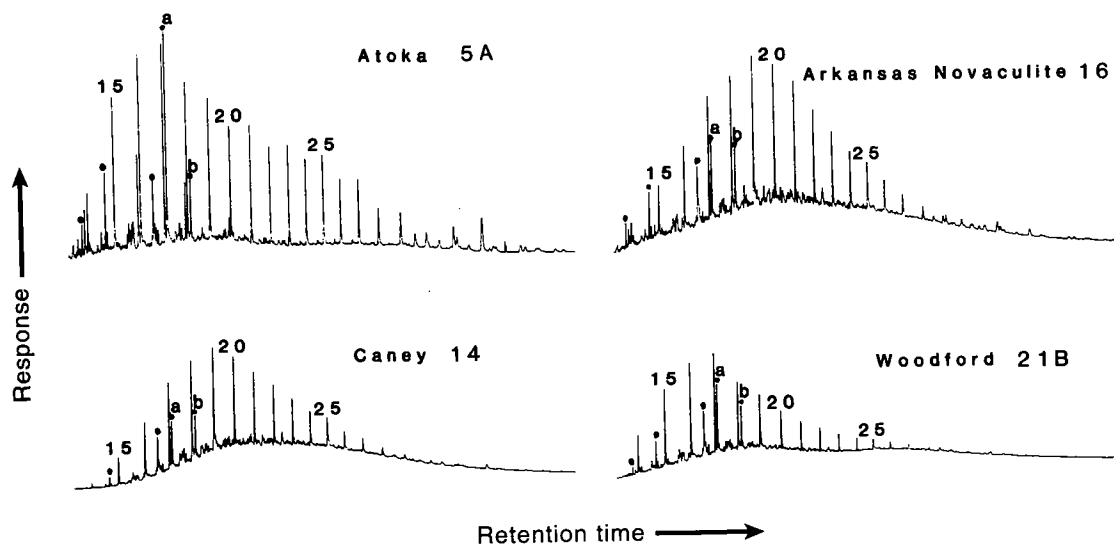


Figure 10. Example gas chromatograms of saturate fraction from Ouachita Mountains rock extracts. Numbers are n -alkane carbon numbers; (●) isoprenoid, (a) pristane, (b) phytane.

In addition to biomarker ratios, secondary bulk parameters such as OEP values (Table 3), percent saturates (Table 3), and *n*-alkane profiles provide further evidence of the mature nature of the oils in this study.

The fact that the Cretaceous oils are biodegraded is probably related to their shallow depth. It is therefore surprising that relatively few oils of the Ouachita tectonic belt show significant biodegradation, since (1) many of them pooled at shallow depths where microbes can survive; and (2) extensive faulting in the northern Ouachitas provides logical conduits for surface water to carry bacteria, oxygen, and nutrients to the oils in that region. Given the maturity level of Ouachita oils, they

were undoubtedly generated at much greater depths. In the subsurface, this same extensive faulting can provide upward-migration pathways by which the oils reach their current near-surface positions.

Considering how vulnerable the exposed tar sand (rock 12 in Fig. 1 and Table 2) is to chemical and microbial attack, it is equally surprising that its bitumen is only moderately degraded. But the presence of trace amounts of *n*-alkanes and isoprenoids confirms that its alteration is limited. This finding could be due to the rock having lower available porosity than other tar sands, thereby restricting the size and type of microbes introduced via meteoric water. A second possible explanation

involves the formation of a tar layer, which would tend to protect underlying oil from further microbial attack.

Rocks

Source Type

On the basis of GC profiles of saturate fractions from the rock extracts (examples shown in Fig. 10), the primary origin of organic material in shales collected from the Ouachita Mountains is marine. Dominant peaks at *n*-C₁₅, *n*-C₁₇, *n*-C₁₉, and *n*-C₂₁ point to an algal and/or bacterial source whereas the low concentration of *n*-alkanes above C₂₅ suggests a limited contribution from land plants. Relative amounts of pristane

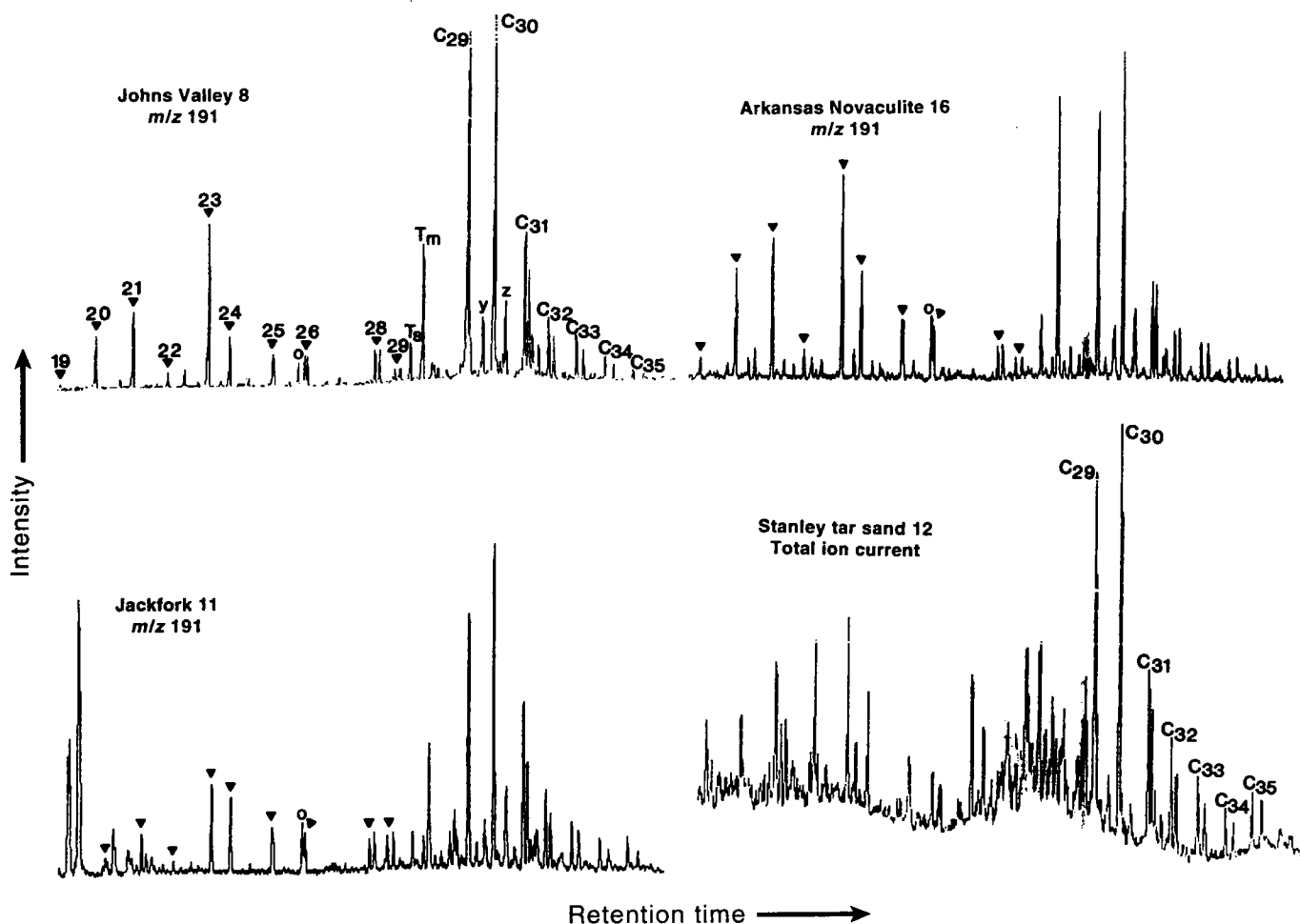


Figure 11. Mass chromatograms showing terpane distributions in some Ouachita Mountains rock extracts. ▼ = tricyclic terpane; ○ = tetracyclic terpane. Peak identifications are given in Table 6. Note: The first two peaks in Jackfork 11 are probably aromatic contaminants resulting from an elution-volume error during fractionation.

and phytane are frequently used to indicate redox conditions at the time of sediment deposition. Low Pr/Ph values (<2) are associated with the rather reducing conditions found in aquatic environments (Jørgensen and others, 1990). Most samples in this study have ratios of <2 (Table 5). Five rocks (Stanley Group 10, Woodford 20B, and Atoka 2, 5A, and 5B) have Pr/Ph ratios in the moderate range (2–4), suggesting that they originated in a slightly more oxic (perhaps nearshore) system.

Other data confirming a primarily aquatic source for the organic matter in shales from the Ouachita Mountains are derived from GC–MS biomarker analysis. All samples analyzed show significant quantities of extended tricyclic terpanes (Fig. 11), a series that Aquino Neto and others (1983) observed to be present in most oils of marine origin but lacking in terrigenous oils

(see also Philp, 1985; Waples and Machihara, 1991). Sterane distributions (Fig. 12) are also consistent with a marine source. Prominent C_{27} steranes have always been associated with marine organisms. Dominant C_{29} steranes, although previously associated with a strong influence from higher land plants, are

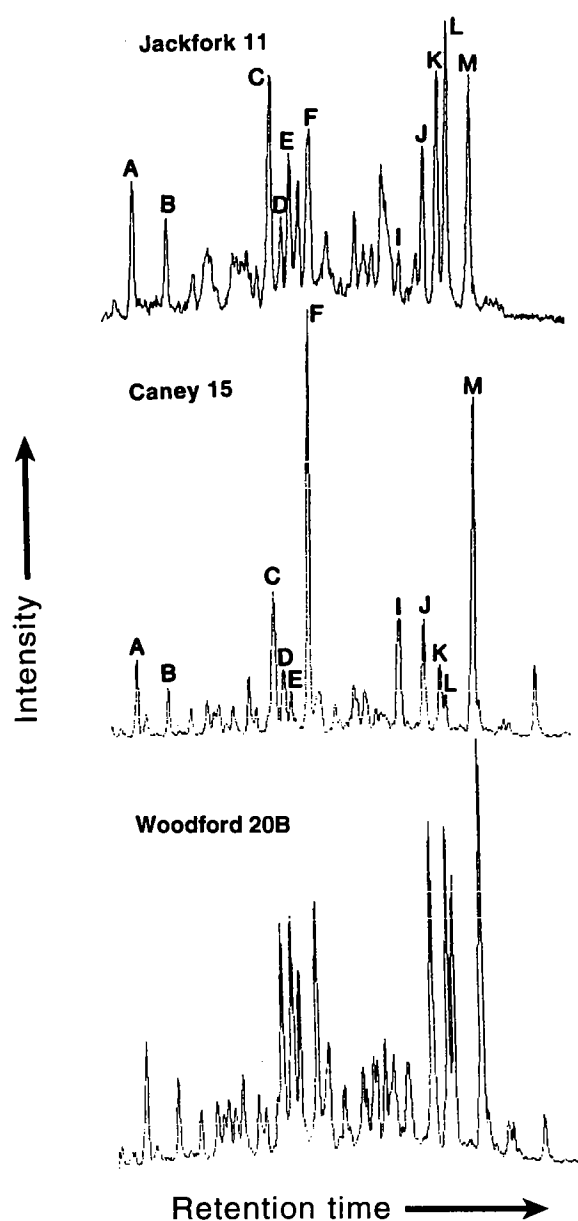


Figure 12. Representative m/z 217 mass chromatograms showing sterane distributions in Ouachita Mountains rock extracts. Peak identifications are given in Table 6.

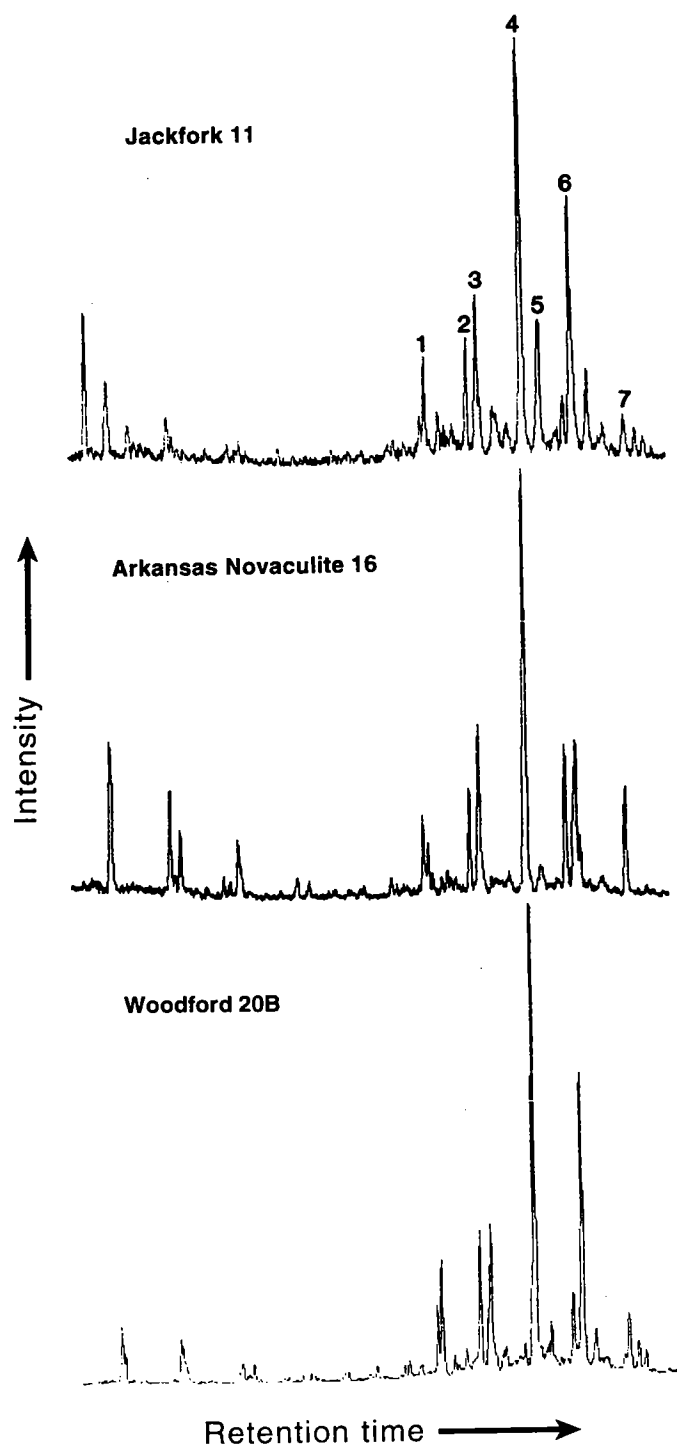


Figure 13. Selected m/z 253 mass chromatograms showing monoaromatic sterane distributions in Ouachita Mountains rock extracts. Numbered peaks refer to those numbered in Figure 8.

now thought to have a second possible source, namely, specific varieties of algae (Fowler and Douglas, 1984; Grantham and Wakefield, 1988).

Whether the peaks eluting after the C_{29} isomers on the m/z 217 mass chromatograms are C_{30} regular steranes or ring-A methylated steranes has not been determined. Methylated steranes commonly have a 4(α or β) ring-placement configuration, although attachment of the methyl group at ring position 2 or 3 has also been observed. The 4-methyl steranes are of two types: 4-methyl-24-ethyl cholestanes and dinosteranes (4,23,24-trimethyl cholestanes); the latter are thought to derive from dinoflagellates. However, dinosteranes have not yet been detected in Paleozoic sedimentary rocks (Summons and others, 1992) and therefore seem unlikely to be present in these rocks. Although this late-eluting group of steranes cannot be fully interpreted until they are completely identified, it should be noted that C_{30} regular desmethyl steranes have been found only in marine deposits whereas 4-methyl cholestanes are present in both marine and freshwater systems (Moldowan and others, 1985; Waples and Machihara, 1990).

Maturity

A combination of whole-rock pyrolysis, vitrinite reflectance, GC, GC-MS, and bulk-composition data was used to assess maturity of possible source rocks. Only gas chromatography was applied to all samples. In some cases, it was the only method applied. Within the limits of the methods used, general agreement on maturity level was found for most samples. Levels range from immature (not yet in oil window) for Arkansas Novaculite 16— $T_{max} = 468^\circ\text{C}$; generation index = 3%; $R_o = 0.47\%$; $20S/(20S + 20R) = 0.24$; $C_{32}S/(S + R) = 0.49$; $M/(M + H) = 0.18$; total hydrocarbons = 33%—to moderately mature (lower half of oil window) for Atoka 2— $T_{max} = 505^\circ\text{C}$; generation index = 30%; total hydrocarbons = 80%—and mature (at or beyond peak oil-generative stage) for Stanley Group 10— $T_{max} = 505^\circ\text{C}$; generation index = 22%; $R_o = 1.12\%$; total hydrocarbons = 59%; concave n -alkane profile.

Atoka 5B produced conflicting

maturity data. Its high concentrations of biomarkers and isoprenoids relative to the n -alkanes; odd carbon-number preference; and low generation index (4%) describe an immature extract. Yet its T_{max} of 501°C suggests a moderately mature kerogen. Possible causes for misleadingly high T_{max} values in pyrolysis data are the presence of recycled and/or inert organic matter or clay minerals (Kingham, 1983; Peters, 1986). The latter can trap hydrocarbons and then release them or their breakdown products at a higher temperature.

A cluster of five Caney (13, 14) and Woodford (17, 18, 19) samples from eastern Latimer County (Fig. 1) are close to or just within the oil window. Average values for this sample group are: $T_{max} = 485^\circ\text{C}$; generation index = 9%; total hydrocarbons = 52%; $20S/(20S + 20R) = 0.42$; $M/(M + H) = 0.15$; and $C_{32}S/(S + R) = 0.56$. Five Atoka (1, 3, 4A, 4B, 6) and two Johns Valley (8, 9) samples from western Latimer County are less mature, as indicated by their average values: $T_{max} = 470^\circ\text{C}$; generation index = 9%; total hydrocarbons = 28%; $20S/(20S + 20R) = 0.33$; $M/(M + H) = 0.16$; and $C_{32}S/(S + R) = 0.58$. High abundances of isoprenoids and other biomarkers relative to the n -alkanes are additional evidence that these latter samples lack maturity.

On the basis of the same factors considered in the preceding paragraphs, four Woodford samples (20A, 20B, 21A, 21B) in T. 2 N., R. 15 E., in Pittsburg County (Fig. 1) are incipiently mature (about to enter the oil window). Located one section north of them, Atoka 7 is low mature (lower part of the oil window). The remaining samples vary in such a way that further grouping by geographic location or formation is not possible. It is of interest to note that all but one of the extracts examined by GC-MS are "mature" according to their $C_{32}22S/(22S + 22R)$ ratios (Table 5). Only the Arkansas Novaculite extract has a ratio less than the equilibrium range of 0.55–0.60. It also has the lowest $20S/(20S + 20R)$ ratio (0.24).

Potential

One approach for predicting source potential of a rock is to compare the amount of convertible or-

ganic matter with total organic carbon content. Results obtained from whole-rock pyrolysis (P_2 per gram of rock) and TOC measurements indicate that the Caney, Woodford, Arkansas Novaculite, and Polk Creek samples have good to very good hydrocarbon-source potential; the Jackfork and one Johns Valley sample have fair potential. The remaining samples for which data are available are unlikely to generate significant quantities of hydrocarbons in spite of their favorable TOC contents (0.5–3.0 wt%). These estimates compare favorably with those made earlier utilizing only pyrolysis data.

It should be pointed out that no testing was done to determine whether these potential source rocks are oil-prone, gas-prone, or both. In general, marine organic matter involves hydrogen-rich type II kerogen, which is oil-prone. However, in his study of Ouachita-facies rocks, Curiale (1983) found mostly vitrinite macerals in the Stanley Group and Arkansas Novaculite and, on that basis, concluded they contained predominantly type III (gas-prone) kerogen. The amount of organic carbon also plays a role in determining whether a rock will produce oil or gas. Some authors (for example, Cooles and others, 1986; Burnham and Braun, 1990) have postulated that organically lean shales (~1.5% TOC or less) are more apt to produce gas, since any oil generated will remain in the rock and be cracked to gas before the fluid volume is sufficient to cause expulsion. Some of the shales in this study that have hydrocarbon generative potential could be considered as moderately lean and therefore more likely to be gas sources.

In summary, shales collected in outcrop from eight stratigraphic units within the Ouachitas were deposited in an environment where the predominant organic source material was marine. Maturation levels vary from thermally immature to mature, following no discernible geographic, stratigraphic, or structural pattern. These findings corroborate Curiale's (1983) thesis that a high-temperature history for this part of the Ouachita province is unfounded. Of 17 samples evaluated, nine have good source potential; two

have fair potential. In particular, four of the Woodford and Caney shales with good source potential are on the threshold or within the lower part of the oil window. Furthermore, the high carbonate content (average 24%) (Table 2) in three of these four rocks may lead to "early" generation of oil. Results from hydrous pyrolysis of kerogen suggest that the presence of CaCO_3 in a source rock lowers the thermal stress necessary to produce oil (Eglinton and others, 1986).

On the basis of the organic richness and thermal maturity demonstrated in this paper for Caney and Woodford outcrop samples in eastern Latimer County, perhaps greater attention is merited by the idea that foreland strata buried beneath the Ouachita allochthon may be a source of Ouachita oils.

Correlations

Geochemical analysis indicates that oils in the Oklahoma part of the Ouachita tectonic belt belong to one family, whereas oils south of the Broken Bow uplift have a distinct, separate origin. Differentiation of these two types of oils is documented with data from every analytical approach used in this study: GC (for isoprenoids); GC-MS; stable carbon isotopes; and elemental analysis (for sulfur). Information on nickel and vanadium contents was not useful for correlation purposes. Significant differences noted in *n*-alkane content (from GC) and bulk-analysis data, such as saturate/aromatic ratios, are not source related for these samples. Rather, they have resulted from a greater degree of biodegradation of the oils found south of the Broken Bow uplift.

Overall sterane and hopane profiles suggest that OTB oils have the same or similar source material. The presence of the unusual compound BNH and its fairly narrow range of concentration vs. C_{30} hopane (0.09–0.25; 0.12–0.25 if oil 19 is excluded) are also evidence for a genetic relation. Correlation is further substantiated by the large number of matching points on normalized distribution curves for tricyclic terpanes (Fig. 6), monoaromatic steroid hydrocarbons (Fig. 8 inset), and triaromatic steroid hydrocarbons (Fig. 9 inset).

Since a ratio can be calculated with relative distribution data from any two points on any two of these curves, the curves actually represent an entire series of correlation ratios.

One oil (19) frequently shows subtle variations from other OTB oils. This oil is produced from the Misenner sandstone immediately below the Woodford Shale and is the only oil sample collected between the traces of the Choctaw and Ti Valley faults. Its differences from other OTB oils are often matched by oil 32, collected farther to the west in the Arkoma basin. Correspondence between these two oils is seen on profiles of their tricyclic terpanes (Fig. 6), monoaromatic steroids (Fig. 8), and triaromatic steroids (Fig. 9); on their gas chromatograms (Fig. 3); and in their isoprenoid ratios (Table 4). Their greatest difference is in their $\delta^{13}\text{C}$ values (Table 3; Fig. 14), which vary by 1.7‰ (–31.2 vs. –29.5) for saturates and 2.1‰ (–30.4 vs. –28.5) for aromatics. Though primarily source-controlled, isotope concentrations of cogenetic oils can vary by as much as 2‰ through the combined effects of natural variation, experimental error, thermal maturity, biodegradation, and/or migration (see review by Weber, 1986). There are no data to support biodegradation as the cause for discrepant $\delta^{13}\text{C}$ values in this case. (If biodegradation is responsible for their high isoprenoid/*n*-alkane ratios, a possibility discussed earlier, the oils have been altered to the same extent. Therefore, one can reasonably expect concomitant changes in other parameters to be roughly "equivalent.") Nor does maturity appear to be the cause. The implied higher maturity of oil 19, based on its heavier isotope values (Clark and Philp, 1989), is not supported by the more reliable molecular maturity parameters listed in Table 4. Both the $\text{C}_{20}/(\text{C}_{20} + \text{C}_{28})$ -20R triaromatic steroid and C_{23} tricyclic/ C_{30} hopane ratios indicate oil 32 to be the more mature oil. Migration factors cannot be ruled out, but the magnitude of the carbon-isotope variation makes it more likely that an actual difference in source material is being reflected. When $\delta^{13}\text{C}$ values for oils 19 and 32 are compared individually with the average for Ouachita oils (excluding oil 19), it becomes

evident that each oil lies within the range of variation permitted for cogenetic oils (Fig. 14). However, oil 19 is ~1‰ heavier than the OTB average of –30.2 for saturates and –29.4 for aromatics, whereas oil 32 is ~1‰ lighter.

A variety of correlation parameters plotted against one another (Fig. 14) further illustrates both similarities and differences among the main group of OTB oils, oil 19, and oil 32. It is important to note that except where carbon isotopes are involved, oils 19 and 32 plot next to one another but at the edge of the OTB cluster. The largest spread of plot points for OTB oils is found in the crossplot of $(\text{Pr} + \text{Ph})/(\text{n-C}_{17} + \text{n-C}_{18})$ and sulfur. The tendency of both these parameters to increase with biodegradation explains the four outliers; 17, 19, and 32 have relatively high isoprenoid/*n*-alkane ratios and 27 has a relatively high sulfur content. All four were discussed previously as biodegraded oils. Differences among OTB oils, oil 19, and oil 32 observable on the remaining crossplots can be attributed to relatively minor changes in depositional material and/or environment. Migration factors could also be involved although their effect on oil composition is not established.

In general, diagnostic features of OTB oils (summarized in Table 7) are *n*-alkane maximum at C_{15} or C_{17} ; decreased amounts of *n*-alkanes above C_{25} ; moderate amounts of isoprenoids with Pr/Ph ratios close to 1.5; average OEP of 1.1; carbon-isotope values around –30‰ (for saturates); moderate sulfur content (~0.4%); C_{29} steranes predominant with abundant C_{27} and C_{29} diasteranes; $\text{C}_{30} > \text{C}_{29}$ hopane; fair abundance of C_{31} – C_{35} homohopanes; prominent tricyclic terpanes extending at least through C_{29} ; C_{24} tetracyclic present in roughly the same amount as C_{26} tricyclic terpanes (ratios range from 0.9 to 1.1, excluding oil 7); and presence of globally rare, source-specific bisnorhopane(s). About 20% of OTB oils exhibit some loss of lower-molecular-weight *n*-alkanes, a minor biodegradation effect.

The source of oil found in Cretaceous strata unconformably overlying Ouachita strata in McCurtain County, less than 10 mi south of the

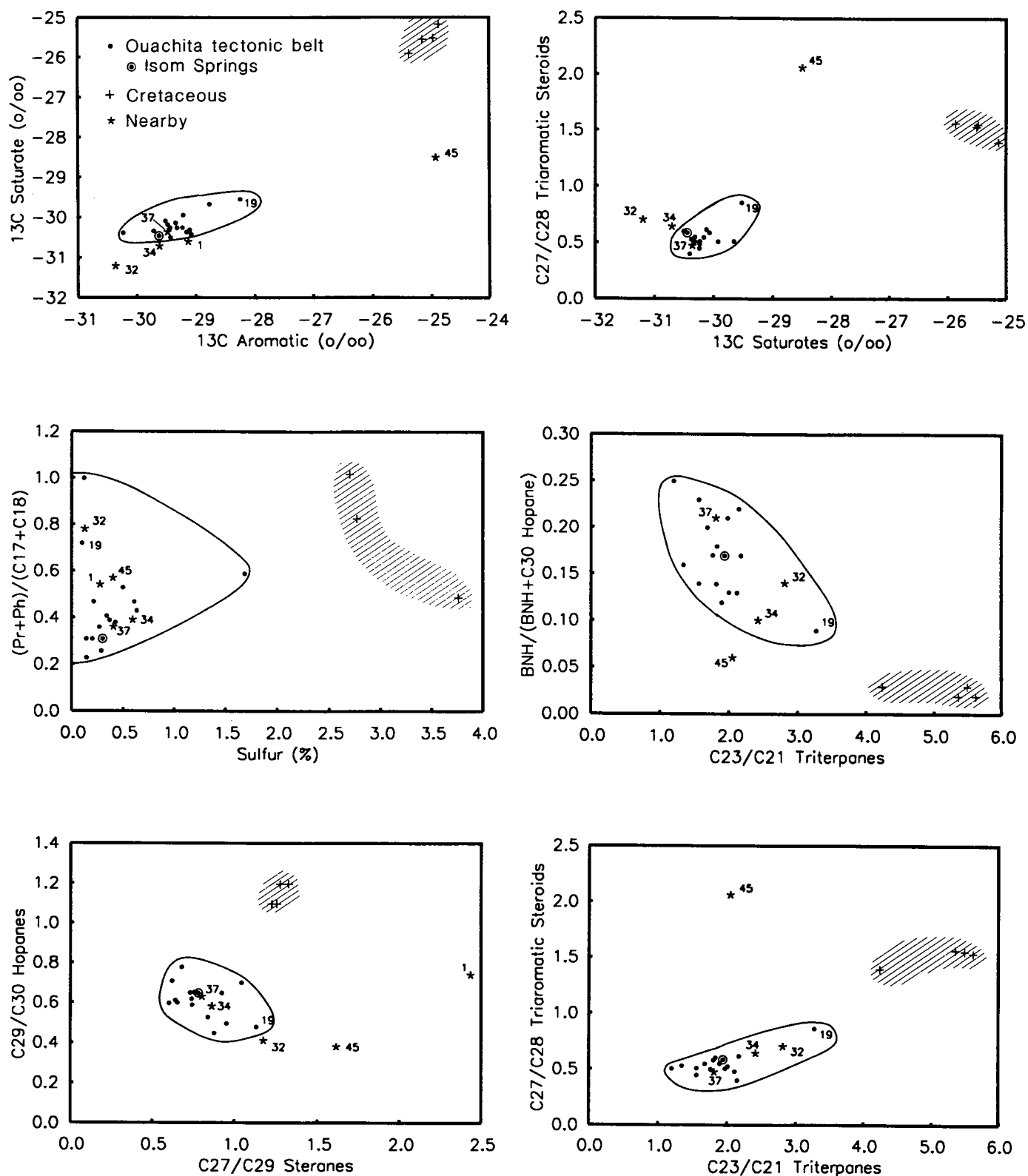


Figure 14. Crossplots of geochemical data showing relations among oils of Ouachita tectonic belt (encircled plot points) and nearby areas. Some oils from nearby areas frequently plot with tectonic belt oils. Hatched area denotes migrated Jurassic Smackover oils from localities near Idabel, Oklahoma, and Talco, Texas.

TABLE 7. — CHEMICAL CHARACTERISTICS OF OUACHITA TECTONIC BELT OILS

		Average (range)
<i>n</i>-Alkanes		
Range	Diminished above C ₂₅	
Maximum	C ₁₅ or C ₁₇	
OEP		1.1 (1.0–1.2)
Isoprenoids		
Pr/Ph	Moderate	1.5 (1.2–2.0)
Steranes		
Predominant homologs	C ₂₉	
Diasteranes	Abundant C ₂₇ and C ₂₉	
Terpanes		
C ₂₉ /C ₃₀ hopanes		0.61 (0.45–0.78)
Homohopanes	Moderate	
28,30-bisnorhopanes	Present (tentative identification)	
Tricyclics	Prominent	
C ₂₄ tetracyclic/C ₂₆ tricyclic		1.0 (0.9–1.3)
Stable carbon isotopes, ‰		
Saturate fraction		–30.2 (–29.5 to –30.5)
Aromatic fraction		–29.3 (–28.3 to –30.2)
Sulfur, %		0.4 (0.1–1.7)

core area of the Ouachitas (Fig. 1), has never been established. Early suppositions included the basal Trinity Group (Cretaceous) and Paleozoic (Carboniferous) strata underlying the Cretaceous (Miser and Purdue, 1919; Honess, 1927; Pitt, 1960). Oils from this locale, the Cretaceous group in this paper, resemble the Type I migrated (Jurassic) Smackover oils of Sassen (1989) and the oils with a (Jurassic) Smackover source from the Mississippi salt basin studied by Sofer (1988). All three sets of oils share similar carbon-isotope compositions (about –25‰) and low Pr/Ph ratios (~0.6). Other compelling source-related similarities between Sofer's oils and the Cretaceous group oils are dominance of C₂₉ over C₃₀ hopane; tricyclic terpane patterns having a large C₂₃ peak; a large C₂₄ tetracyclic peak; relatively high sulfur content (>1%); and slightly elevated C₃₅ homohopanes. All these characteristics are consistent with a carbonate-evaporite origin. Several of Sassen's (1989) East Texas oils were taken from wells between the Idabel W and Talco locations sampled for this paper. He concluded that Type I Smackover oils migrated vertically,

probably along faults, to charge overlying reservoirs along the northern Gulf Rim in East Texas, Louisiana, Arkansas, and Mississippi. In those East Texas and Mississippi fields north of the Smackover updip limit—fields from which the above oil comparisons have been made—he proposed lateral migration to Cretaceous reservoirs. Burgess (1990), in a study of oils from fields of the Mexia-Talco fault system in northeast Texas, also concluded that oils with a (Jurassic) Smackover source had migrated vertically, along fault planes, to reservoirs in younger Cretaceous formations. Recent exploration activity involving updip Smackover production has centered around an area just north of the Talco field (Petzet, 1990).

On the basis of (1) the excellent agreement between key molecular and carbon-isotope compositions presented in this paper and in the references cited above, (2) the geographic proximity of Idabel W and Talco samples to certain of Sassen's (1989) samples, and (3) the location of these samples in Cretaceous strata along the northern edge of the Gulf Coastal Plain, Idabel W oils in south-

east Oklahoma are probably additional examples of Type I migrated Smackover oils as defined by Sassen (1989). Differences in various bulk properties of the Idabel W and Talco oils (Table 3) are attributed to their degree of biodegradation. The higher sulfur, nickel, and vanadium concentrations of the Talco sample imply that it has undergone more severe biodegradation (Waples, 1981). It is worthwhile to point out that although its metals content is higher than Idabel W's by a factor of five, its nickel/vanadium ratio is the same. This finding is consistent with known biodegradation effects. Biodegradation also tends to enrich an oil in its heavier components (Waples, 1981). This type of alteration is evidenced in Talco's lower API gravity, percent saturates, and saturate/aromatic ratio.

Similarities between OTB oils and (Nearby) oils from the Ardmore basin, as presented in chromatograms and normalized distribution plots in this paper, pose some interesting questions regarding the source of Ouachita oils vis-à-vis oils of the Ardmore basin area. The crossplots in Figure 14, which involve correlation parameters based on isoprenoids, steranes, aromatic steroid hydrocarbons, tricyclic terpanes, hopanes, and carbon-isotope ratios, demonstrate the scope of the resemblance between oils found on either side of the leading edge of the Ouachita tectonic belt. It is surprising how few major differences exist. Although a complete set of data is available for only two oils from the adjacent area in the Ardmore basin, oil 37 (Ordovician Oil Creek reservoir) always plots within the Ouachita data cluster and oil 34 (Mississippian Sycamore reservoir) plots within or just outside the cluster. At the very least, the similar geochemistry of these two groups of oils implies that the organic matter in their source rocks must have many of the same attributes.

Assuming the unlikelihood that these Ardmore basin oils have a Ouachita-facies source, do the two groups therefore both have their source in foreland-facies strata? Or could the Silurian-Ordovician Ouachita facies (proposed by Curiale [1983] as the source of Ouachita oils) produce the same organic geochem-

istry profile as the age-equivalent foreland facies? Or, for that matter, is it possible for the Silurian–Ordovician Ouachita facies to produce oils with the same geochemistry as the Devonian Arkansas Novaculite, which has been proposed by Morrison (1980) and Zemmels and others (1985) as the source of Isom Springs oils (viewed as Ouachita oils in this paper)? Faced with geochemically similar oils in Devonian and Ordovician reservoirs of the Michigan basin, Rullkötter and others (1986) dismissed the possibility of a similar biota and depositional environment occurring 100 Ma apart as being too “remote” for serious consideration; they offered migration factors to explain their findings. Perhaps such skepticism is not totally justified. More recently, Curiale (1992) found molecular compositions that support both Devonian and Ordovician sources for oils at both ends of the Marathon–Ouachita fold-and-thrust belt. He suggested that similar organic matter could have been deposited throughout both periods owing to similar basin conditions (anoxic) and similar sedimentation rates (low). He also introduced the possibility of an autochthonous source for the Marathon–Ouachita oils, which, if considered, would involve many of the oils in the present study. In any case, the geochemical similarities between Ouachita and Ardmore basin oils documented in Figure 14 await a fresh, interdisciplinary approach to their interpretation. If this paper accomplishes no more than to engender a reevaluation, from this new perspective, of the origin of Ouachita oils, it will have served a useful purpose.

Considering the relatively minor (known) accumulation of oil in the Ouachitas, corresponding source rock(s) for that oil need not be voluminous. Determining whether Ouachita facies or foreland facies are the source would seem to require uncovering real and distinct differences between the extracts of these two rock types, differences that can be detected in the oils. Unfortunately, this requirement was not met in this study. None of the rocks analyzed appears to be a source for any of the oils. However, on the basis of geochemistry alone, some of their

more mature counterparts, including both foreland and Ouachita rocks, merit consideration as candidate sources. Perhaps the ultimate decision regarding the source of Ouachita oils will rest not on geochemical evidence but on limitations imposed by geologic factors on what appear to be geochemically feasible sources.

CONCLUSIONS

Examination of 45 crude oils from the Ouachita tectonic province and nearby areas has led to the following conclusions:

1. Oils along the entire length of the exposed or buried tectonic belt in Oklahoma are of one genetic type. They can be characterized as having an *n*-alkane maximum at C_{15} or C_{17} ; moderate amounts of isoprenoids; Pr/Ph ratios close to 1.5; OEP close to unity (1.1); carbon-isotope (saturate) values around -30‰ ; average sulfur content of 0.4%; abundant C_{29} and C_{27} steranes and diasteranes; C_{30} greater than C_{29} hopane; fairly abundant homohopanes; prominent tricyclic terpanes; and the presence of 28,30-bisnorhopanes (tentative identification). These combined features describe a moderately mature to mature, algal-based, predominantly marine-type oil, generated in clastic source rocks under mildly reducing conditions.

Oil from Wesley E field, located between the traces of the Choctaw and Ti Valley faults in the western Ouachitas, is a subdivision of this genetic type. Distributions of some of its biomarkers vary subtly but consistently from those of the main family, indicating minor differences in source material and/or depositional environment.

2. Ocone field (western Arkoma basin) oil is molecularly similar to Wesley E oil but has a slightly lighter (by 1.7‰ for saturates and 2.1‰ for aromatics) carbon-isotope ratio.

3. Oils in front of the Ouachita tectonic belt in the Ardmore basin area are remarkably similar in both chemical and carbon-isotope composition to oils within the belt. The implication of this finding warrants a new, interdisciplinary attempt to explain the petroleum system(s) of the Ouachita province.

4. Oils south of the Broken Bow uplift are genetically related to Talco (Texas) oil, whose source is considered to be the Jurassic Smackover (Sassen, 1989). These oils exhibit characteristics consistent with a carbonate-evaporite origin: low Pr/Ph ratios (0.6); heavy carbon-isotope compositions (about -25‰); dominance of C_{29} hopane over C_{30} hopane; relatively high sulfur content ($>1\%$); slightly elevated C_{35} homohopanes; and a relatively large C_{24} tetracyclic terpane peak. Both the Broken Bow and Talco oils are mildly biodegraded, but the Talco oil shows more pronounced effects in its higher concentrations of sulfur, nickel, and vanadium.

Investigation of one tar sand and 25 shale outcrops representing eight stratigraphic intervals in the Ouachitas has led to the following conclusions:

5. Atoka samples are the most organically lean, averaging 1.1 wt% TOC, vs. 4.6 wt% for all other formations combined.

6. In general, the rocks contain primarily marine organic matter deposited where reducing conditions tended to prevail. This conclusion is based on dominant C_{17} , C_{19} , and C_{21} *n*-alkanes; Pr/Ph ratios between 1 and 2 (except for some Atoka samples); significant quantities of tricyclic terpanes; prominent C_{27} and C_{29} steranes; and the presence of C_{30} sterane isomers in the rock extracts.

7. On the basis of a combination of pyrolysis, vitrinite reflectance, GC, GC-MS, and bulk-composition data, maturity levels for the rocks range from immature to mature, following no discernible geographic, stratigraphic, or structural pattern.

8. On the basis of pyrolysis and TOC measurements, nine Caney, Woodford, Arkansas Novaculite, and Polk Creek samples have good hydrocarbon-source potential; the Jackfork sample and one Johns Valley sample have fair potential.

9. None of the rocks with good potential is mature enough to be the source of the Ouachita oils, which bear biomarker signatures of a source rock at peak generating capacity. However, biomarker assemblages of several of the rock extracts resemble those of the oils, suggesting

that where more deeply buried, those formations—both foreland and Ouachita facies—should be considered as possible sources for Ouachita oils.

10. Insufficient geochemical evidence was developed to draw a conclusion regarding the relation of a Stanley tar sand bitumen to its neighboring Ouachita oils. However, the bitumen does have a hopane distribution resembling that of the oils.

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