

# Characterization of Oil Types in the Ardmore and Marietta Basins, Southern Oklahoma Aulacogen

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**ABSTRACT.**—Gas chromatography analyses (GC-FID, GC-FPD, GC-MS) of 385 crude oils from the Ardmore and Marietta basins establishes the presence of seven oil families. These groups (types) are established by the distribution of n-alkanes, acyclic isoprenoids, alkylated cyclic hydrocarbons, alkylated sulfur compounds, steranes, hopanes, aryl-isoprenoids, and carbon isotopes. The type designations are reinforced by the stratigraphic distribution of oil types. In summary, oil Types A through E appear to correlate with source facies within Pennsylvanian (Atoka Formation?), Mississippian (Goddard, Caney, and Sycamore Formations), Devonian-Mississippian (Woodford Shale), upper Middle Ordovician (Viola Group), and Middle Ordovician (Simpson Group) rocks, respectively. The genetic interpretation of Type F oils is uncertain due to geochemical considerations, while Type G oils are complicated by their association with the Ouachita facies. The frequency distribution of these oil types indicates that Type C oils are dominant, but other oil types are locally abundant and provide new exploration targets.

## INTRODUCTION

The southern Oklahoma aulacogen has been an area of significant hydrocarbon exploration for more than 75 years. Despite this fact, basic questions relating to the origins of southern Oklahoma oils remain unanswered. The number of oil families, their source beds, the nature of the migration paths, and the dominant alteration processes have not been adequately addressed. As an initial approach to answer these questions, I define the end-member oil types from gas chromatographic analyses of 385 oil samples collected throughout the study area.

## Geologic Setting

The southern Oklahoma aulacogen has been defined by Hoffmann and others (1974), Pruatt (1975), Thompson (1976), and Wickham (1978a). This report covers the area bounded by the Arbuckle Mountains to the northeast, Ouachita facies to the southeast, Muenster uplift to the southwest, and the Wichita uplift/Anadarko basin to the northwest. Included in this area are the Ardmore basin, Marietta basin, and Criner Hills uplift (Fig. 1).

## Samples

A total of 385 oil samples from 83 fields were obtained as part of a basin modeling research project. These samples provided complete stratigraphic control (Fig. 2), as well as a broad geo-

graphic base (Fig. 3). In some of the multipay fields, samples were obtained from each producing zone and in some cases, where faults offset equivalent producing horizons, samples were collected from both sides of the fault (Fig. 4).

## Analytical Procedures

All oil samples were analyzed by whole-oil, capillary-column, gas chromatography using a Hewlett-Packard 5830 instrument equipped with a flame ionization detector (GC-FID). The capillary column was nonpolar with a bonded phase (Quadrex 007, 50 m × 0.25 mm ID with 0.5 μm film thickness). The oven was programmed from 35°C (10 min) to 300°C at 8°C/min with a final hold-time of 45 min. Other temperature zones include the split inlet (100:1) at 300°C and the detector at 350°C.

A total of 125 oil samples were analyzed for their sulfur-compound distribution by whole-oil gas chromatography using a Hewlett-Packard 5890A instrument equipped with a flame photometric detector (GC-FPD). A temperature programmed injector was used (50–300°C) in the split mode (100:1) along with the capillary column as described above. The oven was programmed from 35°C (2 min) to 225°C at 4°C/min and to 300°C at 8°C/min with a final hold-time of 25 min.

Fifty samples were analyzed by whole-oil gas chromatography-mass spectrometry (GC-MS) using an HP 5890A gas chromatograph interfaced to an HP 5970B mass selective detector. A conven-

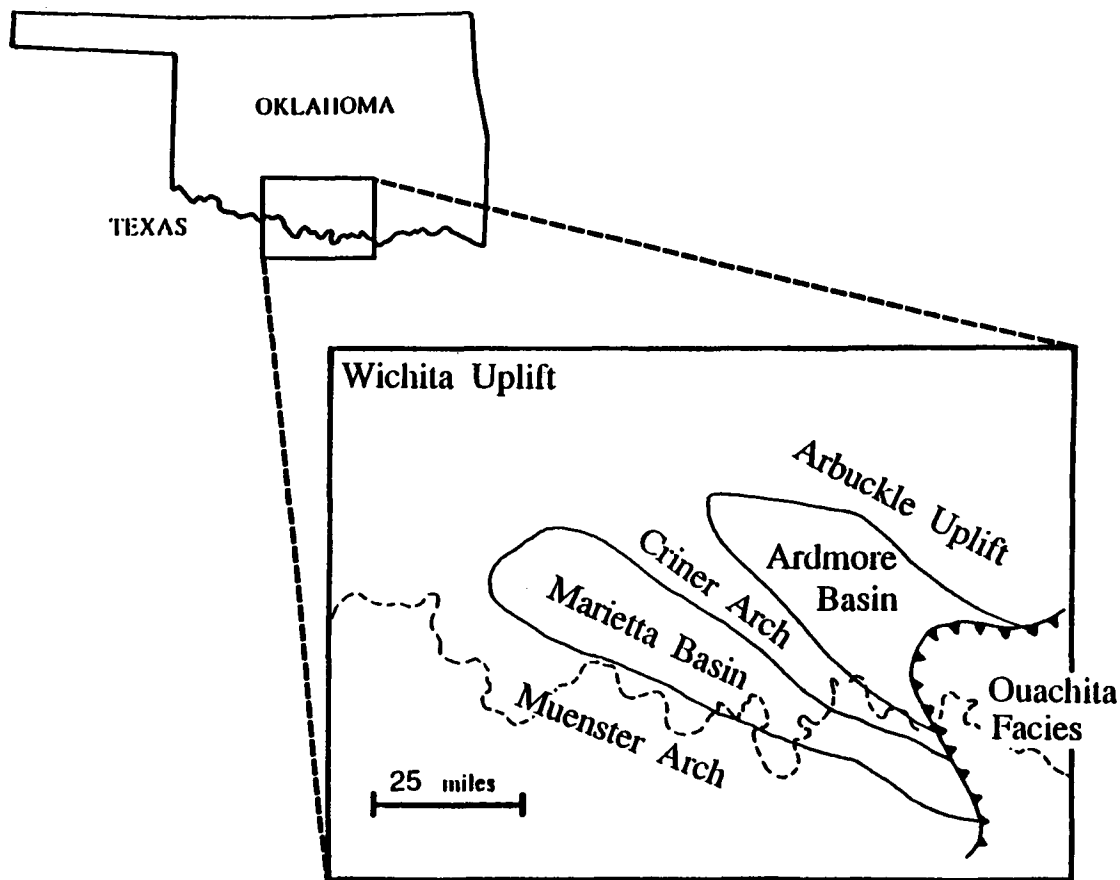


Figure 1. Major geologic provinces in the study area.

tional split injection (100:1) was used at 300°C. The capillary column used on this instrument was a J&W DB-5 (60 m × 0.25 mm ID with 0.25 μm film thickness). The oven was programmed from 35°C (2 min) to 325°C at 2°C/min with a 60 min hold-time. Data were collected in single-ion monitoring (SIM) mode for 20 ions with a 30 msec dwell time.

All chromatograms were quantified by peak height measurement and the data were transcribed to a spreadsheet for further analysis. Detailed data analysis is continuing, but the conclusions regarding the genetic oil types are reported at this time.

## RESULTS

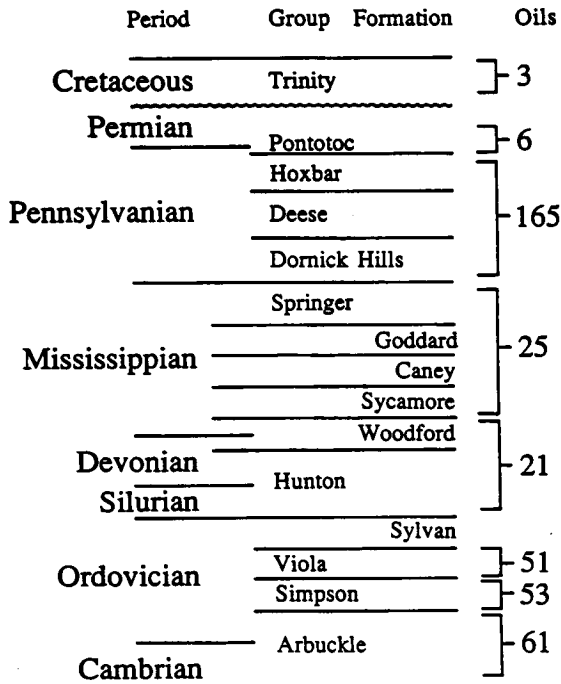
Gas chromatography of whole-oil samples revealed significant differences in the oil types reservoired in the study area. The parameters used to establish the oil groups (types) include the relative n-alkane distribution, acyclic isoprenoids, alkylated cyclic hydrocarbons, alkylated sulfur compounds, aryl-isoprenoids, hopanes, steranes, and carbon isotopes.

### Type A Oils

Oils assigned to Type A are distinguished from the other oil types on the basis of their increased abundance of nC<sub>15</sub> alkanes, very little odd-carbon preference in the nC<sub>11</sub>–nC<sub>20</sub> range alkanes, and their more linear n-alkane profile (Figs. 5,6). They display moderate abundances of isoprenoids with typical Pr/Ph, Pr/nC<sub>17</sub>, and Ph/nC<sub>18</sub> values of 1.31, 0.52, and 0.47, respectively. A moderate amount of aryl-isoprenoids is observed along with minor alkylated cyclic compounds. The per mil carbon-isotope values obtained for two of these oils averaged –30.6, –30.8, and –30.3 for the whole oil, saturate, and aromatic fractions, respectively. Type A oils are generally located in Pennsylvanian reservoirs adjacent to areas where Pennsylvanian sediments are within the oil window (e.g., Leon North, Mountain Creek, and Isom Springs SW fields).

### Type B Oils

Oils assigned to Type B have n-alkane profiles similar to the Type A oils (Figs. 5,6), but have increased abundances of acyclic isoprenoids. Typi-



cal values for Pr/Ph, Pr/nC<sub>17</sub>, and Ph/nC<sub>18</sub> are 1.41, 0.85, and 0.70, respectively. Again, moderate amounts of aryl-isoprenoids are observed along with minor alkylated cyclic compounds. The per mil carbon-isotope values obtained for two of these oils averaged -30.8, -30.9, and -30.3 for the whole oil, saturate, and aromatic fractions, respectively. Type B oils commonly occur in Mississippian-age reservoirs, particularly within the Springer Group (e.g., Aylesworth SE, Sho-Vel-Tum, and Springer fields).

**Type C Oils**

Oils assigned to Type C have n-alkane profiles that decrease exponentially with increasing carbon number from a maximum in the mid-range n-alkanes (Figs. 5,6). These oils display a minor to trace odd-carbon preference in the nC<sub>11</sub>-nC<sub>20</sub> alkane range and contain relatively minor abundances of isoprenoids with typical Pr/Ph, Pr/nC<sub>17</sub>, and Ph/nC<sub>18</sub> values of 1.48, 0.32, and 0.27, respectively. The per mil carbon-isotope values obtained for two of these oils averaged -30.1, -30.4, and -29.9 for the whole oil, saturate, and aromatic fractions, respectively. Similar to Type A and B oils, Type C oils have a moderate amount of aryl-isoprenoids, minor alkylated cyclic compounds,

Figure 2. Stratigraphic distribution of 385 oil samples.

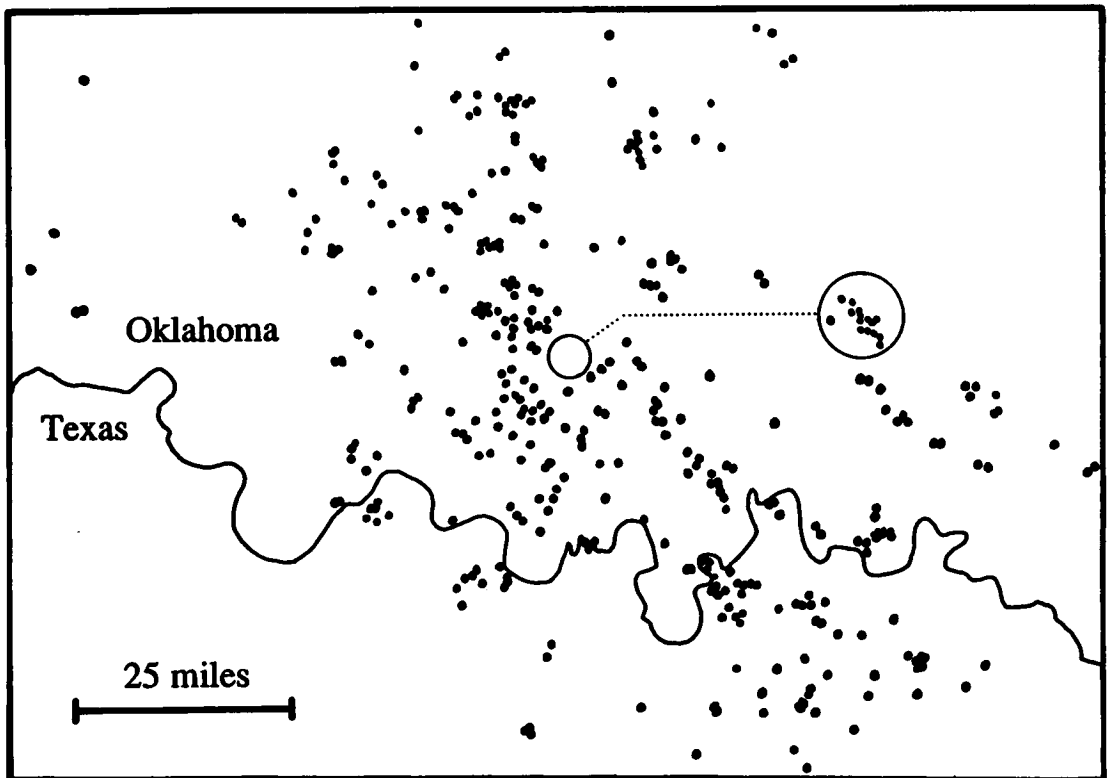


Figure 3. Geographic distribution of 385 oil samples.

SW Enville Field  
COOL CREEK #2-1

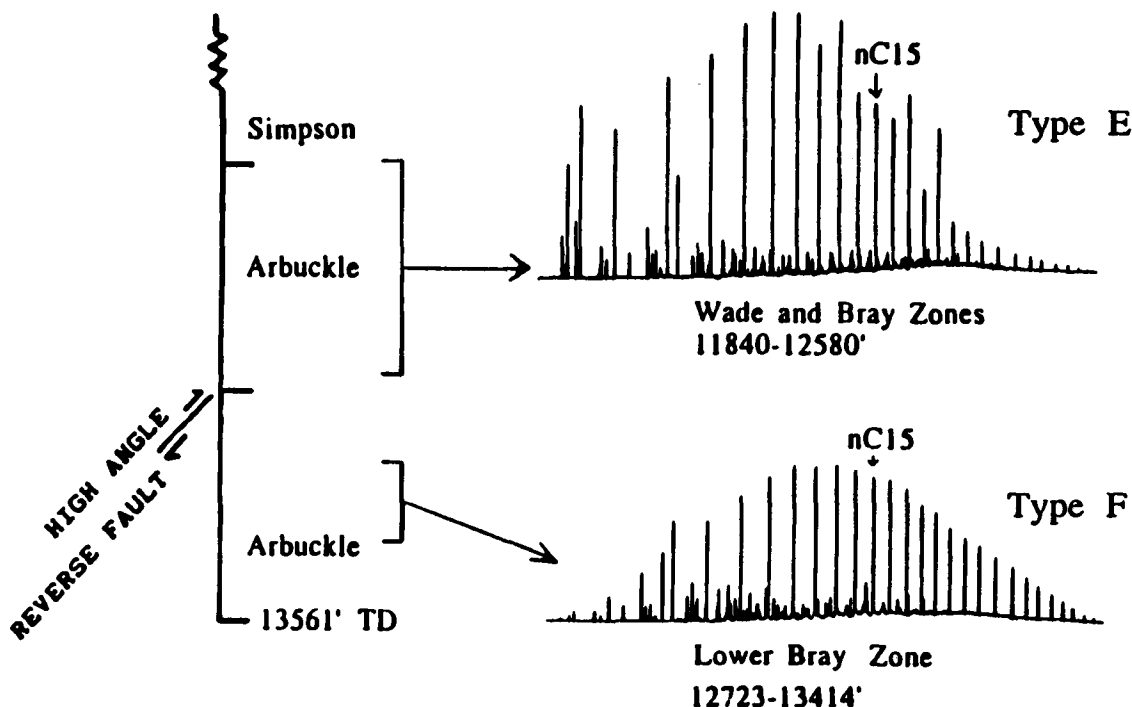


Figure 4. Illustration of the importance of systematic sample collection.

and trace concentrations of alkylated cyclic sulfur compounds. Type C oils are quite common in Hunton Group/Woodford Formation reservoirs (e.g., Aylesworth, Isom Springs, and Springer fields), but also occur in all the producing horizons.

#### Type D Oils

Oils assigned to Type D have some characteristics that may lead some investigators to interpret Type D as a mixed oil type (e.g., mixed Type C + Type E). However, because Type D oils contain some compounds that have not been observed in the other oil groups, a mixing origin is unlikely. Type D oils have an increased abundance of mid-range n-alkanes that contain a moderate odd-carbon preference in the  $nC_{11}$ - $nC_{20}$  range (Figs. 5,6). They contain a moderate amount of aryl-isoprenoids and typical values for Pr/Ph, Pr/ $nC_{17}$ , and Ph/ $nC_{18}$  are 1.10, 0.31, and 0.51, respectively. The per mil carbon-isotope values for two of these oils averaged  $-31.1$ ,  $-31.3$ , and  $-30.9$  for the whole oil, saturate, and aromatic fractions, respectively. The hydrocarbons that make Type D oils unique include the anomalously high concentrations of alkylated cyclic compounds (e.g., n-alkylcyclo-

hexanes and n-alkylbenzenes) with an odd-carbon preference (Fig. 7), and moderate concentrations of alkylated sulfur compounds (Fig. 8). The extended hopanes ( $C_{31}$ - $C_{35}$  triterpanes) are relatively abundant (Fig. 9), but the  $C_{34}/C_{35}$  hopane ratio is generally less than one. The end-member Type D oils commonly occur in Ordovician-age Viola Group reservoirs, particularly within the Marietta basin (e.g., Joiner City, Reck East, and Atlee fields).

#### Type E Oils

Oils that are dominated by n-alkanes with a strong odd-carbon preference in the  $C_{11}$  to  $C_{20}$  range and contain relatively minor amounts of the  $nC_{20}$  hydrocarbons are assigned to Type E (Figs. 5,6). These oils display minor to trace amounts of isoprenoids with typical Pr/Ph, Pr/ $nC_{17}$ , and Ph/ $nC_{18}$  ratios of 1.41, 0.15, and 0.18, respectively. While these oils contain only trace amounts of n-alkylated cyclic hydrocarbons, sulfur compounds, and aryl-isoprenoids, they contain relatively abundant hopanes (vs. steranes) and relatively high  $C_{29}/C_{30}$  hopane ratios. The carbon-isotope values obtained for two of these oils are anomalously light; average values from whole oil, satu-

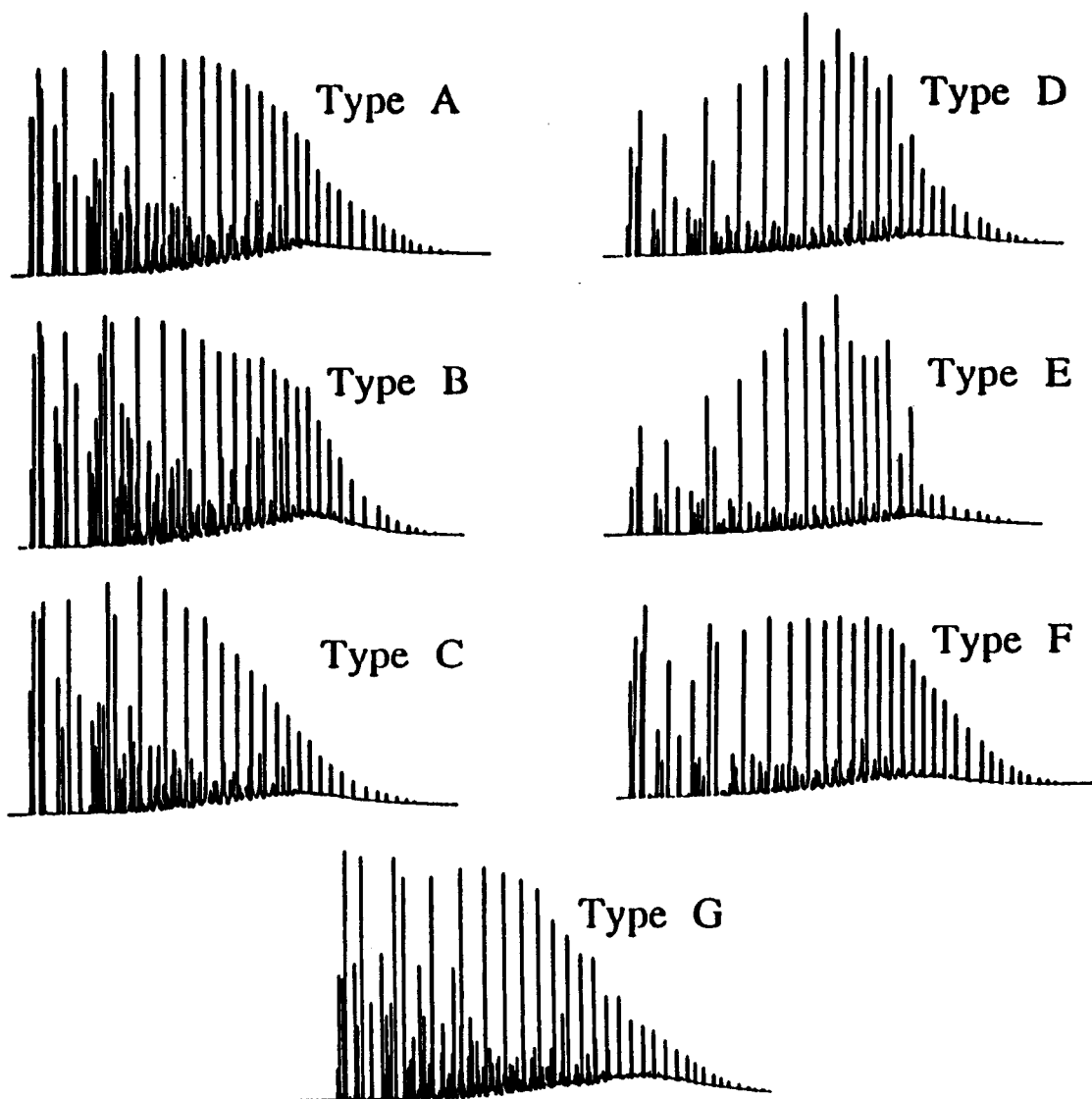


Figure 5. Gas chromatograms (GC-FID) of the end-member oil types.

rate, and aromatic fractions are  $-33.2\%$ ,  $-33.5\%$ , and  $-32.9\%$ , respectively. As a group, Type E oils are generally restricted to Simpson and Arbuckle Group reservoirs (e.g., Robberson SE, Joiner City SE, and Ardmore SW fields).

#### Type F Oils

Oils assigned to Type F are unusual on both geochemical and stratigraphic grounds. These oils have smooth n-alkane profiles, minor isoprenoids (Figs. 5,6), and typical Pr/Ph, Pr/nC<sub>17</sub>, and Ph/nC<sub>18</sub> ratios of 1.64, 0.28, and 0.23, respectively. These oils contain relatively minor amounts of biomarker molecules (e.g., aryl-isoprenoids, hopanes, steranes) and have rather high maturity values (Fig. 10). The per mil carbon-isotope values ob-

tained for two of these oils averaged  $-30.6$ ,  $-30.7$ , and  $-30.3$  for the whole oil, saturate, and aromatic fractions, respectively. These oils are restricted to Arbuckle Group reservoirs (e.g., drill stem test from McKenzie Hill and Cool Creek Formations at Cottonwood Creek field, Cool Creek Formation at Springer field, and the West Spring Creek Formation at Enville SW field).

#### Type G Oils

Oils assigned to Type G have some characteristics that may be interpreted as originating from mixing oil types, but because of their close proximity to the Ouachita facies (Fig. 1) these oils are assigned to one group for the purposes of this report until additional work can be completed.

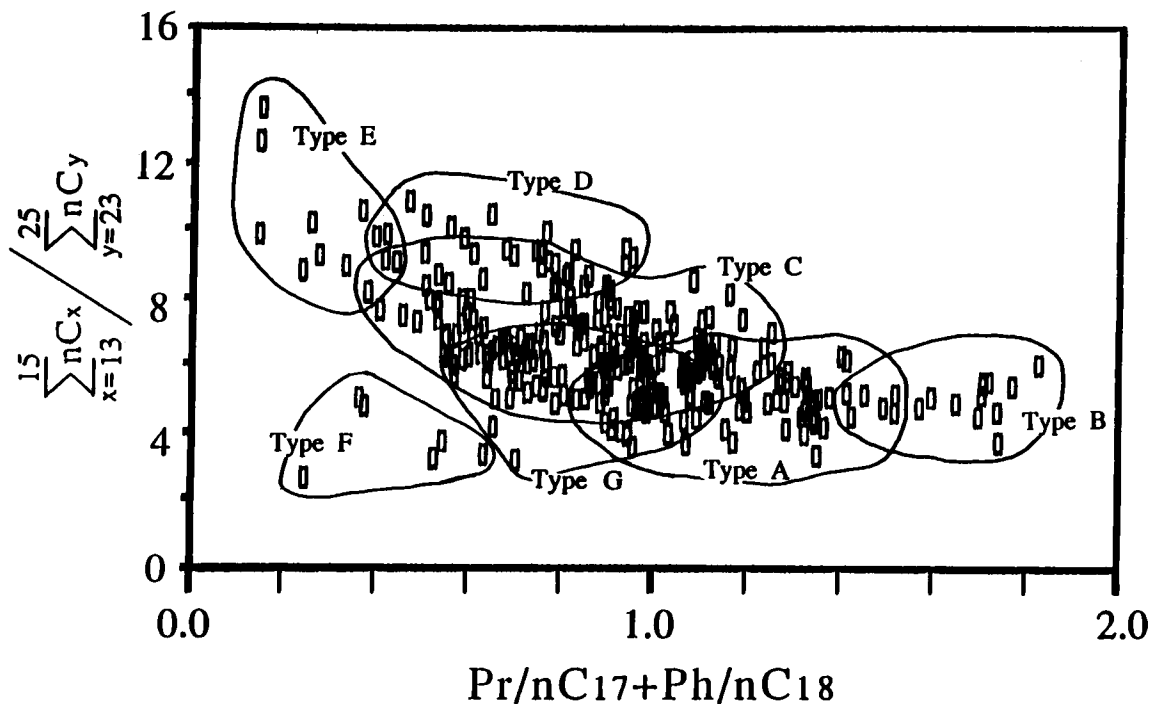


Figure 6. Plot showing typical end-member oil families using *n*-alkane and isoprenoid ratio values.

These oils are somewhat variable in composition, but are generally characterized by their relatively abundant  $C_{20+}$  *n*-alkanes and common odd-carbon preference (relatively minor) in the  $nC_{13}$ – $nC_{20}$  range (Figs. 5,6). Typical values for  $Pr/Ph$ ,  $Pr/nC_{17}$ , and  $Ph/nC_{18}$  can be considered to be 1.51, 0.39, and 0.37, respectively. The per mil carbon-isotope values obtained for two of these oils averaged  $-30.7$ ,  $-30.5$ , and  $-30.5$  for the whole oil, saturate, and aromatic fractions, respectively. These oils are commonly found in Simpson Group reservoirs in geographic proximity to the Ouachita facies (Fig. 1) (e.g., Cumberland and Sherman fields), but also occur in reservoirs in other stratigraphic units (e.g., Pennsylvanian reservoirs at Sherman and Case fields).

## DISCUSSION

While the *n*-alkane and isoprenoid distributions are not universal source indicators, previous studies (e.g., Engel and others, 1988) have demonstrated their merit in Paleozoic geochemical programs. Burruss and Hatch (1989) reported that extracts from organic-rich Pennsylvanian sediments in the Anadarko basin are commonly enriched in higher molecular weight *n*-alkanes when compared to the older stratigraphic units. This relationship is likely to persist into the Ardmore and Marietta basins and remains consistent with a contribution of organic matter from higher plants

(Albrecht and Ourisson, 1971; Tissot and Welte, 1984) in the source rocks for Type A oils. Furthermore, the general restriction of Type A oils to Pennsylvanian-age reservoirs adjacent to areas where Pennsylvanian-age sediments are within the oil window (Wavrek and Ferebee, 1991) supports the interpretation that the Type A oils were derived from Pennsylvanian-age source rocks. It is acknowledged, however, that possible complications involving active hydrocarbon generation (i.e., calculated maturity is increasing at a rate greater than a time function) and the possibility that some oils were derived from distant sources (i.e., Ouachita facies, Fort Worth basin, or Anadarko basin) are still under investigation.

The isoprenoid distributions in oils and source rocks are the result of complex interactions among precursor compounds, mechanisms of preservation, diagenesis, and catagenic alterations (Illich, 1983; Curry and Simpler, 1988). Despite their restricted utility, systematic trends have been observed in this study that help constrain a probable source for Type B oils. The enhanced isoprenoids and relatively abundant  $C_{20+}$  alkanes suggest that the depositional environment for these oils was relatively oxic and contained input from higher plant material (Tissot and Welte, 1984; Curry and Simpler, 1988). Based on the data available, lateral variations in organic content observed within Mississippian organic-rich rocks (e.g., Goddard, Caney, and Sycamore Formations) were appar-

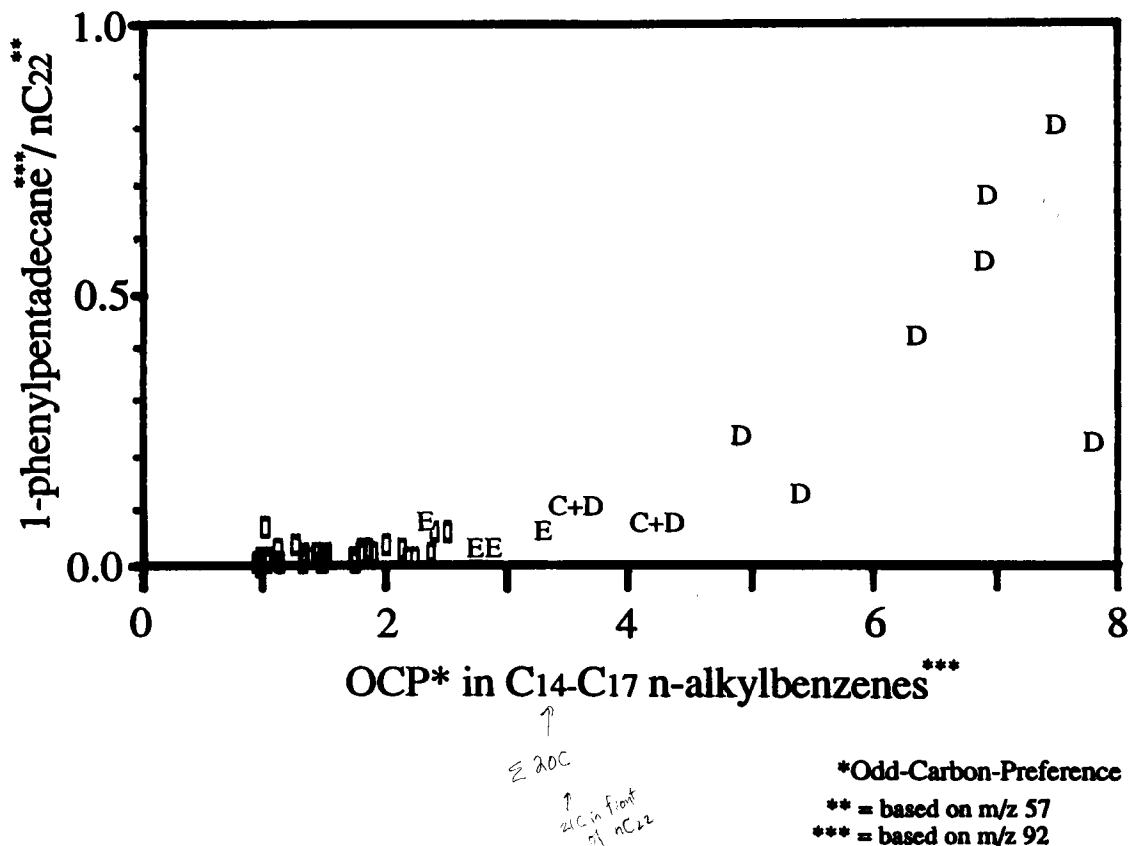


Figure 7. Illustration of the increased abundance and odd-carbon-preference of the n-alkylbenzenes in Type D oils. Data points without a letter designation (i.e., rectangles) are from oil Types A, B, C, F, and G. This figure also demonstrates the use of molecular parameters to unravel mixed oil types.

ently depositionally controlled; gas-prone kerogen facies accumulated on local highs, while oil-prone kerogen facies accumulated in depositional lows. In addition, the stratigraphic restriction of Type B oils to Mississippian-age reservoirs (i.e., particularly Springer Group) reinforces the correlation of Type B oils with Mississippian-age source rocks.

The Late Devonian–Early Mississippian Woodford Shale is a well-known petroleum source rock (Welte and others, 1975; Lewan and others, 1979; Winters and others, 1983; Comer and Hinch, 1987; Lewan, 1987; Burruss and Hatch, 1989; Wavrek, 1989, 1990). It is generally agreed that the Woodford Shale is a laterally persistent, organic-rich rock interval with oil-prone kerogen of sufficient thermal maturity to source liquid hydrocarbons. Previous investigators have observed lateral variations on regional and local scales in organic content (Sullivan, 1985; Hester and others, 1990) and environmentally sensitive microfossils (Urban, 1960), but it is also acknowledged that some Pennsylvanian-age source rocks can yield a “Woodford-appearing” bitumen extract (R. C. Burruss, personal communication). Therefore, the effect of lat-

eral variations in source rock facies will need to be addressed in future research. However, on the basis of the observed hydrocarbon distributions, I correlate Type C oils with the Woodford Shale.

Martin and others (1963) first reported the peculiar distribution of n-alkanes in crude oils from Ordovician-age reservoirs. Since that time, the strong odd-carbon preference in  $C_{11}$ – $C_{20}$  n-alkanes, minor  $nC_{20}$  alkanes, and the minor abundance of acyclic isoprenoids have become accepted as diagnostic of Ordovician-age source rocks on a global scale (Williams, 1974; Alexander and others, 1984; Fowler and Douglas, 1984; Jackson and others, 1984; Reed and others, 1986; Hoffmann and others, 1987; Longman and Palmer, 1987; Jacobson and others, 1988). Since both oil Types D and E share some of the “Ordovician character,” additional clues must be used to distinguish the respective source intervals. Molecular indicators that support a correlation of Type D oils with carbonate source facies include the anomalously high concentrations of n-alkylcyclohexanes and n-alkylbenzenes with an odd-carbon preference (Fowler and Douglas, 1984; Connan and oth-

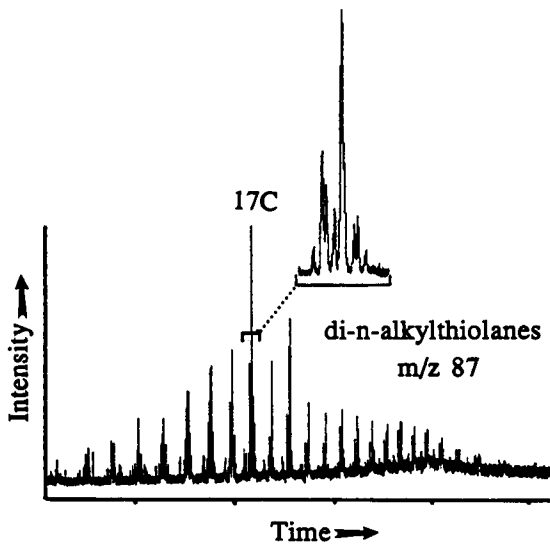


Figure 8. Ion trace of the di-n-alkylthiolanes that are prevalent in Type D oils. Compound identities are tentatively based on published data (e.g., Schmid and others, 1987; Sinninghe Damste and others, 1987; Strausz and others, 1990), although some of the minor peaks may originate from other alkylated molecules.

ers, 1986; Reed and others, 1986; Hoffmann and others, 1987; Williams and others, 1988), extended hopanes (McKirby and others, 1983; Palacas and others, 1984; ten Haven and others, 1985, 1988) and di-n-alkylthiolanes (Schmid and others, 1987; Sinninghe Damste and others, 1987, 1989). Preliminary source-rock data, in conjunction with published reports (Galvin, 1983; Jones and Philp, 1990), support a correlation of Type D oils with the Viola Group. In particular, the Viola unit 1L (terminology of Glaser, 1965; Finney, 1988) contains significant source-rock potential in the basal chert layer (TOC average 1.31%,  $n = 30$ ) and laminated marls (TOC average 2.4%,  $n = 7$ ). While details of this source interval remain under investigation (Garcia, in preparation), the correlation is reinforced by the general stratigraphic restriction of Type D oils to Viola Group reservoirs.

While oil Types D and E share some chemical characteristics, Type E oils have distinct characteristics including a strong odd-carbon preference and the lack of the "carbonate-sourced" molecular indicators that are present in Type D oils. Support for a Type E oil/Simpson Group source-rock correlation is provided by extracts from Simpson Group sediments (TOC as much as 4.5%) within the study area, sedimentologic trends (Schramm, 1964; Wickham, 1978b), carbon isotope anomalies (Hatch and others, 1987), and the general strati-

graphic restriction of Type E oils to Simpson and Arbuckle Group reservoirs.

The oils designated as Type F deserve discussion due to their low biomarker abundance (e.g., aryl-isoprenoids, hopanes, steranes), advanced maturity level, and stratigraphic restriction. The low biomarker abundance may be attributed to the advanced maturity level, low initial abundances, late generation from lean organic source facies, or selective destruction in the presence of sulfur species. While it is noted that Type F oils from the Cool Creek Formation and McKenzie Hill Formation drillstem tests (DST) at Cottonwood Creek are associated with reservoir anhydrite and hydrogen sulfide (David Read, personal communication), the oil samples have low total sulfur contents. Therefore, additional work will be required to unravel the status of Type F oils. Likewise, the genetic implications of Type G oils will require additional research due to their possible derivation from the Ouachita facies. Nevertheless, the compositional variability of Type G oils probably reflects multiple source intervals.

While the frequency distribution of oil types (Fig. 11) provides a useful summary of this research, several points need to be acknowledged. First, sample collection was biased toward the Lower Paleozoic (e.g., Arbuckle Group) and toward reservoirs likely to contain "non-Woodford"-sourced hydrocarbons. Second, oils suspected of being mixed oil types (10%) are included in the group with the closest end-members. This was done since extensive source-rock work will be required to accurately define the lateral variability in source-rock facies and to determine the effects of mixed kerogen types vs. mixed oil types. Third, oils that were mildly biodegraded (4%) were assigned a genetic oil type, but those oils that were severely biodegraded (6.5%) were excluded from the summary. Finally, it is believed that the frequency distribution of oil types (Fig. 11) would have an addi-

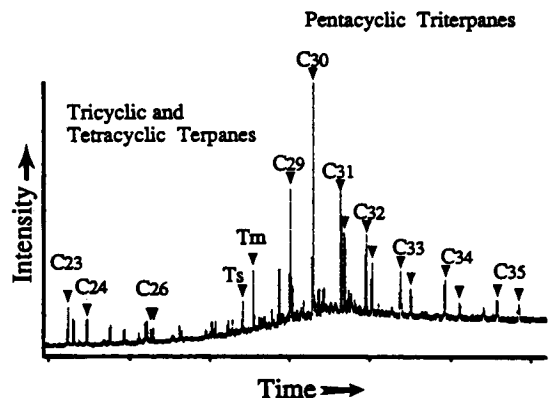


Figure 9. Ion trace of  $m/z$  191 in a Type D oil.



tional skew toward Type C if the data were based on cumulative production.

**CONCLUSIONS**

The gas chromatographic analyses of 385 oils from the Ardmore and Marietta basins reveal the presence of seven oil types. Although the research is "in progress," tentative correlations have been established. Oil Types A through E appear to correlate with source facies within the Pennsylvanian (Atoka Formation?), Mississippian (Goddard, Caney, and Sycamore Formations), Devonian-Mississippian (Woodford Formation), upper Middle Ordovician (Viola Group), and Middle Ordovician (Simpson Group) rocks, respectively. Meanwhile, the "group" status of oil Types F and G along with the study of the lateral variations in source rock facies are still under investigation.

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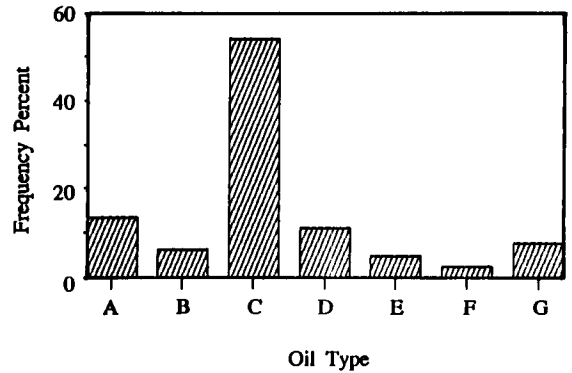


Figure 11. Frequency distribution of oil types reservoired in the Ardmore and Marietta basins.

Tulsa) for his role in the exhaustive task of sample collection from the numerous operators (61), whose names will be published elsewhere.

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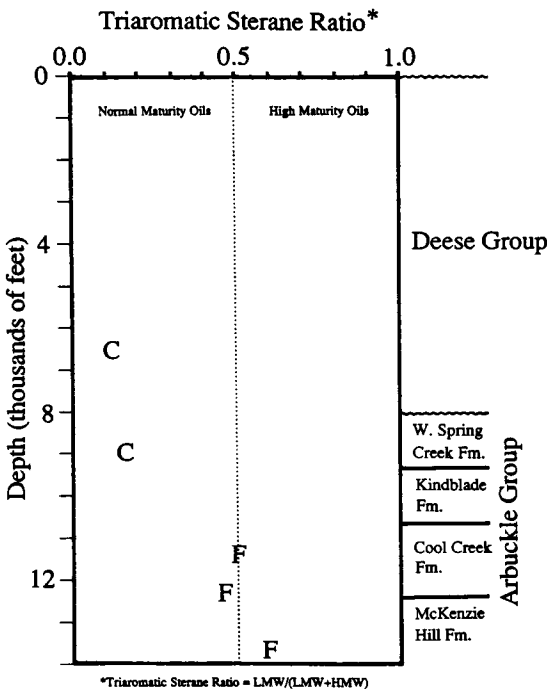


Figure 10. Maturity data plotted against reservoir depth at the Cottonwood Creek field. Letters refer to the oil type in each reservoir. LMW = low molecular weight; HMW = high molecular weight.

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