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, alicylated 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 geographic 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 5890A 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). The 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 5970B gas chromatograph interfaced to an HP 5970B mass selective detector. A conven-
Results

Gas chromatography of whole-oil samples revealed significant differences in the oil types reservoir 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_{16} alkanes, very little odd-carbon preference in the nC_{11}-nC_{20} range alkanes, and their more linear n-alkane profile (Figs. 5,6). They display moderate abundances of isoprenoids with typical Pr/Ph, Pr/nC_{17}, and Ph/nC_{18} 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-
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_{11}-nC_{20} alkane range and contain relatively minor abundances of isoprenoids with typical Pr/Ph, Pr/nC_{17}, and Ph/nC_{18} 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,
and trace concentrations of alkylation of 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 nC11-nC20 range (Figs. 5, 6). They contain a moderate amount of aryl-isoprenoids and typical values for Pr/Ph, Pr/nC17, and Ph/nC18 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 alkylation of cyclic compounds (e.g., n-alkylcyclo-

**Type E Oils**

Oils that are dominated by n-alkanes with a strong odd-carbon preference in the C11 to C20 range and contain relatively minor amounts of the nC20 hydrocarbons are assigned to Type E (Figs. 5, 6). These oils display minor to trace amounts of isoprenoids with typical Pr/Ph, Pr/nC17, and Ph/nC18 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 C29/C30 hopane ratios. The carbon-isotope values obtained for two of these oils are anomalously light; average values from whole oil, satu-
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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
gochemical and stratigraphic grounds. These oils
have smooth n-alkane profiles, minor isoprenoids
(Figs. 5,6), and typical Pr/Ph, Pr/nC17, and Ph/nC18
ratios of 1.64, 0.28, and 0.23, respectively. These
oils contain relatively minor amounts of bio-
maker 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 Forma-
tion at Enville SW field).

Type G Oils

Oils assigned to Type G have some characteris-
tics that may be interpreted as originating from
mixing oil types, but because of their close prox-
imity to the Ouachita facies (Fig. 1) these oils are
assigned to one group for the purposes of this re-
port until additional work can be completed.
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_{15}-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 apparently depositionally controlled by kerogen facies accumulated in different stratigraphic units. In addition, the stratigraphic setting of oil migration from Mississippian to Pennsylvanian (e.g., Springer Group) and Type B oils with Mississippian kerogen facies is important in understanding the depositional environment and thermal maturity of these oils. It is generally accepted that the Late Devonian-Carboniferous-boundary Shale is a well-known source rock interval with oil-prone characteristics and thermal maturity to source Type B oils with Mississippian kerogen facies. The Late Devonian-Carboniferous boundary Shale is a well-known source rock interval with oil-prone characteristics and thermal maturity to source Type B oils with Mississippian kerogen facies. The Late Devonian-Carboniferous boundary Shale is a well-known source rock interval with oil-prone characteristics and thermal maturity to source Type B oils with Mississippian kerogen facies. The Late Devonian-Carboniferous boundary Shale is a well-known source rock interval with oil-prone characteristics and thermal maturity to source Type B oils with Mississippian kerogen facies. The Late Devonian-Carboniferous boundary Shale is a well-known source rock interval with oil-prone characteristics and thermal maturity to source Type B oils with Mississippian kerogen facies.
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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.

- Odd-Carbon-Preference
- ** = based on \( n/2 \ 57 \)
- *** = based on \( n/2 \ 92 \)

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di-n-alkylthiolanes

In the study of hydrocarbons, di-n-alkylthiolanes 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.

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 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 additional skew toward Type G oils on cumulative production.

CONCLUSION

The gas chromatographic presence of seven oil type groups in the study area is “in progress,” tentatively established. Oil Type D oils relate with source facies (Atoka Formation), Caney, and Sycamore Mississippian (Middle Ordovician). Meanwhile, the “group along with the study area” source rock facies are

ACKNOWLEDGMENTS

The work described in this paper was supported by Amoco, Exxon, Mobil, Santa Fe, and others. All authors wish to acknowledge the continuing support of Amoco, Exxon, Mobil, Santa Fe, and others.

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.

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

Figure 10. Maturity depth at the Cottonwood Creek oil type in each reservoir weight; HMW = high m-
of Type D oil.

Type F deserve discussion because anker abundance (e.g., steranes), advanced graphic restriction. The distribution of oil types in the presence of noted that Type F oils are included in the reservoir anhydrite and read, personal comments have low total sulfur concentration, oils suspected of being biased toward the later variability in source rock facies are still under investigation.

ACKNOWLEDGMENTS

The work described in this paper was supported by Amoco Research, ARCO, Chevron, Exxon, Mobil, Santa Fe Energy, and Unocal. I also wish to acknowledge Clive Ferebee (University of 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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