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May 8, 1990

Dr. George Kolstad
Division of Engineering and Geosciences
Office of Basic Energy Sciences
Department of Energy
Washington, D.C. 20545

Gentlemen:

Enclosed are an original and two copies of a progress report entitled "A Study of Source Materials, Depositional Environments, Mechanisms of Generation and Migration of Oils in the Anadarko and Cherokee Basins, Oklahoma." Project Director is Dr. R. Paul Philp, Interim Director of Geology and Geophysics at the University of Oklahoma.

We appreciate your consideration of this progress report. If you need any additional information, please let us know.

Sincerely yours,

Karen M. Petry
Karen M. Petry
Assistant Director
Office of Research Administration

KMP:kk

Enclosures (3)

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A Study of the Source Materials, Depositional Environments,
Mechanisms of Generation and Migration of Oils in the
Anadarko and Cherokee Basins, Oklahoma

Dr. R. P. Philp
School of Geology and Geophysics
University of Oklahoma
Norman, OK 73019

Progress Report for period Sept. 15th, 1989 - Sept. 14th, 1990
Funding for period \$123,843
Report Submitted on May 14th, 1990
Project No: DE-FG05-85ER13412

The following is a brief progress report for work performed in the second year of a three year funded proposal and an outline of the work to be performed in the third year.

The geochemical characterization of oils and source rocks from the Anadarko Basin, Oklahoma has continued in a manner consistent with the original proposal. In the past year we have put most of the emphasis on the geochemical characterization of the Woodford shale. Samples of outcrop and core samples at various maturity levels were collected and their extracts subjected to characterization by gas chromatography-mass spectrometry (GC-MS), isotopic analysis and the insoluble organic residues were examined by various pyrolytic techniques. A paper summarizing the results of this part of the study was recently presented at a meeting held in Norman and organised by the Oklahoma Geological Survey. A draft of the written version of this paper is attached as Appendix I and the information contained in that paper will not be repeated in the main part of the proposal.

In our previous report it was mentioned that we intended to initiate a study of our potential source rocks in the Anadarko Basin, namely the Sylvan, Springer, and Viola formations. This study is now underway and will actually form the main part of the Ph.D. thesis topic of one of our graduate students. A significant amount of time was initially spent on collecting samples from these various formations. This process has been completed and an initial screening of these samples is now underway. Samples are being screened on the basis of their total

organic carbon values, Rock-Eval type analyses to determine petroleum potential and petrographically to determine types of organic matter in the samples. After this initial screening process is complete it is proposed to select a smaller number of samples and exhaustively extract them with organic solvents. The extracts will be fractionated and then analysed by GC and GCMS. Kerogens will be isolated by density separation methods and the kerogen concentrates characterized by pyrolytic techniques combined with GC and GCMS.

From the results of the analyses described above it is anticipated that we can evaluate the source potential of these rocks and also obtain information on the nature of the source material in the samples and its level of maturity. Furthermore the biomarker distributions will be evaluated to try and provide more information on the nature of the original depositional environment. Finally upon completion of the biomarker analysis, isotopic values will be determined for the kerogens and extracts and efforts made to determine whether or not there is any correlation between the oils in the region and these particular formations.

Personnel

Several personnel have been supported on this grant during the past year. These have included Dr. C.P. Yu, a post-doctoral fellow who left in January 1990, who assisted in various aspects of the project including operation of the mass spectrometer. Jon Allen, a technician, has assisted in preparation of samples and

running routine analyses including those on the PYRAN pyrolysis system. Mr. Wang is now a full time graduate student (Ph.D.) on this project and will continue working in this area until he has completed his Ph.D. topic.

Publications and Presentations

Since our last report, a number of the papers cited in the publication list as being submitted or in press have appeared and these are included again in the current listing along with a number of papers funded from this project which has been submitted during the past year.

1. PHILP, R.P., BAKEL, A., GALVEZ-SINIBALDI, A. and LIN, L.H. (1988). A comparison of organosulphur compounds produced by pyrolysis of asphaltenes and those present in related crude oils and tar sands. In "Advances in Organic Geochemistry 1987" pp 915-926.
2. PHILP, R.P., LEWIS, C.A. (1989). The use of the Ion Trap Detector in Petroleum Geochemistry. Org. Geochem. 14(2), 183-187.
3. PHILP, R.P., JONES, P.J., LIN, L.H. and MICHAEL, G.E. (1989). An organic geochemical study of oils, source rocks, and tar sands in the Anadarko Basin. Oklahoma Geological Survey Notes, (Proceedings of Anadarko Basin Symposium, Norman, Oklahoma, April 1988), Circular 90, pp65-76.
4. LIN, L.H., MICHAEL, G.E., KOVACHEV, G., ZHU, H., PHILP, R.P. and LEWIS, C.A. (1989). Biodegradation of tar-sand bitumens from the Ardmore Basin, Carter County, Oklahoma. Org. Geochem., 14(5), 511-523.
5. MICHAEL, G.E., LIN, L.H., PHILP, R.P., LEWIS, C.A. and JONES, P.J. (1989) Biodegradation of tar-sand bitumens from the Ardmore/Anadarko Basins, Oklahoma-II. Correlation of oils, tar sands and source rocks. Org. Geochem., 14(6), 619-634.
6. JONES, P.J. and PHILP, R.P. Oils and source rocks from the Pauls Valley area of the Anadarko Basin. Appl. Org. Geochem. (In

press).

7. PHILP, R.P. and GALVEZ-SINIBALDI, A. Characterization of organic matter by various pyrolysis techniques. AAPG Handbook of Petroleum Geology. (In Press).

8. BAKEL, A.J. and PHILP, R.P. Characterization of Organosulfur Compounds in Oklahoma Coals By Pyrolysis-Gas Chromatography. ACS Meeting, Dallas, April, 1989 (Accepted).

9. BAKEL, A.J. and PHILP, R.P. The distribution and quantification of organic nitrogen compounds in crude oils and kerogen pyrolysates. International Geochemistry Meeting, Paris, Sept. 1989 (Accepted).

Publications and Manuscripts in Preparation

THE EFFECTS OF WEATHERING AND MATURITY ON THE GEOCHEMICAL
CHARACTERISTICS OF THE WOODFORD SHALES

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ABSTRACT

The Woodford Shale is an organic-rich black shale deposited in an euxinic open sea environment and is thought to be one of the principal sources of hydrocarbons in Anadarko basin. The effects of weathering and maturity on geochemical characteristics of the Woodford Shale have been investigated and will be reported in this paper. Five surface rock samples and 13 rock samples from different depths have been collected, extracted and subjected to analysis by GC, GC/MS, Py/GC/MS, isotopic compositions and petrographic characterization.

It has been observed that the surface samples have changed in their hydrocarbon composition and stable isotopic composition as a result of weathering. According to the similarities in various chromatograms, distributions of steranes and terpanes and isotopic data, the surface samples can be divided into two groups. Compared with Group II, the Group I samples contain lower contents of *n*-alkanes, lower tricyclic terpanes (or low values of tricyclic terpanes/hopanes), but higher contents of C₂₁-C₂₂ steranes and $\alpha\beta$ steranes.

The effects of maturity on the geochemical characteristics of Woodford Shale have been also investigated from pyrolysis and the distribution of alkanes, aromatics, steranes and terpanes. The thermal maturity parameters of steranes and terpanes are used to assess the maturation. The hydrocarbon generation has increased greatly below 8,500 feet based on the data of S₁/S₁+S₂ from Py/GC analysis. The MPI values are observed to increase with increasing depth and maturity.

In conclusion it can be observed that significant alteration can occur to the Woodford shale as a result of weathering. Hence as previously noted, a great deal of care needs to be exercised when collecting and selecting rock samples for source rock characterization.

INTRODUCTION

During evolution of a sedimentary basin, the source rocks containing efficient Organic Matter are expected to produce liquid hydrocarbons and these liquid hydrocarbons will be expelled out of from source rocks to migrate a trap via carrier and a reservoir will be formed. Among all of these processes, the thermal maturation of organic matter in source rocks is a principal step to provide the formation of oil accumulations. Thermal maturation is also a major effect on the compositions of organic matters in source rocks and crude oils. Other effects on the compositions of organic matter might be bacterial attack, water washing, oxidation by free oxygen, etc. A detail information on the effects of various process on the distribution of organic matters in source rocks would help us acquire better knowledge of the evolution of the source rocks.

The Anadarko basin, located in western Oklahoma, is one of the greatest oil and gas provinces the United States (Johnson, 1989). The geological evolution of Anadarko basin has been extensively studied by many researchers and recently briefly described by Johnson, (1989). Some geochemical researches were also carried out in the basin recently. Philp et al. (1989) presented results of a geochemical study evolving the oils, source rocks and tar sands in this basin. In this paper, they concentrate their interest on the biodegradation of oils and their origin (or source). Meanwhile another geochemical study directed by Burrus and Hatch (1989) presented the evidence for

multiple source of oils and long-distance oil migration. The Woodford Shale is an organic-rich black shale deposited in an euxinic open sea environment and is thought to be one of the principal sources of hydrocarbons in Anardarko basin. In the present study. the effects of weathering and maturity on geochemical characteristics of organic matters in the Woodford Shale have been investigated and will be reported in this paper.

EXPERIMENTAL

Sample preparation

Five surface rock samples and 13 rock samples of woodford shale were collected from Arbuckle mountains and Anardarko basin in Oklahoma respectively (Fig.1). TOC values for these samples were obtained by Core Lab Company. The rock samples were cleaned, crushed and then extracted with methylene dichloride. The rock extracts and crude oils were treated to remove asphaltenes by precipitation with n-pentane and the n-pentane soluble fraction were further fractionated by TLC into fractions containing aliphatic hydrocarbons, aromatic hydrocarbons and NSO components and analyzed by GC, GC-MS and the stable isotopic compositions of the various fractions were also determined.

Analytical procedures

Gas Chromatography (GC): The saturate and aromatic fractions were analyzed by GC, using a Hewlett-Packard 5890 A GC. The GC was equipped with a 30m x 0.25mm i.d. DB-5 column. The GC temperature

condition for saturates was as following: injection temperature was 300°C; column temperature was initially 40 °C and then programmed at 10°C/min. for the first 10 minutes and the 3°C/min. to 300°C. and held for 20 minutes. And the GC temperature condition for aromatics was: injection temperature was 300°C; column temperature was initially 40 °C for 1.5 min. and then programmed at 4°C/min. to 300°C and held for 30 minutes. Helium was employed as carrier gas. Peak heights were determined from on the chromatograms used for quantitative analysis purposes.

Gas Chromatography-Mass Spectrometry (GC-MS): GC-MS analyses were performed to determine steranes and terpanes using a Finnigan TSQ-70 interfaced to a Varian 3340 GC and equipped with a 30m x 0.25mm i.d. DB-5 column. The GC conditions were as following: injection temperature was 300°C; column temperature was isothermal at 40 °C and then programmed at 10°C/min. to 140°C and then to 300°C at 3°C/min. and held isothermally for 20 minutes.. Helium was employed as carrier gas. The ion source temperature was 200°C; Electron energy and current were -70eV and 200uA, respectively.

Pyrolysis/GC/MS: A Pyran System was employed for the pyrolysis analysis. The pyrolysis conditions are as following: Isothermal at 300°C for 1 min. then programmed to 610°C at 300C/min.; Kept isothermally at 610°C for 5 min., then cooled down to ambient; Helium used as carried gas (60 ml/min. in level I; 30ml/min. in level II). Samples weight from 10-50mg depending upon their TOC content, with a size of 200 mesh.

¹³C isotopic Composition: The extracts and their fractions of

core samples were statically combusted according to the methods of SOFER (1980). Following combustion, the tubes were opened on a vacuum line (2×10^{-3} torr) and water was removed by trapping at -70°C (Neslab Cryocool CC-60 cooling unit). The CO_2 was collected in a gas sampling ampoule at -196°C (liquid N_2) and then transferred directly to the inlet system of a Finnigan MAT Delta E isotope ratio mass spectrometer equipped with a 90° sector magnetic deflector. The stable carbon isotopic composition is expressed as:

$$\delta^{13}\text{C} (‰) = [\text{R}_{\text{sample}}/\text{R}_{\text{standard}} - 1] \times 10^3,$$

where R is the abundance ratio of the heavy to light isotope of carbon ($^{13}\text{C}/^{12}\text{C}$). The values are expressed relative to PDB carbonate (0 ‰) and are corrected for ^{17}O contribution.

RESULTS and DISCUSSIONS

Thermal Maturation

The occurrence of hydrocarbons in organic rich source rocks has been one of the major targets of petroleum geochemistry. Thermal maturation is a main factor affecting the formation and occurrence of hydrocarbons. With increasing temperature, hydrocarbons will increase in their content in source rocks which were mainly formed from kerogen. During their formation from kerogen, the composition of hydrocarbons, including biomarkers, will undergo some changes. Examining and studying these changes with depth are the direct way to know what happened to hydrocarbons during thermal maturation and to evaluate the source rocks.

Bulk Composition Pyrolysis/gas chromatography (Py/GC) is a fast, convenient method to evaluate the source rocks. Peak S1 on the Py/GC chromatograms represents the free hydrocarbons already formed mainly from kerogen and ready for migration and accumulation. Peak S2 represents the hydrocarbons formed from kerogen during pyrolysis under high analytical temperature (Fig.2). The ratio of S1/S1+S2 (calculated from peak area) have been used a geochemical parameter for source rock evaluation (ref.). The increase in the peak S1 or the ratio of S1/S1+S2 with increasing depth (Fig.2) indicated that the hydrocarbon content in Woodford shale were enhanced with the increasing thermal maturity. From Fig.2, it can be also noted that the ratio begins to increase at greater rate at a depth of around 8,500 feet with a vitrinite reflectance of about 0.6% where the oil-threshold was generally believed to be on. It was also noted that the ratio of S1/S1+S2 of some samples is lower than other samples just below or above them while general trend in increasing with depth. One reason for this shift in the ratio of S1/S1+S2 could be the facies change which could cause some changes in composition of organic matter, which in turn cause the change in this ratio. There could be reasons for deeper samples at 11,714 feet (BJC-27) and 14,250 feet (BJC-16), respectively. A depth range from 11,000 to 11,900 feet was thought to be the main phase of oil expulsion in Woodford Shale in Anadarko Basin (Cardott, 1989). These two samples are among or already through this oil expulsion phase. The low values of for the ratio of S1/S1+S2 might be caused by depletion in the liquid hydrocarbons which undergo primary

migration.

n-Alkanes While the hydrocarbons were formed with increasing maturity, their compositions were also observed to be changed. The n-alkanes are the most abundant hydrocarbons. A major change to n-alkanes observed in Woodford shale is that the relative content of light hydrocarbons were increased compared with that of higher molecular weight n-alkanes with increasing depth (Fig.3). This is supposed to be caused by the breakdown of long chain molecules into short chain molecules under higher temperature.

Terpanes and Steranes Terpanes and steranes are important cyclic biomarkers in crude oils and oil source rocks although their generally lower concentrations compared to n-alkanes. The distributions of these biomarkers are also subjected to change under maturation. A major change was that the relative contents of tricyclic terpanes ($C_{19}-C_{30}$) and low molecular weight steranes ($C_{27}-C_{28}$) were increased with increasing maturity compared to pentacyclic terpanes (mainly $C_{29}-C_{30}$ hopanes) and regular steranes ($C_{27}-C_{28}$) (Fig.4). The probable reason for the change among steranes is that the $C_{29}-C_{28}$ steranes were broken down through cracking of side chain into low molecular weight steranes without changes in cyclic nucleus. The situation for terpanes is presumably more complicated because the pentacyclic terpanes are very difficult to be transformed into tricyclic terpanes through cracking of D-ring according to dynamics (ref.). One possible explanation for terpanes is that the tricyclic terpanes are more thermally stable than hopane series. The relative high

concentration of high molecular hopanes up to C_{36} were observed occurring in shallow (or immature) source rocks (e.g. KAC-37, Fig.4a). In contrast, the C_{30} - C_{35} hopanes of the deep samples, for example KAC-37 etc., were almost not detected. It is probably caused by the transformation of high molecular weight hopanes through side-chain cracking under thermal maturation into low molecular weight hopanes. Meanwhile, the deeper source rocks (e.g. BJC-27, 12,955 ft.) have generally weaker responses of steranes and terpanes in GC/MS analysis (Fig.4) This was probably caused by the dilution of *n*-alkanes formed from kerogen during thermal maturation.

The isomerization of steranes and hopanes is one of the important reactions under thermal maturation. The ratios 20S/20S+20R of $\alpha\alpha$ - C_{29} steranes, $\beta\beta/\alpha\alpha+\beta\beta$ C_{29} steranes and 22S/22S+22R C_{32} -hopanes are the mostly used thermal parameters. Those two sterane ratios in Woodford shales were observed to increase from the depth of 5,700 ft. to about 10,000 ft. (where is the oil-threshold), then decrease with increasing depth. Meanwhile the hopane ratio remained relatively stable with depth (Fig.5).

The decrease in sterane ratios after oil-threshold may be explained by the add of immature molecules (here 20R and $\alpha\alpha$ -isomers) from kerogen (RULLKOTTER, 1989). But it is very difficult to explain why same thing doesn't happen to other compounds such as hopanes and phenanthrenes.

Aromatics From GC traces of aromatics (Fig. 6), it was noted that phenanthrenes are the important components of organic

matters in Woodford shale. Recently, the phenanthrene ratios have been also used as thermal maturity parameters (RADKE, 1987). The similar distribution of phenanthrene ratios with increasing maturity has been observed in Woodford shales. The MPI (Methyl Phenanthrene Index), MPR-2 and MPR-3 increase with increasing maturity, at a higher rate after oil-threshold. Meanwhile, MPR-1 and MPR-9 increase first and then decrease after oil-threshold (Fig.7).

Weathering Effects

The characteristics of organic matters in source rocks will be affected under weathering conditions. Five surface samples of Woodford shales were collected from Arbuckle Mountains area for the study of weathering effects on organic matters of Woodford shales.

According to the distributions of organic matters, the five samples were divided into two groups: Group I--KAC-34 and CAL-2; Group II--CAL-1,3,4. These two group surface samples differ from each other in the distributions of n-alkanes, aromatics, terpanes and steranes. The results of GC, GC/MS, Py/GC analysis of KAC-34 and CAL-4 are presented in Figures 8-13 to display how these two group samples differ from each other.

n-alkanes The GC traces of saturates (Fig.8) indicated that the n-alkanes in KAC-34 and CAL-4 were removed in different extent compared to the subsurface samples. The n-alkanes have been almost removed from the group I samples (e.g. KAC-34). The group II samples (e.g. CAL-4) have relatively higher content of

n-alkanes left compared with group I samples. The relative content of isoprenoid alkanes in group II is much higher than that of normal subsurface samples (Fig.3). The previous studies indicated that n-alkanes are the components which are most easily removed by bacterial activities. The lowest n-alkane content in group I samples implies that these surface samples are more severely biodegraded than those surface samples belonging to group II.

Terpanes and Steranes KAC-34 and CAL-4 have low vitrinite reflectance of 0.37% and 0.34% respectively. Low values of vitrinite reflectance indicate that these surface samples have low thermal maturity. The isomerization values of steranes and hopanes are widely used as maturity parameters of organic matters in crude oils and source rocks. One advantage of the use of these sterane and hopane parameters is that these parameters could be easily available even when the vitrinite is impossible or difficult to be measured (eg. in oils and carbonates). But one disadvantage is that the distributions of steranes and hopanes are sometimes easily affected by other factors besides maturation such as bacterial activity and water-washing. The surface samples are believed to be more easily affected by these geochemical and biological processes under weathering conditions. Some changes under weathering conditions are also observed in surface samples of Woodford shales. Although of its low vitrinite reflectance value of 0.37% (or lowly actual maturity), KAC-34 has similar distributions of steranes to those of more mature samples. For examples, KAC-34 has also higher content of pregnanes and $\beta\beta$ -

steranes. Previous studies indicated that the ease of biodegradation was in such order: 20R-5 α ,14 α ,17 α steranes > 20S-5 α ,14 α ,17 α steranes and 5 α ,14 β ,17 β steranes > 5 α ,14 α ,17 α steranes.

The high relative content of $\alpha\beta\beta$ and 20S- $\alpha\alpha\alpha$ steranes in group I samples indicated that biodegradation made these immature samples more "mature" according to sterane thermal parameters.

The distributions of hopanes in these two group of surface samples looks very different. In the m/z 191 mass chromatograph of group II samples (e.g. CAL-4, Fig.10), There are many "abnormal" peaks observed, especially in tricyclic and tetracyclic compound range. The group I samples (e.g. KAC-34, Fig.10) have similar terpane distribution to the immature subsurface samples (e.g. KAC-37, 5819 ft., Fig. 4a). Although of the similarity, some phenomena related to the biodegradation were observed. The preferential removal of 22R hopanes and the decreasing susceptibility to biodegradation of hopanes in the order $C_{35} > C_{34} > C_{33} > C_{32} > C_{31} > C_{30} > C_{29}$ has been previously documented by Goodwin and others (1983). It was observed again that the relative content of $C_{31}-C_{35}$ hopanes to $C_{29}-C_{30}$ was depleted in the surface samples. But the 22S/22R ratio seems not to be affected in the surface samples (especially in KAC-34). The high relative content of moretanes to hopanes in surface samples could be caused by low maturity and/or biodegradation. Previous study indicated that moretanes are relatively more resistant to biodegradation (for examples compared with hopanes) (Philp et al., 1989).

Aromatics The GC traces of aromatics of surface samples showed that there are some differences in their aromatic composition (Fig.11). The group II samples have high content of high molecular weight component which eluted last on the GC. Compared with subsurface samples, the content of phenanthrenes of these surface samples are lowered.

Isotope Composition The data of the stable carbon isotopic composition of saturates and aromatics of Woodford shale samples plot in figure 12. Almost all of the subsurface samples (non-weathered) plot in the "marine" area. In the beginning of the paper we have introduced the Woodford shale was deposited in an euxinic open sea environment. The group I surface samples plot also in the area where subsurface samples are. It seems that no much change occurred to the stable isotopic compositions of this group samples. But the group II surface samples are shifted in the direction of enhancement in the value of $\delta^{13}C$ aromatics (Fig.12).

Bulk Composition The surface samples were also subjected to the pyrolysis analysis. The Py/GC traces (Fig. 13) showed the low peak of S1. It could be caused by low maturity and/or weathering. The free hydrocarbons corresponding to S1 peak are believed to removed from samples by washing and biodegradation.

CONCLUSIONS

1. The effects of maturity on the geochemical characteristics of Woodford Shale have been investigated by pyrolysis and isotopic data and the distribution of alkanes, aromatics,

steranes and terpanes. The hydrocarbon generation has increased greatly below 15,000 feet based on the data of S1/S1+S2 from Py/GC analysis. The MPI values are observed to increase with increasing depth and maturity.

2. It has been also observed that the surface samples have changed in their hydrocarbon composition and stable isotopic composition as a result of weathering. According to the similarities in various chromatograms, distributions of steranes and terpanes and isotopic data, the surface samples can be divided into two groups. Compared with Group II, the Group I samples contain lower contents of n-alkanes, lower tricyclic terpanes (or low values of tricyclic terpanes/hopanes), but higher contents of C₂₁-C₂₂ steranes and $\alpha\beta\beta$ steranes.

3. In conclusion, it can be observed that significant alteration can occur to the Woodford shale as a result of weathering. Hence as previously noted, a great deal of care needs to be exercised when collecting and selecting rock samples for source rock characterization.

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(7-85)

U.S. Department of Energy
Grant Application Budget Period Summary
(See Reverse for Definitions and Instructions)

OMB Approval
No. 1910-1400

Please Print or Type

Organization: University of Oklahoma		Period Covering: From: 10-1-88 To: 9-30-89		FOR DOE USE ONLY Proposal No: Award No.:	
Principal Investigator (P.I.)/Project Director (P.D.): Paul Philp		DOE Funded Person-Mos.		Funds Requested By Applicant	
A. SENIOR PERSONNEL (PVPD Co PIs, Faculty and Other Senior Associates) (List each separately with title. A 6 show number in brackets. Attach separate sheet if required.)		CA	ACBC	Sum	\$
1 Paul Philp - Principal Investigator		3			18,000
2					
3					
4					
5					
6 () TOTAL SENIOR PERSONNEL		3			18,000
B OTHER PERSONNEL (SHOW NUMBERS IN BRACKETS)					
1 () POST DOCTORAL ASSOCIATES		12			26,000
2 () OTHER PROFESSIONALS (TECHNICIAN, PROGRAMMER, ETC.)					
3 () GRADUATE STUDENTS					
4 () UNDERGRADUATE STUDENTS					
5 () SECRETARIAL-CLERICAL					3,000
6 () OTHER					7,600
TOTAL SALARIES AND WAGES (A + B)					54,600
C FRINGE BENEFITS (IF CHARGED AS DIRECT COSTS)					12,908
TOTAL SALARIES, WAGES AND FRINGE BENEFITS (A + B + C)					67,508
D EQUIPMENT (LIST ITEM AND DOLLAR AMOUNT FOR EACH ITEM)					
TOTAL EQUIPMENT					
E TRAVEL 1 DOMESTIC (INCL. CANADA AND U.S. POSSESSIONS)					4,500
2 FOREIGN					
F OTHER DIRECT COSTS					
1 MATERIALS AND SUPPLIES					16,000
2 PUBLICATION COSTS/PAGE CHARGES					1,150
3 CONSULTANT SERVICES					
4 COMPUTER (ADPE) SERVICES					
5 CONTRACTS AND SUBGRANTS					
6 OTHER					300
TOTAL OTHER DIRECT COSTS					17,450
G TOTAL DIRECT COSTS (A THROUGH F)					89,458
H INDIRECT COSTS (SPECIFY RATE AND BASE) 43% MTDC as set by DHHS on 12/22/86					38,467
TOTAL INDIRECT COSTS					
I TOTAL DIRECT AND INDIRECT COSTS (G + H)					127,925
J APPLICANT'S COST SHARING (IF ANY)					
K TOTAL AMOUNT OF THIS REQUEST (ITEM I LESS ITEM J)					127,925
PVPD TYPED NAME & SIGNATURE R. Paul Philp		DATE 5-8-90			
INST. REP. TYPED NAME & SIGNATURE Karen M. Petry		DATE			

BUDGET
10/1/90 to 9/30/91

DOE

A. SALARIES AND WAGES

1. Principal Investigator Paul Philp 25% FTE for 12 mos.	\$ 18,000
2. Post-Doctoral Research Fellow 100% FTE for 12 mos.	26,000
3. Secretary 25% FTE for 12 mos.	3,000
4. Laboratory Technician 50% FTE for 12 mos.	<u>7,600</u>
Total Salaries & Wages	\$ 54,600

B. FRINGE BENEFITS

25% x \$44,000 = \$11,000	
18% x 10,600 = 1,908	\$ 12,908

C. TRAVEL*

One professional meeting of AAPG and GSA	\$ 4,500
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D. EXPENDABLE SUPPLIES

Cappillary columns, gases, solvents, glassware, MS spare parts	16,000
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E. PUBLICATION COSTS

1. Journal page charges @ \$100/pg.	\$ 600
2. Interim and final reports	<u>550</u>
Total Publication Costs	\$ 1,150

F. OTHER DIRECT COSTS

Communications and postage	<u>\$ 300</u>
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G. TOTAL DIRECT COSTS	\$ 89,458
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*Travel expenses will be reimbursed at actual, reasonable and necessary costs.

BUDGET - Continued
10/1/90 to 9/30/91

DOE

H. INDIRECT COSTS

43% MTDC as set by DHHS on 12/22/86

\$ 38,467

I. TOTAL COSTS

\$127,925

ОКЛАНОМА

--- RETENTION TIME --->

----- RELATIVE INTENSITY ----->

--- RETENTION TIME --->

--- RELATIVE INTENSITY --->

--- RETENTION TIME --->

--- RETENTION TIME --->

PHENANTHRENE RATIOS

PHENANTHRENE RATIOS

KAC-34 SURFACE

CAL-4 SURFACE

--- RETENTION TIME --->

--- INTENSITY --->

RETENTION TIME --->

--- INTENSITY --->

RETENTION TIME --->

KAC-34 SURFACE

CAL-4 SURFACE

--- RETENTION TIME --->

Biodegradation of tar-sand bitumens from the Ardmore and Anadarko Basins, Carter County, Oklahoma

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Abstract—A series of tar-sand bitumens collected from a single shallow well in the Ardmore Basin, Carter County, Oklahoma has been characterized by various geochemical techniques. Particular emphasis has been placed on determination of variations in biomarker distributions, both hydrocarbons and porphyrins, as a function of biodegradation. The tar-sand bitumens have been severely biodegraded and most of the *n*-alkanes, low molecular weight cycloalkanes, isoprenoid alkanes, C_{27} – C_{29} steranes, light aromatics and sulfur compounds have been removed. In addition, the hopane distributions have been altered to differing degrees with the pseudohomologues above C_{20} decreasing in concentration prior to the C_{27-29} hopanes. The triaromatic steroid hydrocarbons were also altered with preferential removal of 20R epimers (C_{28-29} and C_{27-28}). Diasterane and C_{28} -sterane distributions appear to be relatively unaffected by biodegradation. The high resistance of tricyclic terpanes, the C_{24} -tetracyclic terpane and monoaromatic steroid hydrocarbons to biodegradation indicate that the distributions of these compounds are well suited to serve as correlation parameters in heavily altered samples. It was also observed in this study that the main ring structure of the porphyrin molecule was not affected by these very high levels of biodegradation. Previously hypothesized changes in porphyrin structure, due to biodegradation, have included *n*-alkyl side chain cleavage and possible conversion from DPEP- to ETIO-type porphyrins. An investigation has also been made with an active seep collected from Sulphur in the Anadarko Basin, Oklahoma and the results show that the relative rate of biodegradation of various classes of biomarkers differs between these two locations, although it was proposed that the original oil responsible for these two seeps is derived from the same source rock formation.

Key words—tar sand, biodegradation, hopanes, steranes, porphyrins, GC-MS, pyrolysis

INTRODUCTION

Tar-sands have been defined by the Interstate Oil Compact Commission (1980) as being a sedimentary rock containing a crude oil which is too viscous at natural reservoir temperature to be commercially producible by conventional primary recovery techniques. The tar-sand deposits of the world have been divided into two types: The breaching and exposure of an existing oil trap leading to *in situ* deposits and oil migrating to the surface producing active seeps (Walters, 1980). There are, of course, gradations and various combinations of these two types of deposits. Heavy oil accumulation and tar-sand formation are thought to be created by water washing and/or bacterial degradation of conventional crude oils (Winters and Williams, 1969; Bailey *et al.*, 1973; Milner *et al.*, 1977; Rubinstein *et al.*, 1977). Water washing removes the more water-soluble light hydrocarbons, especially aromatics, whereas biodegradation preferentially removes *n*-alkanes prior to removal of the more complex molecules. In a recent laboratory study, Lafargue and Barker (1988) showed that water washing removes the hydrocarbons in the sequence aromatics, *n*-alkanes, and then the naphthenes. No loss of pristane, phytane, steranes or terpanes was observed to occur but some

aromatics and sulfur compounds were depleted. Lafargue and Barker (1988) concluded that water washing is probably the dominant process affecting crude oil composition where conditions are unfavorable for bacterial degradation. Severe biodegradation removes isoprenoids as well as polycyclic molecules, making oil–oil and oil–source rock correlations and maturity determinations considerably more difficult, when using methods based on these compounds (Philp and Lewis, 1987). Therefore, a knowledge of the compositional changes caused by biodegradation is highly desirable for making accurate assessments of genetic relationships among oils, especially severely degraded heavy oils, seeps and tar-sand bitumens.

In the past two decades, the effect of biodegradation on petroleum composition has been studied extensively. The preferential removal of *n*-alkanes followed by *iso*- and *anteiso*- alkanes and then isoprenoids are well recognized phenomena of biodegradation (Winters and Williams, 1969; Bailey *et al.*, 1973). Recently, Philp and Lewis (1987) reviewed the effects of biodegradation. The relative extents of biodegradation described by them are not necessarily applicable to all situations, and a few exceptions have been reported. For example, McKirdy *et al.* (1983) have shown that steranes and diasteranes are degraded prior to the hopanes,

whereas Volkman *et al.* (1983) showed that hopane degradation immediately followed the initial alteration of (20R)-5 α (H),14 α (H),17 α (H)-steranes. A number of studies have shown that extensive biodegradation of hopanes produces ring A/B demethylated hopanes (Seifert and Moldowan, 1979; Rullkötter and Wendisch, 1982; Philp, 1983; Volkman *et al.*, 1983), whereas Howell *et al.* (1984) reported a series of demethylated hopanes and tricyclic terpanes in oils that are non-biodegraded or only mildly degraded. These discrepancies demonstrate that biodegradation is locally controlled by the population of microbes, nutrient supply and oxygen content and probably pH, Eh and temperature of the water in contact with the petroleum in a reservoir (Philp, 1983). Few data are available as to how porphyrin distributions change with biodegradation and/or water washing of oils.

In general, the progressive effects of biodegradation initially involve the removal of light *n*-alkanes, followed by the removal of *iso*- and *anteiso*-alkanes, steranes, diasteranes and the alteration and removal of hopanes followed by moretanes. Light aromatics are preferentially removed by water washing (Connan, 1984), but it is unclear when the C₁₅ aromatic fraction is biodegraded relative to the *n*-alkanes. Since the majority of porphyrins in oil are decarboxylated and contain multiple alkyl substituents, it is believed that the porphyrin distribution will not be altered by water washing due to their insolubility in water. It should be noted, however, that monocarboxylated porphyrins have been reported in very low concentrations in some oils (Baker and Louda, 1986). Severe biodegradation of aromatics is not always coupled with a drastic alteration of alkanes. Some aromatics, such as long chain *n*-alkylbenzenes are readily metabolized by bacteria adapted for *n*-alkane consumption via biooxidation (Connan, 1984). However, alternate methods for degradation of the aromatic components, as well as bacterial species adapted for aromatic hydrocarbon degradation, may very well exist. The typical order of susceptibility to biodegradation within the aromatic hydrocarbon fraction is monoaromatics > diaromatics > triaromatics. Within this broad grouping different isomers are degraded at different rates (Rowland *et al.*, 1986). By analogy, it may be proposed that porphyrins will have certain similarities to various NSO components and hence it may be anticipated that their susceptibility to biodegradation will be less than that of triaromatics.

Porphyrin side-chains are commonly methyl, ethyl, more rarely, *n*-propyl and longer *n*-alkyl groups (Quirke *et al.*, 1980) which could be degraded in a similar manner to *n*-alkyl aromatic compounds. This *n*-alkyl cleavage could occur with either deoxophylloerythroeno-porphyrins (DPEP) or etioporphyrins (ETIO). Biodegradation of this type would lead to an increase of one isomer over the other, or the possible formation of a porphyrin species not normally ob-

served in non-degraded oils. Another possibility would be cleavage of the isocyclic ring in DPEP porphyrins, similar to that of the C-ring cleavage for pentacyclic triterpanes (Rullkötter and Wendisch, 1982). It has been assumed in this study that the primary tetrapyrrole ring structure of the porphyrin is not altered and therefore absolute concentrations of porphyrins were not quantitatively measured. However, semi-quantitative observations, with respect to concentration, were made by absorption spectroscopy.

In a study similar to the present one, Barwise and Park (1983) found no change in porphyrin distribution for a suite of oils derived from a common source and of similar maturities but reservoirs at different depths and subjected to different degrees of biodegradation. A study by Palmer (1983) showed that DPEP/ETIO ratios of porphyrins are good maturity parameters when biodegradation has already affected parameters such as API gravity, *n*-alkane, sterane and triterpane distributions. In the same study, Palmer (1983) found porphyrin distributions to be a useful correlation tool between an oil seep and genetically-related degraded and non-degraded reservoir oils. The absolute concentration of vanadyl porphyrins was observed to increase with the degree of biodegradation while the amount of nickel porphyrins, relative to the vanadyl species, decreased (Palmer, 1983).

Main study area

The South Woodford Asphalt deposits are located approximately 1.5 miles south of Woodford, Carter County, Oklahoma in the Ardmore Basin (Fig. 1). This deposit is in Upper Mississippian-Lower Pennsylvanian strata, and the tar sand deposits are distributed along the crest of the South Woodford Anticline. A geological map of the South Woodford Asphalt deposits (Fig. 1) shows the location of quarry sites and tar sand outcrops. Several active oil seeps exist along the axis of the South Woodford Anticline in the Rod Club Sandstone (Harrison and Burchfield, 1984).

Well OGS-5-Fitzgerald was chosen for this study because it was the deepest well (270ft) cored by the Oklahoma Geological Survey in this area. The core was taken near the axis of the anticline in near vertically dipping Rod Club Sandstone. Lithologically, the sandstone consists of brown to tan, fine to very fine sands with abundant clay laminations and strings. The bitumen-bearing sands ranged from 7 to 270ft in depth. Average bitumen content is 10.8% based on the analysis of 66 samples (Harrison and Burchfield, 1984). Sixteen tar sand samples were selected at depths ranging from 16 to 256ft in the Fitzgerald well for this study.

Secondary study area

For comparative purposes, active seep samples were also collected from the Middle Ordovician Oil

Fig. 1. Location of the Fitzgerald No. 5 well.

Creek Formation at the South Sulphur Asphalt deposits north of the Fitzgerald area. This study site has been previously described by Müller *et al.* (1984).

Previous studies of this area

At the present time, the most comprehensive geochemical study of the South Woodford tar sand deposit is a recent publication by Weber (1988). Bitumens isolated from the Middle Ordovician Oil Creek Formation at the South Sulphur Asphalt deposits, to the north of the Fitzgerald area, have been previously studied by Williams (1983) and Müller *et al.* (1984).

Müller *et al.* (1984) reported that *n*-alkanes, isoprenoids, low molecular weight aromatic hydrocarbons and thiophenes had been completely removed from the tar sand bitumen of South Sulphur

Asphalt deposits. In the most severely degraded samples, the sterane distribution was found to be partially altered. The preferential loss of C_{30} -hopanes, relative to their C_{27} - C_{29} pseudohomologues, was observed even in the sample with intact sterane distribution. The partial loss of $18\alpha(H)$ -22,29,30-trisnorhopane (T_1) was also observed in the biodegraded sample. Diasteranes, triaromatic steroid hydrocarbons, tricyclic terpanes, the C_{24} -tetracyclic terpane, C_{29} -hopane and $17\alpha(H)$ -22,29,30-trisnorhopane (T_m) appear to be resistant to biodegradation in the South Sulphur samples (Müller *et al.*, 1984). Müller *et al.* (1984) also gave a list of susceptibility for various classes of compounds, excluding porphyrins which were not studied, towards biodegradation in decreasing order: thiophenes, naphthalenes, *n*-alkanes, *n*-alkylcyclohexanes, alkylbenzenes, iso-

prenoids, C_{30} , hopanes, moretanes, 18 α (H)-22,29,30-trisnorhopane, and steranes.

EXPERIMENTAL PROCEDURE

Asphaltene removal

Tar sand bitumens (0.3–0.5 g), provided by the Oklahoma Geological Survey, had been obtained from the corresponding tar sand sample by extraction with dichloromethane (Harrison and Burchfield, 1984). Asphaltenes were removed from the bitumens by precipitation with *n*-pentane. This process was repeated 3 or 4 times to ensure complete precipitation of the asphaltenes.

Hydrocarbon fractionation

After removal of the asphaltenes, the bitumens were separated into saturate, aromatic and polar (NSO) fractions by column chromatography using silica gel (100–200 mesh) and alumina (80–200 mesh). Saturate hydrocarbons were eluted from the column with *n*-pentane (c. 80 ml) and aromatic hydrocarbons with toluene (c. 80 ml). Polar components were obtained using dichloromethane/methanol (1:1, c. 50 ml). Fractions were evaporated either on a rotary evaporator or under a stream of nitrogen. Alkanes were removed from the saturate fraction by use of Union Carbide S115 molecular sieve (3–4 g) in 150 ml of isooctane (Fisher, HPLC grade). The mixture was refluxed (20 h), and the solvent containing the branched cyclic hydrocarbons was removed and evaporated. No attempt was made to recover the *n*-alkanes from the molecular sieves since for the most part the *n*-alkane content of these samples was extremely low or non-existent.

Gas chromatography

Saturate and aromatic fractions were analyzed by gas chromatography (GC) using either a Hewlett-Packard 5890 or Varian 3300 instrument. Both the total saturate fraction and the branched/cyclic fraction were analyzed by GC. Both instruments were equipped with a J & W Scientific DB-5 fused silica capillary column (30 m $\times$ 0.25 mm; 0.25 μ m film thickness). The Varian 3300 was equipped with flame ionization and flame photometric detectors (FID and FPD, respectively), whilst the HP 5890 had only a FID. Helium was used as carrier gas with a flow rate of c. 1 ml min⁻¹. Injector and detector temperatures were 300°C. Temperature program was 40°C (1.5 min) to 130°C at 15°C min⁻¹ and then to 300°C at 4°C min⁻¹ (final temperature held isothermal for 25 min). Organic sulfur compounds in the aromatic fraction were determined by use of the FPD.

Biomarker analyses

Biomarkers present in the saturate and aromatic fractions were analyzed using a Hewlett-Packard 5890 A gas chromatograph interfaced to a Finnigan MAT Model 700 Ion Trap Detector (ITD). The GC

was equipped with a J & W Scientific DB-5 fused silica capillary column (c. 25 m $\times$ 0.25 mm, 0.25 μ m film thickness). A split-splitless injection technique was used with helium as the carrier gas at a flow rate of c. 1 ml min⁻¹ and injector temperature of 300°C. The temperature program was started from 40°C (1.5 min) and increased initially to 140°C at 10°C min⁻¹ and then to 300°C at 4°C min⁻¹ (final temperature held for 20 min).

The emission current of the ITD was 80 μ A, electron energy 70 eV, multiplier voltage 1400–2100 V and scan speed of 1 s scan⁻¹. The ITD was used in the multiple ion detection mode monitoring *m/z* ratios of 191, 217, 231, 253, for di- and tripterpanes, steranes, triaromatic and monoaromatic steroids, respectively. Data were collected on an IBM PC-XT using Finnigan MAT ITDS V # 3.00 and PC-DOS 2.1 software. Compound identification was made by comparison with mass chromatograms from samples previously analyzed on the GC-ITD system and by comparison with published data. Selected samples were also analysed using a Finnigan MAT triple stage quadrupole mass spectrometer operated under similar conditions.

Porphyrim isolation

Column chromatography (100–200 μ m mesh silica 80–200 μ m mesh alumina activated at 240°C for 3 h) was performed on tar sand extracts to determine the predominant porphyrin metal chelate species present. Nickel porphyrins were eluted with 10 and 20% toluene/hexane, and vanadyl porphyrins were eluted with 10% ethyl acetate/toluene (Barwise and Whitehead, 1979). Metallo-porphyrins were identified by visible absorption spectrometry, and vanadyl porphyrins were found while the nickel porphyrins could not be observed.

Demetallation and thin layer chromatography of porphyrins

Porphyrins were demetallated before HPLC analysis using methanesulphonic acid (MSA = 98%; Aldrich Chemical Co.). Crude oil or tar sand bitumen plus a five fold excess of MSA was heated for 4 h at 100°C. The reaction was quenched by pouring the mixture into distilled water (1–2 times the amount of acid used). The organic coagulate was separated from the aqueous acid by filtration. The organic residue was washed with MSA diluted with distilled water (50% v/v) until the organic filtrate was colorless (Marriott *et al.*, 1984). The porphyrins were extracted from the aqueous phase with methylene chloride and conversion to the free-base was achieved by neutralization with sodium acetate or sodium bicarbonate solution (5%, w/v). The methylene chloride eluant was dried with sodium sulfate and transferred to a rotary evaporator to remove solvent. The methylene chloride and aqueous phases were monitored with visible spectrophotometry during the procedure in

order to check the completeness of isolation and the degree of porphyrin purity.

Thin layer chromatography (20 cm × 20 cm × 0.25 mm silica gel 60, Merck) was used prior to HPLC analysis to remove unwanted aromatic components from the demetallated porphyrin fraction. The porphyrin fraction was eluted by benzene/methylene chloride (1:1, v/v) or toluene/methylene chloride (1:1, v/v) (Alturki *et al.*, 1972). This step was ultimately replaced by using a Bond Eluates (trade-mark) column filled with 1 g of C₁₈-silica and elution with methylene chloride until no further porphyrins eluted.

High performance liquid chromatography

HPLC separation of demetallated porphyrins was performed using three silica columns (4.6 × 150 mm, 3 µm) connected in series. An Eldex 9600 ternary solvent system and a Rheodyne 7125 injector fitted with a 10 µl loop were used. Porphyrins were detected using a Kratos 783 spectrophotometer set to monitor a wavelength of 400 nm. A typical flow rate for this system was 0.9 ml min⁻¹, with backpressure at 1450–1550 psi and the following solvent mixtures were used: (A) methylene chloride:acetone (4:1, v/v); (B) hexane:pyridine (99:1, v/v); (C) hexane:acetic acid (99:1, v/v) (Barwise *et al.*, 1986; Chicarelli *et al.*, 1986).

RESULTS AND DISCUSSION

Bulk composition

The tar-sand bitumens contain significant amounts of aromatic and polar compounds, as seen from the ternary diagram in Fig. 2. Gas chromatograms of selected tar-sand bitumen hydrocarbon fractions are shown in Fig. 3 and most are so severely degraded that all *n*-alkanes and isoprenoids have been removed, as expected for severely biodegraded samples (Connan, 1984). The only exception was the sample

from 240ft which contained *n*-C₁₄–C₂₄ alkanes, pristane and phytane, and was possibly contaminated. For all the samples tricyclic terpanes, pentacyclic terpanes, and steranes can be observed at the tail of the large unresolved hump. The aromatic hydrocarbons of the tar-sand bitumens also showed effects of severe degradation/water washing to the extent that only a large hump of unresolved components was present in chromatograms of the aromatic hydrocarbons along with triaromatic steroid hydrocarbons. The lower molecular weight aromatic hydrocarbons are more water soluble than saturated hydrocarbons (Price, 1980), and their rate of biodegradation is known to decrease with increasing aromatic ring number and increasing chain length of alkyl substituents (Rowland *et al.*, 1986; Volkman *et al.*, 1984; Williams *et al.*, 1986).

Biomarker distributions

Biomarkers have been used extensively in recent years to provide information on depositional environments (Moldowan *et al.*, 1985); types of preserved source materials (Philp and Gilbert, 1984; Huang and Meinschein, 1976); and the thermal maturity of a sample (Mackenzie *et al.*, 1982). In the case of oils, biomarker distributions can provide information on the extent of biodegradation (e.g. Seifert and Moldowan, 1979; Volkman *et al.*, 1983) and, to some extent, relative migration distance (Seifert and Moldowan, 1978; Mackenzie, 1984). One of the aims of the work described in this paper was to examine the extent of biodegradation of steranes, hopanes and porphyrins in the tar-sand bitumens.

Steranes. It has often been shown that steranes are degraded much more rapidly than diasteranes (Seifert and Moldowan, 1979; Volkman *et al.*, 1983; Goodwin *et al.*, 1983). Furthermore, the 20R-5 α (H),14 α (H),17 α (H) sterane isomers are degraded more readily than their 20S isomers, and the C₂₇ steranes are removed prior to the C₂₈ and C₂₉ species. The *m/z* 217 chromatogram for the tar sand bitumen from 144 ft shows that the regular C₂₇–C₂₉ steranes have been removed, leaving the C₂₇–C₂₉ rearranged steranes and relatively small, but significant, quantities of C₃₀-steranes. The C₃₀-steranes have been shown by MS/MS to be regular, or side-chain substituted, and not 4-methyl steranes (Fig. 4). The similarity in distributions of the diasteranes and C₃₀-steranes for all of the tar-sands studied suggests that the bitumens from this core have a common source. The apparent resistance of the C₃₀-steranes to biodegradation, as shown by these results, may be useful in correlation studies. Moldowan *et al.* (1985) have stated that C₃₀-steranes may have wide-ranging applicability as marine source indicators, except for oils derived from Cambrian and older source rocks.

Aromatic steroid hydrocarbons. The biodegradation of monoaromatic and triaromatic steroid hydrocarbons under simulated and natural conditions has been studied by Wardroper *et al.* (1984). The major

Fig. 2. Ternary diagram showing relative proportions of saturate, aromatic and NSO – asphaltene fractions for the tar sand extracts and oils from the surrounding area.

Fig. 3. Chromatograms of saturate fractions from extracts of the tar sands recovered at 16, 144 and 256 ft sub-surface.

effects they observed were: (i) loss of low molecular weight triaromatic hydrocarbons (C_{20-21} species); (ii) preferential degradation of mono- and tri-aromatic hydrocarbons with the $20R$ configuration; (iii) resistance of low molecular weight monoaromatic hydro-

carbons to biodegradation as compared with their higher molecular weight pseudohomologues. Biodegradation of aromatic steroids is not apparent until the C_{27-29} steranes, hopanes and C_{27-29} diasteranes have been severely degraded. Hence, these com-

Fig. 4. SIM chromatogram (m/z 217) for the sterane region of the saturate hydrocarbons isolated from the extract of the sample from 144 ft sub-surface.

Fig. 5. Mono- and tri-aromatic sterane chromatograms (m/z 253 and 231, respectively) for bitumens from samples recovered at 16, 116 and 248 ft sub-surface. (Peak identifications given in Table 1).

pounds are useful for correlation and maturation studies (Mackenzie, 1984; Seifert and Moldowan, 1978).

Examples of the monoaromatic steroid (m/z 253) and triaromatic steroid hydrocarbon (m/z 231) distributions for three tar-sand bitumens are shown in Fig. 5. The similarity of these mass chromatograms further supports our proposal that these tar-sand bitumens are genetically related. The absence of C_{20} and C_{21} triaromatic steroid hydrocarbons is probably due to their preferential removal during water washing and/or biodegradation, as documented by Wardroper *et al.* (1984) and Volkman *et al.* (1984).

A slight decrease in C_{27-28} 20R triaromatic steroid hydrocarbons, relative to the corresponding 20S isomers, could be observed (Fig. 5; see Table 1 for peak identifications). The preferential removal of the 20R species is analogous to the preferential decrease of 20R-5 α (H), 14 α (H), 17 α (H) steranes during biodegradation (Goodwin *et al.*, 1983; Seifert and Moldowan, 1979; Volkman *et al.*, 1984). The monoaromatic steroid hydrocarbons of these tar-sand bitumens, are very similar in distribution to those of a conventional oil from the same area. Therefore, it is proposed that in these tar sands, the monoaromatic steroid hydro-

carbons are more resistant to biodegradation than the triaromatic steroid hydrocarbons, an observation previously made by Wardroper *et al.* (1984).

Table 1. Peak identifications for the mono- (m/z 253) and tri- (m/z 231) aromatic steroid hydrocarbon distributions shown in Fig. 5. [Based on data in Wardroper *et al.* (1984) and Mackenzie (1984).]

Peak	Carbon number	Stereochemistry
1	21	5 β H
2	22	5 β H
3	27	5 β H, 20S
4	27	—?
5	27	5 β H, 20R
6	27	5 α H, 20S
	28	5 β H, 20S
	27	5 α H, 20R
7	28	5 α H, 20S
	28	5 β H, 20R
	29	5 β H, 20S
8	29	5 α H, 20S
9	28	5 α H, 20R
	29	5 β H, 20R
10	29	5 α H, 20R
11	26	20S
12	26	20R
	27	20S
13	28	20S
14	27	20R
15	28	20R

Terpanes. Unlike the steranes and aromatic steroid hydrocarbons, terpane distributions show a number of variations resulting from differences in the extent of biodegradation (Fig. 6). The preferential removal of the 22R isomers of C_{31} , C_{32} , C_{33} hopanes is clearly indicated in the terpane distributions of the sample from a depth of 16 ft (Fig. 6). The preferential removal of 22R hopanes and the decreasing susceptibility to biodegradation of hopanes in the order of $C_{33} > C_{34} > C_{31} > C_{32} > C_{31} > C_{30} > C_{29}$ has been previously documented by Goodwin *et al.* (1983). However, with these tar-sand extracts, the susceptibility of the hopanes to biodegradation appears to be partially reversed. That is, the order of removal by biodegradation is $C_{29} > C_{31-33} > C_{34}$ and C_{33} homologues. Moretanes and 17 α (H)-22,29,30-trisnorhopane (T_m), 18 α (H)-22,29,30-trisnorhopane (T_s) and 17 α ,21 β -29-norhopane (C_{29}) appear to be relatively stable to biodegradation, in this particular sample suite. The resistance of T_m , T_s and the C_{29} -hopane to biodegradation has also been reported by Seifert *et al.* (1984). However, relative to the tricyclic terpanes, which show no detectable changes resulting from biodegradation, there is a slight decrease in

the concentrations of the C_{29} -hopane, T_m and T_s , particularly for samples at 116 and 168 ft. On the basis of changes occurring within the hopane distributions, the samples from 144 and 204 ft appear to be the least biodegraded with the other samples (Fig. 6) showing extensive evidence for alteration of the terpane distributions.

Tricyclic and tetracyclic terpanes are widely distributed in ancient sediments and crude oils and are fairly resistant towards biodegradation (Aquino Neto *et al.*, 1983). Tricyclic terpanes (C_{27-29}) were first reported by Anders and Robinson (1971) in the Green River Formation of the Uinta Basin, Utah. The same series of compounds were also found unaltered in extracts from outcrops and cores of oil-impregnated sandstones of Rozel Point Spring Seep of the Uinta Basin (Reed, 1977), whilst the steranes and hopanes from those samples had been altered by biodegradation and water washing. The resistance of the tricyclic terpanes to biodegradation has been confirmed by other authors, such as Seifert and Moldowan (1979), Connan *et al.* (1980) and Goodwin *et al.* (1983). However, in a few severely biodegraded oils, such as the St Aubin Asphalt,

Fig. 6. Hopane chromatograms (m/z 191) for 6 tar-sand samples recovered from increasing depths within the Fitzgerald No. 5 well. (Numbers correspond to carbon number of individual hopanes.)

Switzerland, it has been shown that the tricyclic terpanes can be demethylated in a similar manner to the hopanes (Connan, 1984).

The enhanced degradation of the hopanes from samples below 240 ft, as manifested by removal of the C_{30} and higher hopane pseudo-homologues, is probably due to their increased contact with the ground water in the area. Examination of the core showed the upper 7–16 ft and the lower 256–270 ft to be composed of grayish-brown to brown colored sandstone. Most of the intermediate section was composed of dark brown to black, highly bitumen-saturated sandstone, with a few fractures and light brown sandstone strings. This observation suggests that the upper and lower parts of the tar-sand deposit are more accessible to the ground water and, ultimately, the bitumen will be more severely degraded than in the middle section of the core. It is well documented that bacterial degradation will occur at the oil–water interface, since bacteria preferentially abide in the aqueous phase and do not thrive in oil (Connan, 1984). Some microorganisms produce extracellular materials that can absorb, emulsify or wet a hydrocarbon phase, thus increasing the contact area and producing sub-micron droplets which can be phagocytized (Zajic and Gerson, 1977). However, more complex mechanisms may be involved in the present study area. Since some heavy oil is seeping out along the crest of the South Woodford Anticline, active migration of oil from a reservoir in the vicinity of the seep may be occurring and mixing with the tar-sand bitumens.

subsequently causing contamination of the indigenous hopanes.

It has been proposed that ring A/B demethylated hopanes (25-norhopanes) isolated from biodegraded asphalts and oils (Rullkötter and Wendisch, 1982) are the biodegradation products of $17\alpha(H)$ -hopanes. In severely biodegraded crude oils, it has been proposed that the demethylated hopanes can be used as maturity parameters, in the same way as the regular hopanes are used in nondegraded oils (Volkman *et al.*, 1983). However, the biodegradation of hopanes does not always produce ring A/B demethylated hopanes (Connan, 1984) and no evidence for the presence of 25-norhopanes could be found in these tar-sand extracts. An *in vitro* study carried out by Goodwin *et al.* (1983) also failed to produce demethylated hopanes, although the $17\alpha(H)$ -hopanes were degraded.

Porphyrins. In order to study the effects of biodegradation upon porphyrin distributions it was proposed to monitor either distinct destruction of certain isomers or dealkylation of a specific group of isomers. Changes in DPEP- to ETIO-type porphyrin ratios were monitored by observing the percentage of DPEP relative to porphyrins ratio. This was achieved by integrating peak areas from HPLC chromatograms with the knowledge that there was some overlap between ETIO and DPEP porphyrins in the region of the chromatogram containing these components (Fig. 7). The co-elution problem was not considered to be significant and the peaks which

Fig. 7. HPLC chromatogram (400 nm absorbance) for the demethylated porphyrins isolated from the Fitzgerald well No. 5 sample recovered at 128 ft sub-surface.

Fig. 8. (a) Plot of the DPEP-to-ETIO ratio versus depth of recovery for samples from the Fitzgerald No. 5 well. (b) Cross plot of the chromatographically same members of C_{32}/C_{31} vs C_{32}/C_{30} DPEP-series porphyrins (m/z 476 = 14 n ; n = integer) for tar sand samples from the Fitzgerald No. 5 well. Sample numbers are same as for Fig. 8(a) and hence can be used to relate samples with depth.

eluted in that region were not defined in this study, as they accounted for less than 10% of the total area. Within the error limits set by repeated analyses of the porphyrins isolated from Boscan crude oil, Venezuela, there were no observable changes in percent DPEP of total DPEP + ETIO porphyrins or the DPEP-to-ETIO ratio within the tar-sand core samples with increasing depth [Fig. 8(a)].

Ratios of C_{32}/C_{31} and C_{32}/C_{30} DPEP type porphyrins were determined to identify possible methyl cleavages from the porphyrins and plotted against the ratio of C_{32}/C_{30} DPEP which was also determined to investigate possible ethyl cleavages (Fig. 8(b)). Data points falling outside the central grouping in both of these plots are interpreted to be due to changing column conditions. The variation of the ratios is considered to be insignificant in this context and once again within normal variation, as defined by several analyses of the Boscan porphyrins. Based upon the porphyrin ratios measured for extracts from the OGS-5-Fitzgerald tar-sand core, it was concluded that there were no observable effects upon the porphyrin distributions resulting from biodegradation. It should be noted that porphyrins with alkyl substituents longer than ethyl were not determined, but such extended n -alkyl substituents are known to exist up to C_{11} (Quirke *et al.*, 1980). The analytical technique of normal phase HPLC is not without limitations and such data do not prove conclusively that there was no alteration of porphyrins due to biodegradation. However, results of this study support previous work by Palmer (1983) and Barwise and Park (1983) which also showed no effect on the porphyrin distribution resulting from biodegradation.

Surface weathering effects. In a related study we have re-examined the biomarker composition of active seep samples from the Oil Creek Formation in the Sulphur region of Oklahoma previously analysed by Müller *et al.* (1984). Samples were collected over a period of several months to see whether or not any variations could be observed in the biomarker distributions as a result of surface weathering. Furthermore, samples from the active Oil Creek Formation seep which had been exposed to the atmosphere for several months and bitumen from the water into which it was moving were also collected. Some interesting differences between the active seep and the Fitzgerald tar sand extracts were observed. First, samples of the active seep and the water had low concentrations of the C_{20} - C_{21} steranes, relative to the C_{27} - C_{30} regular and rearranged samples. However, the sample collected from outside the seep, and which had experienced additional weathering due to atmospheric exposure, showed a significant increase in the concentration of the C_{20} - C_{21} steranes, relative to the higher carbon number regular and rearranged steranes. Based on peak heights in the m/z 217 chromatogram, the ratio of C_{20}/C_{29} steranes in the seep was 0.34 compared with 1.2 in the seep sample exposed to additional atmospheric weathering. In comparison to the Fitzgerald samples, there was also a much higher concentration of regular steranes relative to the rearranged steranes [cf. Fig. 4 and 9(a)].

A similar effect could also be seen in terpane concentrations. The active seep sample, although exhibiting significant removal of the extended and C_{30} hopanes, had a high concentration of hopanes relative to tricyclic terpanes [Fig. 9(b)]. On the con-

Fig. 9. (a) Sterane (m/z 217) and (b) hopane (m/z 191) SIM chromatograms for the saturated fraction isolated from the Sulfur region active seep bitumen.

trary, the sample from the water and that exposed to the atmosphere outside the seep had significantly higher concentrations of tricyclic terpanes relative to hopanes. (In the active seep sample the ratio of the C_{27} tricyclic/ C_{27} trisnorhopane was 1.5 whereas in the exposed sample this ratio was approximately 4.2.) This suggests enhanced destruction of the hopanes, although their overall distribution was unaltered [Fig. 9(b)]. Interestingly enough, the terpanes showed a similar distribution to that observed in the most biodegraded Fitzgerald sample at 256 ft. However, it must be remembered that, in contrast to the Fitzgerald sample, the regular steranes were still present in these Sulphur seep samples. The degraded sterane (m/z 124) chromatograms were virtually identical to those observed for Oil Creek oils and those of the Fitzgerald seep samples. As discussed previously (Jiang *et al.*, 1988), these A/B-ring degraded steranes are extremely useful for correlating oils and seeps which have undergone differing degrees of biodegradation.

SUMMARY

In summary, the tar-sand bitumens from the Fitzgerald well were so severely biodegraded that n -alkanes, isoprenoids, light aromatic hydrocarbons, thiophenes, benzothiophenes and regular C_{27} - C_{29} steranes had been removed. The sample from a depth of 240 ft differed from the others since it still con-

tained C_{14-24} n -alkanes, pristane and phytane. However, the lack of steranes and severely altered hopanes implies that the n -alkanes, pristane and phytane had most likely been recently added to this sample, either by contamination during coring, extraction, or by *in situ* mixing with migrated less degraded oils. Diasteranes, C_{29} -steranes, tricyclic terpanes and monoaromatic steroid hydrocarbons appeared to be rather resistant toward biodegradation in these samples and thus are suitable for correlation studies. The triaromatic steroid hydrocarbons were slightly altered with the result that C_{29} and C_{21} species were absent and there was a slight reduction of C_{27-29} 20R isomers.

The biodegradation effects summarized from the study of tar sand bitumens of the OGS-5-Fitzgerald core, when compared to that of the tar sand bitumen from the South Sulphur Asphalt deposits, in which the C_{30-} hopanes degraded faster than C_{27-29} steranes (Miiller *et al.*, 1984), illustrates the unpredictability of the relative order of degradation of hopanes and steranes. Porphyrin distributions were found not to be altered by biodegradation and, as such, represent a useful class of biomarkers for correlation studies.

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Biodegradation of tar-sand bitumens from the Ardmore/Anadarko Basins, Oklahoma—II. Correlation of oils, tar sands and source rocks

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Abstract—In an earlier paper we reported the effects of biodegradation on tar-sand bitumens from the southern part of the Ardmore and Anadarko Basins. In this paper we wish to describe geochemical correlations that have been made between the tar-sand bitumens and oils produced from various formations in the Pauls Valley area, 25 miles to the north. It was determined that the tar-sands were formed from a source similar to many of these oils whose reservoir ages ranged from Ordovician to Pennsylvanian. The oils had been previously divided into two major groups, on the basis of their biomarker distributions, with one group (80% of the oils studied) proposed to have been sourced from the Woodford Shale (Devonian) and the other group from the Viola Limestone (Ordovician). The tar sand bitumen-oil correlation study, based on hydrocarbon and porphyrin biomarker distributions, and pyrolysis-gas chromatography of asphaltenes, has shown that the tar-sand bitumen appears to be genetically related to the group of oils derived from the Woodford Shale and more specifically to those present in the Oil Creek Formation (Ordovician) of the Anadarko Basin.

Key words—biodegradation, tar-sand bitumens, oils, source rocks

INTRODUCTION

Over 300 occurrences of heavy oils and bitumen impregnated rocks have been reported in Oklahoma (Harrison *et al.*, 1981) with a total of 45 tar-sands occurring in Carter and Murray Counties in south-central Oklahoma. In the present study nineteen tar-sand samples were taken from a drill core, at depths ranging from 16 to 256 ft, obtained from a tar-sand quarry site in the Ardmore Basin, Carter County, Oklahoma (Fig. 1). The samples were cored in the Upper Mississippian Rod Club sandstone within the local structure known as the South Woodford Anticline (Harrison and Burchfield, 1984). Geochemical characteristics of these samples have been described in a preceding paper (Lin *et al.*, 1989).

The major aim of the second part of this study was to determine possible sources for the tar-sand bitumen. It was proposed to undertake the correlation using hydrocarbon and porphyrin biomarker distributions and subsequently use pyrolysis-gas chromatography (py-GC) of the asphaltene fraction to confirm any correlations that were made. It was of interest to use porphyrin, as well as hydrocarbon, distributions for correlation purposes since there have been few specific studies published on porphyrin distributions in genetically related oils or source rocks (Branthaver and Filby, 1987). Jones (1986) previously undertook a study of hydrocarbon biomarkers present in several oils along with possible source rocks from the Pauls Valley-Hunton Uplift area of southern Oklahoma. The same group of oils and

source rocks were examined in this study in order to determine their porphyrin distributions.

Study area and previous work

The tar and sand deposits are in Upper Mississippian-Lower Pennsylvanian strata within the crest of the NW-SE trending South Woodford Anticline, T3S, R1W (Fig. 1). There are shallow wells (165–480 ft) that produce heavy oil from vertical Pennsylvanian (probably Otterville) sandstone in section 4, T3S, R1W (Harrison and Burchfield, 1984). Several active oil seeps exist along the axis of the South Woodford Anticline in the Rod Club Sandstone (Harrison and Burchfield, 1984). The study area for the tar sand deposit has been described in the first part of this study and will not be described in detail again (Lin *et al.*, 1989).

Regional structure setting

The Ardmore Basin is set in what is recognized as the Southern Oklahoma Aulacogen (Feinstein, 1979) which in the context of plate tectonics is the failed arm of a triple junction rift system which was active during Precambrian and early Paleozoic times (Maley, 1986). The original aulacogen set the scene for an early northwest-southeast trending trough which was the connected Ardmore-Anadarko Basin. The two basins, Ardmore and Anadarko, did not become separate until the latter half of the Pennsylvanian, possibly during the Arbuckle Orogeny (Tomlinson and McBee, 1959). The development of the

Fig. 1. Map indicating location of tar sand core and general location of oil samples collected for use in this study. In addition a generalized cross section along A-A' in Southern Oklahoma through the study area is also shown.

aulacogen is divided into three stages, namely rifting, subsidence and deformation. The rifting stage is characterized by extrusives and intrusives. There are at least 15,000 ft of graywacke, argillite, quartzite, and embedded chert of late Precambrian to Early Cambrian age associated with the igneous rocks. The subsidence stage of the aulacogen was the time of deposition of a thick sequence of marine sediments of primarily carbonates, however the Ordovician Simpson Group was dominated by clastic deposition of shales and thick sandstone of regional importance.

The carbonates contain paleontologic evidence of shallow water deposition, which would tend to indicate that the trough subsided at a rate that was equal to sedimentation. The deformational stage is the time of tight folding and reactivation of older faults. Conglomerates within the upper Mississippian and early Pennsylvanian indicate several periods of uplift for the Ardmore Basin. Major uplift is indicated for the (Middle Pennsylvanian) Morrowan and Atokan time by the much thicker Joliff and Bostwick conglomerate members at the base of both series, respec-

tively. The Criner Hills (Fig. 1) is believed to be the major uplift which provided material for the conglomerates. The Upper Mississippian conglomerate is reported to contain limestone pebbles from Ordovician and Lower Mississippian carbonates (Meek, 1983). The Morrowan Joliff member conglomerate contains Mississippian Sycamore Limestone and Devonian Woodford chert cobbles with younger material present, while the Atokan Bostwick conglomerate member contains pebbles of all older Paleozoic formations down to and including the Early Ordovician Arbuckle Limestone (Tomlinson and McBee, 1959). The presence of the conglomerates provides evidence in support of a probable post-Atokan, or later, oil generation since none of the clasts have been found to be bitumen impregnated. A generalized cross section for the southern Oklahoma area illustrating the position of the Ardmore Basin relative to the Pauls Valley-Hunton Uplift area is shown in Fig. 1 (Ham *et al.*, 1964).

A number of oils and source rocks from the Pauls Valley-Hunton Uplift area, southeast Anadarko Basin, have been analyzed for *n*-alkane, terpane and sterane distributions (Jones, 1986) in an attempt to perform an oil-source rock correlation. Based on the biomarker distributions, Jones (1986) concluded that of thirty oils, 80% had a possible common source, probably the Woodford Shale. Some of the oils reservoirized in the Viola Limestone exhibit distinct geochemical characteristics similar to the Viola rock extract which was thus proposed as the probable source rock (Jones, 1986).

EXPERIMENTAL PROCEDURE

All of the experimental procedures, except pyrolysis-gas chromatography (py-GC) of asphaltenes, have been previously described in the first part of this study (Lin *et al.*, 1989) and will not be described again in this paper.

Flash pyrolysis-GC of asphaltenes

The asphaltenes from the oils and tar-sands were dissolved in a small amount of dichloromethane and reprecipitated with *n*-pentane three times before being subjected to py-GC, using a CDS (Chemical Data Systems) 122 extended temperature pyroprobe. The sample was pyrolyzed at 610°C for 20 s using a pyrolyser coupled to a Varian 3300 gas chromatograph with a split injection system (split ratio 1:30) via a heated interface (300°C). The pyrolysis products were transferred directly onto the GC column by helium (*c.* 30 ml/min) passing through the interface. Chromatographic separation was performed on a J&W Scientific DB-5 fused silica column (30 m × 0.25 mm, film thickness 1.0 µm). The carrier gas flow rate through the column was *c.* 1 ml/min, and the temperature program was held at -25°C for 2 min during the pyrolysis and then increased to 300°C at 4°C/min (final temperature was held for

30 min). The column effluent was split (1:1) and monitored by a flame ionization detector (FID) and a flame photometric detector (FPD) mounted in parallel to determine hydrocarbons and sulphur containing compounds respectively. All data were collected with Nelson Analytical Chromatography Software Model 2600, running on an IBM PC-XT under PC-DOS #3.6.

RESULTS AND DISCUSSION

Bulk composition

It was apparent from the relative distributions of the saturate, aromatic, and polar fractions of oils and tar sand bitumens that the oils which were not biodegraded contained mainly saturated hydrocarbons (71.6–83.2%) while the tar sand bitumens contained major amounts of aromatic and polar compounds. Fluctuations observed for the saturate/aromatic ratio from the tar-sand bitumens probably reflect different rates, or extents, of bacterial degradation and water washing on the saturates and aromatics. Two of the Oil Creek oils (#29 and #30) exhibited low API gravity of 12° and 10° respectively and further GC analysis of saturates, aromatics and sulfur compounds indicated that these two oils have been degraded.

Gas chromatography of oils

The gas chromatograms of the saturate fractions for the Oil Creek Formation oils #3, #18, #29, and #30, proposed by Jones (1986) to be sourced from the Woodford Shales, are shown in Fig. 2. In these chromatograms, the two shallow oils show a decrease in the concentration of their *n*-alkanes relative to the isoprenoids as a result of early stage biodegradation (Winters and Williams, 1969; Bailey *et al.*, 1973; Connan *et al.*, 1980; Alexander *et al.*, 1983). The gas chromatograms of the aromatic and sulfur components for these same four oils [Figs 3(a) and 3(b)] also show a decrease in the relative concentration of lower molecular weight components with decreasing reservoir depth. The lower molecular weight aromatics are known to be more water soluble than the saturate hydrocarbons (Price, 1980), and their biodegradation rate decreases with increasing aromaticity and increasing chain length of alkyl substituents (Rowland *et al.*, 1986; Volkman *et al.*, 1984; Williams *et al.*, 1986). The alteration to the aromatic and organosulfur compounds is far more severe than that which has occurred to the saturated hydrocarbons. This phenomenon has been observed previously by Connan (1981, 1984) who showed that intensive alteration of both aromatics and alkanes is generally encountered only in the surface or at shallow depth, while in deeper reservoirs, highly altered aromatics and sulfur compounds are associated with only mildly altered alkanes. The preferential degradation of aromatics, including sulfur compounds, is not clearly understood, although it is probably related to

Fig. 2. Chromatograms showing the distribution of the *n*-alkanes of four oils examined in this study. Oils 29 and 30 are partially biodegraded.

sulfur-decomposing bacteria and possibly to some species of sulphate-reducing bacteria (Connan, 1981, 1984). Laboratory results have also shown that biodegradation of the aromatic hydrocarbons will prevail when essential nutrients such as nitrate and phosphates are absent (Fedorak *et al.*, 1983). A similar phenomenon has been observed in mangrove swamps where preferential biodegradation of alkanes and aromatics is directly related to nutrient supply (Scherrer and Connan, 1989). The preferential biodegradation of the sulfur-containing aromatics relative to aromatics and alkanes, within the depth limits of the oils examined in the current study of 5800–8200 ft, commonly suggests an anaerobic degradation pathway for the process (Connan, 1981, 1984). However, decomposition of sulfur-containing aromatics as observed in outcrop samples (Aquitaine Basin, France) implies an aerobic degradation path-

way cannot be definitely ruled out (Connan, 1981, 1984).

CORRELATION OF TAR-SAND BITUMENS WITH OILS AND SOURCE ROCKS FROM THE PAULS VALLEY AREA

In view of the fact that Jones (1986) had previously classified oils from the Pauls Valley area into two major groups on the basis of their biomarker distributions, only representative samples from these two groups, namely the Viola oil #20 and the Oil Creek oil #29, were used in this study to attempt oil/tar-sand bitumen correlations based on the hydrocarbon distributions. However porphyrin distributions for all oils were used for the attempted correlation studies to determine whether the oils could be classified according to Jones (1986) but based only on porphyrin distributions (Michael, 1987). The Viola oil #20 was

Fig. 3. FID chromatograms of the aromatic fractions from the same four oils as shown in Fig. 2. The extent of alteration of oils 29 and 30 is more clearly shown here by the extensive removal of the substituted naphthalenes (N) and phenanthrenes (P). The right hand chromatograms are FPD chromatograms for the same four oils. An increase in the extent of biodegradation is again indicated by removal of the organosulphur compounds which are dominant in the unaltered sample oil #18. The major compounds are all substituted benzothiophenes (BT) or dibenzothiophenes (DBT). A = Alkyl; M = Methyl; DM = Dimethyl and TM = Trimethyl.

Fig. 4. A comparison between the terpanes of typical Viola and Oil Creek oils and the tar sand extract from a depth of 204'. Tricyclic terpanes are labelled by 19^* , tetracyclic terpanes by 24 and hopanes by C_{29} , etc.

characterized by a high ratio of the C_{24} -tetracyclic terpane (peak labelled 24) to the C_{24} -tricyclic terpanes (26*); reduced concentration of the C_{23-30} tricyclic terpanes (28*–30*) relative to 17 α (H)-22,20,30-trisnorhopane (T_m) and 18 α (H)-22,29,30-trisnorhopane (T_s); a predominance of the C_{33} over the C_{34} extended hopanes (Fig. 4) and a reduced concentration of C_{30} -steranes relative to their C_{29} counterparts. Aquino Neto *et al.* (1983) observed that components in the C_{24} and higher, tricyclic terpane series may be relatively weak in carbonate samples, compared to their lower molecular weight homologues. A high ratio for the C_{33}/C_{34} extended hopanes is a characteristic of carbonate sourced oils or highly reducing environments (McKirdy *et al.*, 1983; Rullkötter *et al.*, 1985), as is an even-odd predominance of *n*-alkanes and a predominance of phytane over pristane. Collectively, these features were used to conclude that the Viola oil #20 from this study was sourced from a carbonated source rock, probably the Viola Limestone itself (Jones, 1986). Oil Creek Oil #29 was chosen not only because it is representative of the majority of oils from the Pauls Valley area, but also because it is of similar maturity to that of the tar-sand bitumen based on the (T_m/T_s) ratio. Despite the fact that oil #29 shows signs of biodegradation in the *n*-alkane and aromatic fractions, comparison of the *m/z* 191 and *m/z* 217 chromatograms with those of oils #3 and 18 it is clear that no alteration had occurred to the polycyclic terpane and sterane components at this level of biodegradation.

Biomarker distributions in oils and tar-sand bitumens

Biomarkers have been used to provide information on depositional environments (Moldowan *et al.*, 1985), nature of source materials (Philp and Gilbert, 1984; Huang and Meinschein, 1976), and thermal maturity of a sample (Mackenzie *et al.*, 1982). In the case of an oil, biomarker distributions can also provide information on the extent of biodegradation (e.g. Seifert and Moldowan, 1979; Volkman *et al.*, 1983) and, possibly, relative migration distances (Seifert and Moldowan, 1978; Mackenzie, 1984). The use of total porphyrin distributions, as determined by high performance liquid chromatography (HPLC), for correlation studies has been proven to be effective by Eglinton *et al.* (1979) in a study of Eocene reservoired oils and their correlation with Cretaceous source rocks of the Maracaibo Basin. In the present study it was anticipated that the porphyrin distributions, which were unaltered by biodegradation (Michael, 1987), could be used to support the oil/oil, oil/tar-sand and oil/source rock correlations based on hydrocarbon distributions.

The *m/z* 191 mass chromatograms of oil #20, #29, and the tar-sand bitumen from a depth of 204 ft, are shown in Fig. 4. It is apparent from these chromatograms that there are similarities between the tricyclic, tetracyclic, and pentacyclic terpane distributions in oil #29 and the tar sand bitumen. Oil #20

differs from the tar-sand bitumen by possessing a higher concentration of the C_{24} -tetracyclic terpane (24) and the C_{31} - C_{33} extended hopanes are all present in higher concentrations relative to the C_{30} hopane but particularly so in the case of the C_{33} extended hopanes. The sterane distributions of oils #20 and 29 are very similar apart from the higher concentration of $\beta\beta$ -steranes in the former. It is difficult to correlate these distributions with the tar sand extract due to the removal of the regular steranes by biodegradation from the tar sand. It is proposed that although on the basis of *n*-alkane/isoprenoid distributions, oil #29 is slightly biodegraded, neither hopane or sterane distributions have been affected.

Aromatic steroid hydrocarbons are not readily affected by biodegradation until after the C_{27} - C_{29} steranes, hopanes, and C_{27} - C_{29} diasteranes have been severely altered (Wardroper *et al.*, 1984) and therefore are useful for correlating severely biodegraded oils (Seifert *et al.*, 1984). The distribution of monoaromatic steroid hydrocarbons of oil #20 and #29 and the tar sand bitumen (204 ft) are shown in the *m/z* 253 chromatograms (Fig. 5). As with the terpanes, there is clearly a similarity in the distributions of the monoaromatic steroid hydrocarbons for oil #29 and the tar sand bitumen while oil #20 has relatively high concentrations of C_{21} and C_{22} components and a different distribution of the C_{27} - C_{29} components. The C_{21} and C_{22} monoaromatic steroid hydrocarbons are thought to be more thermally stable than their higher molecular weight homologues, thus oil #20, collected from a reservoir at 8900 ft and with the higher concentration of C_{21} and C_{22} species, is probably more mature than oil #29 (reservoir depth 3925 ft) and the tar-sand bitumen. It should be noted that concentrations of low molecular weight aromatic steroid hydrocarbons have also been shown to increase with increasing migration distances (Riolo *et al.*, 1986).

The distributions of triaromatic steroid hydrocarbons in oils #20 and #29 and the tar-sand bitumen (204 ft) as determined from their *m/z* 231 chromatograms are also shown in Fig. 5. Oil #29 and tar sand bitumen again show a good similarity in their C_{24} - C_{25} distributions. The absence within the tar sand of C_{20} and C_{21} components and the slight decrease in C_{23} -20R(14) epimer relative to the C_{23} -20S(13) epimer, is probably an indication that the triaromatic steroid hydrocarbons have been altered by biodegradation. It has been previously reported by Wardroper *et al.* (1984) that the C_{20} and C_{21} triaromatic steroid hydrocarbons are more readily degraded compared to their higher molecular weight homologues.

The major components of the *m/z* 217 mass chromatograms for the tar sand bitumens were diasteranes since the regular steranes had been removed by biodegradation. Diasteranes are thought to be relatively resistant to biodegradation and hence useful for correlation purposes. The distributions of the diasteranes in all of the tar sand bitumens were very similar.

Fig. 5. Distribution of monaromatic and triaromatic steroid hydrocarbons as determined by SIM of m/z 253 and m/z 231 for Viola oil # 20; Oil Creek oil # 29 and the tar sand extract from a depth of 204'.

Fig. 6. A plot of %DPEP in total porphyrins versus reservoir depths for all oil samples used in this study. The oil generation window commences at depth of approximately 6500' in the Pauls Valley area. Note the gradual decrease in this value at shallow depths and then a constant value between 0 and 25% below the approximate oil generation window.

The m/z 217 mass chromatograms of the oils, which were not biodegraded, still possess both normal and rearranged steranes, and correlation with the tar-sand bitumen is difficult. Thus, the correlation of rearranged steranes between oil and tar sand bitumen was not made. In a recent paper a series of AB-ring degraded steranes has been shown to be present in both altered and unaltered oil samples (Jiang *et al.*, 1988). The distribution of these compounds was

extremely useful for demonstrating that a relationship exists between the tar sand bitumen and the Oil Creek oil despite the absence of regular steranes in the tar sand bitumen.

Porphyrins are sensitive to maturation changes and hence before attempting any correlation it is necessary to ensure that the samples being correlated are of similar maturities. The percent of deoxyphytylerythrothiophosphorylins (DEP) to total porphyrins (i.e. DPEP + ETIO species) reflects thermal maturity in that this value decreases upon increasing thermal maturity (Barwise and Park, 1983). The reason for the decrease in %DPEP is probably due to conversion of DPEP to ETIO and thermal breakdown (Baker and Louda, 1986). A plot of the percent DPEP versus reservoir depth (Fig. 6) was used to evaluate the relative maturities of all oils examined in this study and also in the work of Jones (1986). There is a good correlation of percent DPEP with reservoir depth which is assumed to be due to maturation since Jones (1986) had previously found that 80% of the oils had a common source based upon other biomarker distributions. The increase in DPEP observed for sample 23 at 9500 ft has been tentatively interpreted as arising from the expulsion of additional porphyrins from the asphaltene. This is similar to the proposed porphyrin expulsion from kerogens in shales of the Paris Basin (Mackenzie *et al.*, 1979). Interestingly enough it can be seen in Fig. 7 that the increase in the DPEP concentration of oil sample 23 is due mainly to an unknown porphyrin tentatively identified as a C_{33} or higher DPEP porphyrin. Mackenzie *et al.* (1979) have previously noted the generation of a higher molecular weight species (C_{33-39}) in shales from the Paris Basin below the onset of the oil generation window.

Fig. 7. The porphyrin distribution in oil sample # 23 recovered from the Bromide Formation at a depth of 9530'.

Fig. 8. A plot of the %DPEP porphyrins vs %C₂₈ + C₂₉ ETIO (B) for all of the oil samples and the average values for the tar sand extract.

It is also useful to look at porphyrin distributions in terms of their series A (fully substituted pyrrole) and series B (β -unsubstituted at one or more pyrrole positions) (Mackenzie *et al.*, 1979). In general, the average carbon number of the series A decreases and percent of series B increases as maturity increases due to alkyl cleavage. A plot of %DPEP versus %C₂₈ + C₂₉ ETIO series B shows good correlation of these two maturity parameters (Fig. 8). A negative correlation would indicate either (1) a possible mixing of oils of different maturity or (2) different sources. The average %DPEP and %C₂₈ + C₂₉ ETIO series B for the tar-sand extract plots closest to oil samples 29 (Oil Creek) and 17 (Bromide), suggesting that these are the oils of similar maturity to the tar-sands based on porphyrin distribution. Oil samples 29 and 17 correlate best with the tar-sand as seen in the porphyrin distributions (Fig. 9). Sample 29 shows the best qualitative correlation with the tar-sand extract, with the exception of an increased C₂₉ and C₃₀ ETIO series A concentration, which is interpreted to arise from a slight increase in maturation. The average ETIO series A carbon number for oil sample 29 is C₂₉, and C₃₀ for the tar-sand. The relatively higher level of maturity for sample #29 could be due to in-reservoir maturation or an influx of lower maturity oil into the tar-sand bitumens. Oil sample 17, from the Bromide Formation, has a similar porphyrin distribution to sample 29, the exception being the absence of the C₃₃ DPEP isomer peak. The C₃₀ and C₂₉ ETIO series A components are also present in higher concentrations and the C₃₁ DPEP peak has increased in concentration relative to C₃₂ DPEP. The above mentioned differences between the tar sand porphyrins and those present in the oils are believed to be due to maturational effects of carbon-carbon bond breakage on alkyl substituents.

Oil-source rock correlation based on porphyrin distributions

Five different formations from early Ordovician through early Pennsylvanian were sampled as possible source rocks for the oils and tar-sand bitumens. The amount of extractable material from the Pennsylvanian Hart Formation was very low and therefore no attempt was made to obtain a porphyrin distribution from this formation.

The porphyrin distribution for the Pennsylvanian Springer Shale (core depth 7202 ft) consisted entirely

Fig. 9. Porphyrin distributions for the tar sand sample at a depth of 128' compared with oil samples from the Oil Creek Formation (3925') and the Bromide Formation (5110').

Fig. 10. Porphyrin distributions from an extract of a core from the Pennsylvanian Springer Shale collected at a depth of 7202'.

of ETIO-type porphyrins with a C_{32} ETIO series A predominance (Fig. 10). The predominance of the C_{32} ETIO series A is indicative of low maturation as suggested by Mackenzie *et al.* (1979). If this is true, then the porphyrin distribution observed in this sample, lacking DPEP components, results predominantly from source variations not maturity. Support for the proposal that the Springer extract has not been altered extensively by maturation comes from a slight odd/even predominance and distinct bimodal distribution of n -alkanes and a predominance of $\alpha\alpha$ -20R-steranes (Philp, 1985). The vitrinite reflectance value of the Springer Shale sample was not measured, but the approximate R_o for Woodford Shale samples from a depth of approximately 600 ft shallower in the same area was 0.45%. The extract of the Springer Shale does not correlate with any of the oils or the tar-sand bitumens. The high proportion of C_{32} ETIO series A and the presence of the unknown porphyrin (Fig. 10) was not observed in any of the other oils, or tar-sand extracts, examined in this study. Other possible source rock samples which did not correlate with the oils or tar-sand bitumens are the Viola Limestone (8330 ft) and the Arbuckle Limestone (8796 ft). Neither sample is considered to have reached maturity levels much beyond that of the Springer Shale sample, but both have unique porphyrin distributions with only the ETIO porphyrins and the unknown porphyrin present. The C_{32} ETIO series A is thought to be a possible thermal product from the cleavage of the exocyclic ring on DPEP porphyrin or it could be a product of heme-type compounds under diagenesis rather than a chlorophyll precursor (Baker and Louda, 1986). These characteristics are not easily explained by any diagenetic or maturation effects which are currently known. Primary migration and expulsion cannot be

used to explain the distributions since it would then be expected that more polar DPEP porphyrins would be concentrated and not the ETIO porphyrins as observed. A possible difference in source input might produce a unique porphyrin distribution which is very probable in the case of the Ordovician Viola and Arbuckle Formations. Recent research has indicated a unique and predominant source organism for several Ordovician sourced oils namely *Gloeocapsamorpha priscas* (Reed *et al.*, 1986; Longman and Palmer, 1987). This is possibly a blue-green alga or large bacterium, which was either non-photosynthetic or utilized chlorophyll which did not contain a phytol side chain (Reed *et al.*, 1986; Longman and Palmer, 1987).

It is possible that the depositional environment for the three possible sources mentioned above was oxidizing or at least partially oxic at times. Depositional conditions of shallow water marine carbonates and shales, i.e. slightly more reducing, might also support these observations, and pristane/phytane ratios for all samples are greater than one, typically taken as being indicative of oxic conditions. If the conditions were anoxic, then DPEP porphyrins should predominate (Baker and Louda, 1986). Another possible explanation for this discrepancy may be that the DPEP porphyrins had already been converted to the ETIO form. However such a conversion could not be readily detected at similar depths in Woodford Shale samples of similar maturity.

The porphyrin distributions from the Woodford Shale samples (approximate maturity 0.5% R_o ; Cardott and Lambert, 1985) correlates very well with that from the tar-sands and many of the oils (Fig. 11). One diagnostic component which should be noted is the C_{32} ETIO series A porphyrin which is predominant in the Woodford Shale extracts and Oil Creek

oil samples (Fig. 11). This peak is also predominant in many oil samples of sufficient maturity such that the %DPEP porphyrins has decreased substantially. It is probable, based on vitrinite reflectance data, that the Woodford Shale outcrop samples used in this study were not mature enough to be responsible for the generation of the oil which has sourced the

reservoirs in the Pauls Valley area or the Fitzgerald tar-sand. The major source for the oils is proposed to be from the Woodford Shale in deeper parts of the basin where the shale has reached higher levels of maturity.

Oil-tar sand correlations by pyrolysis-GC of asphaltenes

Asphaltenes are macromolecular compounds with certain structural similarities to kerogens (Tissot and Welte, 1984). However, they do have lower molecular weights, are not totally insoluble, and can migrate into reservoirs with associated hydrocarbons (Behar *et al.*, 1984). Pyrograms of kerogens and associated asphaltenes shown similar distributions of pyrolysis products and can be used for oil/source rock correlation (Behar *et al.*, 1984). An *in vitro* experiment carried out by Teschner and Wehner (1985) demonstrated that the py-GC products of asphaltenes showed no difference before and after biodegradation of the oil containing the asphaltene. The resistance of asphaltenes towards biodegradation was also demonstrated by Rubenstein *et al.* (1979) and Bonnamy *et al.* (1987) who compared the asphaltene pyrograms of biodegraded and non-biodegraded oils. The components released by pyrolysis of asphaltenes might have been occluded in a molecular framework which is inaccessible to microorganisms (Rubenstein *et al.*, 1979). Therefore, py-GC of asphaltenes is a useful tool for correlation of biodegraded and non-biodegraded oils, especially in the case of severely altered samples where commonly used compounds have been altered or completely removed.

The asphaltene pyrograms of Viola oil #20, Oil Creek oil #29 and the tar-sand bitumen (204 ft) consisting of a series of *n*-alkanes and their corresponding *n*-alk-1-enes are shown in Fig. 12. The tar-sand bitumen and oil #29 show a good correlation in the distribution of their pyrolysis products suggesting similarities in asphaltene structures and hence source materials. However, the asphaltene pyrogram of oil #20 (Fig. 12) shows a distribution dominated by *n*-alkanes extending up to C₃₅, containing less aromatics and no detectable pristene. The absence of pristene and an increase in normal hydrocarbons over isoprenoids, other branched hydrocarbons, phenolic and aromatic compounds, with increasing maturity has been observed in the pyrolysates of kerogens isolated from sediments of increasing maturity (van de Meent *et al.*, 1980; van Graas *et al.*, 1981; Solli *et al.*, 1984; Philp and Gilbert, 1985; Solli and Leplat, 1986; Curiale, 1986). An artificial maturation study of kerogens also showed an increase in the aliphatic nature of the pyrolysates with increasing heating time and temperature (Eglinton *et al.*, 1988). Hence from the chromatograms in Fig. 12 it can be said that oil #20 is more mature than oil #29 and the tar sand bitumen. However in spite of this higher level of maturity the difference in original source input between samples

Fig. 11. A comparison of the porphyrin distributions present in an extract from an outcrop of the Woodford Shale outcrop, a tar sand extract at a depth of 128' and an Oil Creek oil sample from a depth of 3925'.

Fig. 12. Pyrograms produced by characterization of the asphaltenes from an Oil Creek oil (#29) and a Viola oil (#20) compared with that from the asphaltenes from one of the tar sand samples.

#20 and #29 is reflected by a predominance of higher molecular weight hydrocarbons in the region above C_{20} for the Viola oil (#20) asphaltene.

CONCLUSION

Extracts of tar-sand bitumens from the Fitzgerald-5 well have been analysed by gas chromatography and gas chromatography-mass spectrometry. *N*-Alkanes, isoprenoids, naphthalene, alkyl-naphthalenes, phenanthrene, C_1 -, C_2 -phenanthrenes, benzo- and dibenzothiophenes have been removed from the tar-sand bitumens, and the biomarker distributions are also altered as a result of biodegradation. C_{27-29} steranes and $C_{20}-C_{21}$ triaromatic steroid hydrocarbons are absent. C_{27} and $C_{28}(-20R)$ triaromatic steroid hydrocarbons decrease slightly and there is hopane degradation with preferential removal of $22R-C_{30}$ hopanes. Preferential degradation of $C_{27}-C_{28}$ steranes prior to alteration of hopanes can be observed in certain samples but diasteranes, C_{30} -steranes, tricyclic terpanes, C_{24} -tetracyclic terpane and monoaromatic steroid hydrocarbons appear to be resistant towards biodegradation, and are useful for correlation purposes.

Porphyrim distributions are useful for correlation purposes in shallow reservoired oils and tar sands which have undergone degradation. Care must be exercised to separate the effects of maturation from source and this can be done, to a certain extent, if maturation of the oil is at least less than 0.7% R_o equivalent. The use of total demetallated porphyrin distributions in the present study was not sufficient to establish undisputable correlations possibly due to maturity differences but could be used in conjunction with information obtained from other biomarkers.

The correlations made in this study are based on tricyclic terpanes, C_{24} -tetracyclic terpane, hopane, mono- and triaromatic steroid hydrocarbon distributions, porphyrins and asphaltene py-GC. The results show that the tar-sand bitumen appears to be derived from the same source material as oil #29 and others reservoired in the Oil Creek Formation of the Pauls Valley area. These oils were in turn, previously proposed to be sourced from the Woodford Shale (Jones, 1986).

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