1976

Experimental Diagenetic Study of a Modern Lipid-Rich Sediment.

William Earl Harrison

Louisiana State University and Agricultural & Mechanical College

Follow this and additional works at: https://digitalcommons.lsu.edu/gradschool_disstheses

Recommended Citation

Harrison, William Earl, "Experimental Diagenetic Study of a Modern Lipid-Rich Sediment." (1976). *LSU Historical Dissertations and Theses*. 3021.

https://digitalcommons.lsu.edu/gradschool_disstheses/3021

This Dissertation is brought to you for free and open access by the Graduate School at LSU Digital Commons. It has been accepted for inclusion in LSU Historical Dissertations and Theses by an authorized administrator of LSU Digital Commons. For more information, please contact gradetd@lsu.edu.

INFORMATION TO USERS

This material was produced from a microfilm copy of the original document. While the most advanced technological means to photograph and reproduce this document have been used, the quality is heavily dependent upon the quality of the original submitted.

The following explanation of techniques is provided to help you understand markings or patterns which may appear on this reproduction.

- 1. The sign or "target" for pages apparently lacking from the document photographed is "Missing Page(s)". If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting thru an image and duplicating adjacent pages to insure you complete continuity.**
- 2. When an image on the film is obliterated with a large round black mark, it is an indication that the photographer suspected that the copy may have moved during exposure and thus cause a blurred image. You will find a good image of the page in the adjacent frame.**
- 3. When a map, drawing or chart, etc., was part of the material being photographed the photographer followed a definite method in "sectioning" the material. It is customary to begin photoing at the upper left hand corner of a large sheet and to continue photoing from left to right in equal sections with a small overlap. If necessary, sectioning is continued again — beginning below the first row and continuing on until complete.**
- 4. The majority of users indicate that the textual content is of greatest value, however, a somewhat higher quality reproduction could be made from "photographs" if essential to the understanding of the dissertation. Silver prints of "photographs" may be ordered at additional charge by writing the Order Department, giving the catalog number, title, author and specific pages you wish reproduced.**
- 5. PLEASE NOTE: Some pages may have indistinct print. Filmed as received.**

University Microfilms International

300 North Zeeb Road

Ann Arbor, Michigan 48106 USA

St. John's Road, Tyler's Green

High Wycombe, Bucks, England HP10 8HR

77-10,373

HARRISON, William Earl, 1942-
EXPERIMENTAL DIAGENETIC STUDY OF A MODERN
LIPID-RICH SEDIMENT.

The Louisiana State University and
Agricultural and Mechanical College,
Ph.D., 1976
Geology

Xerox University Microfilms, Ann Arbor, Michigan 48106

EXPERIMENTAL DIAGENETIC STUDY OF A MODERN
LIPID-RICH SEDIMENT

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Geology

By
William E. Harrison
B.S., Lamar University, 1964
M.S., University of Oklahoma, 1966
December, 1976

ACKNOWLEDGMENTS

I would like to express my appreciation to Dr. J. S. Hanor and Dr. G. F. Hart for directing this study. Their suggestions and advice, especially during the planning stage of the project, were very helpful. I would also like to thank Dr. R. F. Ferrell for his help with experimental apparatus and for critically reviewing this dissertation.

Dr. Clara Ho of the Coastal Studies Institute suggested the study area and her studies on the sediment and water chemistry provided valuable background information for this project. Thanks are also extended to Dr. Prentice Schilling of the Experimental Statistics Department who designed the statistical analysis program. Dr. Thomas Whelan III of the Coastal Studies Institute provided data on in situ carbon dioxide measurements in the study area.

Finally, I would like to express my gratitude to my wife, Nancy. Her patient understanding and encouragement contributed greatly to this research effort.

Samples for this study were contributed by The University of Texas Marine Science Institute, Sun Oil Company Research Laboratory, Exxon Production Research, and Amoco Production Research Corporation.

This project was supported by grants from Amoco Production Research Company, Superior Oil Company, Tenneco Oil Company, and by an American Association of Petroleum Geologists Grant-In-Aid.

TABLE OF CONTENTS

	<u>Page</u>
ACKNOWLEDGMENTS	i
LIST OF TABLES.	v
LIST OF FIGURES	vi
ABSTRACT	ix
INTRODUCTION	1
Purpose of Investigation	1
Previous Investigations	3
Theories of Hydrocarbon Generation	3
Inorganic Origin	3
Organic Origin	8
BIOGENIC COMPOUNDS IN SEDIMENTS	20
General Statement.	20
Carbohydrates.	21
Proteins	24
Lipids	28
KEROGEN STUDIES	35
General Statement.	35
Formation of Kerogen	35
Types of Kerogen	38
Thermal Maturity	40
Thermal Indicators	49
PROCEDURE	52
General Statement.	52
Sample Location and Collection	53
Modern Organic-Rich Sediments	53
John-The-Fool Lake Samples	53
Gulf of Mexico Samples	55
Ancient Organic-Rich Sediments.	55
Sample Treatment	57
Homogenizing the Samples	57

	<u>Page</u>
PROCEDURE - Continued	
Experimental	59
Bomb Equipment.	59
Description.	59
Operating Conditions	60
Extraction Procedures	61
Lipid Extraction	61
Hydrocarbon Extraction	63
ANALYTICAL TECHNIQUES	65
Gas Chromatography	65
Gas Analysis	70
Fatty Acid and Hydrocarbon Analysis.	70
Miospore Carbonization Measurements.	71
Eh and pH Measurements	72
X-Ray Diffraction Patterns	73
SAMPLE IDENTIFICATION	76
STATISTICAL ANALYSIS.	78
GENERAL DISCUSSION OF EXPERIMENTAL DATA	86
Carbonization.	86
Gaseous Products	86
Carbon Dioxide.	86
Nitrogen.	93
Methane	95
Extractable Lipid, Fatty Acid, and Hexane-	
Soluble Fractions.	96
Extractable Lipids.	96
Fatty Acids	101
Hexane-Soluble Fraction	102
Paraffinic, Aromatic, and Hetero-Compound	
Components	104
Distribution of Fatty Acid and Paraffinic Components	110
POSSIBLE ROLE OF DECARBOXYLATION.	134
SUMMARY AND CONCLUSIONS	137
REFERENCES.	142

	<u>Page</u>
APPENDIX	
I. Extraction Data for Four Samples of John-The-Fool Lake Mud	152
II. Elemental Analysis of John-The-Fool Lake Kerogen.	154
III. Temperature Controller Settings versus Measured Temperatures for the Barnes Hydrothermal System.	155
IV. Relation between Occupied Vessel Volume (fill factor), Temperature, and Pressure	156
V. Lipid Extraction Scheme.	157
VI. Flow Chart of Extraction Procedure	158
VII. Description of Gas Chromatograph and Operating Conditions	159
VIII. Drawing of Eh-pH Measuring Device.	161
IX. Eh and pH Values	162
X. Concentration of Paraffinic and Aromatic Hydrocarbon and Hetero-Compound Fractions.	163
XI. Graph Showing Increased Lipid Fraction as a Function of Exposure Time at 160°C	166
VITA.	167

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1. Fatty Acids in Ancient Shales.	31
2. Fatty Acids in Modern Sediments.	33
3. Carbon, Hydrogen, and Oxygen Content of Selected Organisms and Kerogens.	37
4. Thermal Alteration Index Scheme of Staplin	51
5. Characteristics of Thermal Conductivity (TCD) and Flame Ionization (FID) Detectors Used in Gas Chromatography.	69
6. Model for Analysis of Variance	79
7. Individual n-Paraffins and Fatty Acids and Groups of Compounds whose Concentrations Were Significantly Affected by Temperature, Extractions, and Temperature x Extraction Interaction.	82
8. Maximum System Pressure and Partial Pressures of Carbon Dioxide, Nitrogen, and Methane after Allowing Reaction Vessel to Cool to Ambient Temperature (in atmospheres)	88
9. Absolute Concentrations of Extractable Lipid, Fatty Acid, and Hexane-Soluble Fractions (expressed as mg/gm dry sediment).	97
10. Absolute Concentrations of Fatty Acids Extracted from the Sediments and Fluid at the Conclusion of Each Experiment (in mg/442 ml slurry)	121
11. Absolute Concentrations of n-Paraffins Extracted from the Sediments and Fluid at the Conclusion of Each Experiment (in mg/442 ml slurry)	124

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1. Structural Formulas of the Fundamental Unit (isoprene) and Terpenoid Hydrocarbons Formed by Two Isoprene Units (Limonene) and Three Isoprene Units (selinene).	11
2. Possible Degradational Scheme for Converting Chlorophyll to a C ₁₉ Hydrocarbon (pristane) or a C ₃₀ Hydrocarbon (phytane).	13
3. An Example of the Dehydrogenation Mechanism Suggested by Mair which Could Yield Aromatic Hydrocarbons	14
4. Range of Carbon Isotope Ratios in Naturally-Occurring Carbonaceous Material.	15
5. Simplified Scheme of the Generation and Migration of Oil	19
6. Thermal Decomposition of Amino Acids as a Function of Time	27
7. Typical Representatives of the Three Major Biochemical Groups	34
8. Gas Chromatograms of Hydrocarbons Generated by Pyrolyzing Sediments at 280°C for 10 Minutes . . .	41
9. Yield of Light Hydrocarbons Resulting from Pyrolysis of Organic-rich Sediments.	43
10. Gas Chromatograms of Hydrocarbons from Modern Sediments	44
11. Variation in n-paraffin Distribution as a Function of Depth (temperature)	47
12. Depth-Temperature Relation of Pusey's "Liquid-window" Concept.	48
13. Location of John-The-Fool Lake	54
14. Location of Gulf of Mexico Samples	56

<u>Figure</u>	<u>Page</u>
15. Illustration of GC Pattern of n-Paraffins and Fatty Acids.	67
16. X-Ray Diffractograms of Clays from Modern Samples. .	74
17. X-Ray Diffractograms of Clays from Ancient Samples .	75
18. Graphs Showing Variation in Concentrations of Fatty Acids when Statistical Interaction is Significant (A) and when Interaction is not Significant (B).	81
19. Effect of Temperature on Carbonization of <u>Pinus spp.</u>	87
20. The Substituent Structure Suggested for Kerogen. . .	92
21. Ternary Diagrams Showing Variation in Paraffinic, Aromatic, and Hetero-Compound Components as a Function of Temperature.	106
22. Ternary Diagrams Showing Variation in Paraffinic, Aromatic, and Hetero-Compound Components as a Function of Temperature.	107
23. Ternary Diagrams Showing Variation in Paraffinic, Aromatic, and Hetero-Compound Components as a Function of Temperature.	108
24. Ternary Diagrams Showing Variation in Paraffinic, Aromatic, and Hetero-Compound Components as a Function of Time	109
25. Ternary Diagrams Showing Variation in Paraffinic, Aromatic, and Hetero-Compound as a Function of Temperature	111
26. Ternary Diagrams Showing Variation in Paraffinic, Aromatic, and Hetero-Compound Components as a Function of Temperature.	112
27. Distribution and Concentration of Fatty Acids From US-H ₂ Experiments	113
28. Distribution and Concentration of n-Paraffins From US-H ₂ Experiments	115
29. Distribution and Concentration of Fatty Acids From LE-H ₂ Experiments	117

<u>Figure</u>	<u>Page</u>
30. Distribution and Concentration of n-Paraffins From LE-H ₂ Experiments	119
31. Semi-Log Histograms Showing Distribution of Fatty Acids and n-Paraffins.	127
32. Semi-Log Histograms Showing Distribution of Fatty Acids and n-Paraffins.	128
33. Semi-Log Histograms Showing Distribution of Fatty Acids and n-Paraffins.	129
34. Semi-Log Histograms Showing Distribution of Fatty Acids and n-Paraffins.	130
35. Semi-Log Histograms Showing Distribution of Fatty Acids and n-Paraffins.	131
36. Carbon Content of Fatty Acid, Paraffin, and Carbon Dioxide Fractions for NPC Experiments . . .	136
37. Ternary Diagrams Showing Increasing Paraffinic Fractions with Maturity.	139

ABSTRACT

Sedimentary organic matter can be divided into two broad groups on the basis of solubility in non-polar organic solvents. Material which can be removed from sediments by a methyl alcohol : chloroform solvent system constitutes the soluble or extractable lipid fraction. The material unaffected by such extractions is kerogen and is generally considered to be the source of petroleum. The effects of these two types of organic matter on the generation of petroleum is evaluated in a series of simulated diagenetic studies.

Samples were heated for 50 hours at temperatures of 80°C, 160°C, and 240°C. Lipid extractions were made on one-half of the samples prior to heating in pressure vessels. The remaining samples were heated with all biochemical components intact. After heating, samples were extracted with a methyl alcohol : chloroform mixture (1 : 1 vol./vol.) and fatty acids, paraffinic and aromatic hydrocarbons, and hetero-compounds were quantitatively determined.

Modern organic-rich muds used in this study display variation in paraffinic, fatty acid, aromatic, and hetero-compound products as a function of (1) temperature and (2) the presence/absence of soluble lipids. Hetero-compounds, which dominate the soluble organic fraction of the natural sediments, became minor components as samples were subjected to increased temperature conditions. Sediments from which soluble lipids were extracted prior to heating had product mixtures which were rich in paraffins.

Head-space analysis of gaseous products showed CO₂ and nitrogen to be major components; methane was detected in most samples but was never a dominant constituent.

A major result of the study is a tentative assessment of fatty acid diagenesis. Samples heated at 80°C had lower fatty acid yields than the reference sediment. At 160°C, unextracted sediments had two times as much total fatty acid material as the reference; lipid-free samples experienced an 8- to 10-fold increase. The 240°C samples had lower fatty acid yields than samples heated at 160°C. Thus, the pattern is one of depletion of fatty acids at 80°C, enrichment at 160°C, and a second degradational phase at 240°C. The general scheme of fatty-acid diagenesis appears to include: (1) early decarboxylation of free and slightly bound fatty acids, (2) cleavage of bound fatty acids from the kerogen matrix, and (3) final decarboxylation of the acids released from kerogen at lower temperatures.

EXPERIMENTAL DIAGENETIC STUDY OF A MODERN
LIPID-RICH SEDIMENT

INTRODUCTION

Purpose of Investigation

The purpose of this study is to determine quantitatively the variations in abundance of normal or n-paraffin, aliphatic fatty acid, and other organic fractions which occur as a result of subjecting a uniform organic-rich sediment matrix to different temperatures and pressures under laboratory conditions. The main objectives of the study are to:

1. Determine the approximate physical conditions required to initiate hydrocarbon generation from a specific modern organic-rich sediment.
2. Determine the n-paraffin and aliphatic fatty acid variations which result from different thermal conditions.
3. Evaluate the hydrocarbon generating potential of both the material which can be extracted in the laboratory with organic solvents and that portion of the organic matter which exists in a solvent insoluble form.

The project attempts to establish a set of documented observations on the behavior of lipid components as these components are subjected to physical conditions which simulate those encountered in sedimentary basins. The lack of such basic information on a single

hydrocarbon source rock has been pointed out by Welte (1965). In discussing the relation between petroleum generation and source rocks, Welte concludes that a single hydrocarbon source should yield an evolutionary series of crude oils. He further states (p. 2249) that, ". . . no such evolutionary series have heretofore been described. The reason may lie in the strong scatter of analyzed oils with regard to regional and age provenance. . ."

By conducting experiments on sediments of uniform properties and by measuring the hydrocarbon and fatty acid constituents at the end of each hydrothermal run, this study was designed to provide a laboratory analog for the "evolutionary series" mentioned above.

Extrapolating data obtained in laboratory experiments to natural conditions must always be done with full realization of the limitations of laboratory studies. In this study, the experiments were conducted in a closed system and early-formed products were not removed from the site of the initial reactions as must happen in nature as primary products migrate out of source beds. The role of geologic time can be only approximated in laboratory studies by variation in temperature and, perhaps, pressure. Such temperature and pressure variations in laboratory work may not instill the same response in organic and inorganic components as natural diagenesis would instill. Nonetheless, confirming the relation between precursor material, temperature conditions, and final generated products is a necessary exercise. It establishes a data framework upon which second-generation research projects may be based.

Previous Investigations

Theories of Hydrocarbon Generation

Inorganic Origin.--Two of the earliest and most important inorganic theories of petroleum generation were proposed by Bertholot and Mendeleeff in 1866 and 1877, respectively. Translations of portions of the original investigations of Berthelot and Mendeleeff are presented in Dott and Reynolds (1969) and are reviewed here briefly.

Bertholot's concept involved downward-percolating carbonic acid which came in contact with alkali metals at high temperatures. This reaction, as demonstrated by Bertholot's laboratory experiments, yields alkaline acetylides. These acetylides decompose in the presence of water vapor to produce the alkyne hydrocarbon, acetylene, and hydrogen. If the acetylene and hydrogen are immediately removed from the source of heat, the acetylene condenses to bitumens and tar or produces other hydrocarbons. Berthelot suggested that a great variety of hydrocarbons could be produced in this manner and that naturally-occurring petroleum-like compounds could result from purely inorganic reactions.

The reaction of water and calcium carbide yields acetylene and calcium hydroxide as products and typifies the mechanism which Mendeleeff proposed as being responsible for the presence of natural hydrocarbons. Mendeleeff thought that iron carbides in the interior of the earth would be exposed to downward-flowing water during upheavals produced by mountain-building processes. Dott and Reynolds (1969, p. 29) point out that Mendeleeff's standing in the academic community, coupled with laboratory investigations which showed that hydrocarbons

can be produced from metal carbides, firmly established the inorganic theories for many years.

Weismann (1971) postulated that natural gas in west Texas and eastern New Mexico might be the result of high-temperature inorganic reactions. The mechanism, as presented by Weismann, involves molten rock coming in contact with carbonate rocks at a temperature of 1000°C or greater. The carbon dioxide created at the magma-carbonate interface would be reduced to methane by hydrogen associated with the igneous rock. Weismann used stable carbon isotope analyses to show that hydrocarbon gases from fields in Texas and California were formed at temperatures much higher than those which normally exist in sedimentary basins. The principle of significant carbon isotopic variation resulting from different mechanisms of formation for methane was proposed by Sackett (1966, 1968) and he suggested (1968, p. 856) that increasing geologic time and temperature have a tendency to establish isotopic equilibrium in methane and significant isotopic differences are not to be expected from methane produced at high temperatures.

Recently, Porfir'ev (1974) has reviewed the salient features of investigations by Russian and East European workers and contends that the organic origin of petroleum is highly questionable. Because Porfir'ev's summary is the latest synopsis of arguments for an inorganic origin and because his work brings together much of the data frequently cited by subscribers to inorganic theories, a critical review of Porfir'ev's paper is warranted. It is believed that Porfir'ev's views are those of the minority among Soviet geologists.

Porfir'ev points out that the abiogenic models proposed by USSR workers are subject to criticism from a geologic viewpoint and

that the models will be confirmed or rejected only with the passing of time. He states (p. 14) that the only aspect of the origin of petroleum which can be viewed completely and objectively is that pertaining to geologic facts which, he contends, ". . . flatly contradict organic theory. . ."

Two of Porfir'ev's main geologic arguments are based on (1) the difficulties of lateral migration in sedimentary sequences, and (2) the presence of petroleum accumulations in crystalline metamorphic and igneous rocks.

It is true that the migration of petroleum is one of the most poorly understood phenomena of petroleum geology. Cordell (1973) has brought together all of the major theories of migration and the reader is referred to his paper for a comprehensive summary on the subject. Porfir'ev's major objection to lateral migration is the low solubility of hydrocarbons in water under crustal conditions of temperature and pressure. Price (1973) however, has recently conducted solubility studies on hydrocarbon and hetero-compound molecules and has shown that solubilities increase drastically over a temperature range of 100-180°C. One of Price's experiments shows that the solubility of an Arabian crude oil in aqueous solution increases from 0.042 ppm at 25°C to 17.0 ppm at 180°C. This constitutes a 400-fold increase at temperatures which are well within those encountered in most sedimentary basins. Changes in solubilities due to the addition of hetero-atoms to hydrocarbons also are quite pronounced. The aqueous solubility of the aromatic hydrocarbon benzene at 25°C as determined by Price is 1740 ppm. Addition of a nitrogen-containing molecule, pyrrole, forms indole and the solubility of this compound under the

same conditions, is 3558 ppm. Also, Price's data show that the most insoluble petroleum fractions in cold water are most strongly affected by increased solubility at higher temperatures. Thus it would appear that migration arguments based on the insoluble nature of hydrocarbons in water must be reevaluated in terms of newly-acquired experimental evidence.

Porfir'ev discusses commercial petroleum production in crystalline basement rocks and mentions several regions in the world where such resources exist. Although many of the localities used as examples by Porfir'ev are in close proximity to sedimentary sections, several deposits do exist in igneous or metamorphic rocks isolated from sediments. However, by omission of certain key geologic details, Porfir'ev fails to completely describe the relationship of igneous and sedimentary rocks for some of the examples he used to support an inorganic origin. One such example is Dineh-Bi-Keyah Field in Arizona.

There is no question that the productive unit in Dineh-Bi-Keyah Field is a highly fractured, porous, igneous sill. Examination of the electric logs and descriptions of the Kerr-McGee-Navajo wells, #1 and #2 show that the sill is encased vertically by several hundred feet of sedimentary rock (McKenny and Masters, 1968). However, the most important feature of the stratigraphic sequence is that the sill, in many places, is immediately overlain by a black carbonaceous shale. In fact, one of McKenny and Master's original explanations for the genesis of the accumulation involved distilling the hydrocarbons from the black shale as a result of heat accompanying sill emplacement.

Hedberg (1964) mentions several occurrences of petroleum-like material in igneous rocks but indicates that the igneous rock was

important only as a source of heat for the genesis of the material, the source of hydrocarbon precursors being in adjacent sedimentary rocks. Hedberg cites (p. 1746) a study in which shale samples were collected at various distances from a shale-igneous dike contact. Total organic carbon was low for samples taken within a few inches of the contact but increased rapidly to a constant value for samples taken a few feet away from the contact. Baker and Claypool (1970) have further documented the above relationship by measuring the extractable organic material and the hydrocarbon content as well as total organic carbon in a similar shale-intrusive igneous rock setting.

Contrasting with the above situations, there are occurrences of petroleum-related material in igneous rocks which preclude derivation from sediments. One such example is discussed by Hedberg (1964) and also is mentioned by Porfir'ev. The alkalic igneous rocks of the Khibina Massif in the USSR contains gaseous hydrocarbons as well as bitumen material. Analysis of the rocks intruded by the massif revealed an absence of hydrocarbon gases and bitumens. The conclusion is drawn that the hydrocarbons are the result of chemical processes which accompanied the intrusion.

Evans et al. (1964) reported n-paraffins with carbon numbers of 10 to 22 from a dolerite dyke in Norway. Detailed petrographic analysis indicates that the hydrocarbon-filled vesicles were enclosed by dolerite at a temperature of 600°C. The presence of pyrite indicates a low oxygen fugacity and Evans et al. postulate a system where carbon dioxide, carbon monoxide, water, and hydrogen are the major species. Evans et al. explain (p. 144) the genesis of hydrocarbons from such a system as follows:

At 600° C and 50 atm pressure such a system would also have methane as an equilibrium reaction product (Krauskopf, 1959). Paraffins of higher molecular weight than methane are stable only below 450° C and are produced by the Fischer-Tropsch reaction between 200 and 250° C in the presence of a catalyst. Since the crystallization of the analcime was at about 275° C, the paraffins were formed at a lower temperature, the chalcedony possibly behaving as a catalyst.

Thus the inorganic chemical reactions required to generate hydrocarbons abiogenically are well established and have doubtlessly taken place periodically during geologic time. However, that significant portions of the earth's naturally-occurring hydrocarbons are the result of inorganic reactions has not been established.

Organic Origin.--Although knowledge regarding the series of chemical reactions which generate hydrocarbons is far from complete, general agreement does exist that hydrocarbons and petroleum which occur in commercial quantities in sedimentary basins are the result of processes which began with biologic precursors. Several lines of evidence, both individually and collectively, have established the organic theory as a fundamental working concept in petroleum geology.

One of the earliest and most important investigations supporting an organic origin was the work of Triebs (1934). He discovered complexed organic pigments in a variety of bitumen products and crude oils and proposed a relation between the complex porphyrins and organisms.

Organic pigments or porphyrins are respiratory catalysts, chlorophyll and heme being the characteristic porphyrins for plant and animal life, respectively. Free porphyrins are not present in crude oils but exist as metal complexes, primarily involving vanadium and nickel (Dunning, 1963). These complexed forms are very stable and

account for most of the vanadium and nickel found in petroleum. Garner et al., (1953) have found nickel concentrations of 100 to 1000 ppm in South American and Middle East petroleum. They found that vanadium concentrations for the same samples varied from 200 to 20,000 ppm. Although porphyrins have not been identified in all crude oils and are noticeably low in all paraffinic oils and Paleozoic American crude oils, these biologically-derived components occur with such frequency that they provide a strong basis for assuming an organic origin. Because porphyrins decompose rapidly at temperatures above 200°C, the presence of these compounds is used to support a history of low temperature conditions for petroleum (Breger, 1963).

Another field of chemistry which has yielded information at least as important as the discovery of porphyrins is stereochemistry. Bergmann (1963, p. 515) credits Walden with first suggesting the relation between optically active petroleum fractions and biologic precursors. Organic molecules which have the ability to rotate plane polarized light do so by means of an asymmetrical arrangement of atoms around a central carbon atom (Eglinton, 1969; Hart and Schuetz, 1972). Production of organic compounds in the laboratory using optically inactive chemicals and reagents invariably results in optically inactive molecules whereas the same molecules produced by biological activity are optically active (Eglinton, 1969). Establishing this phenomena as being uniquely biologically controlled makes the presence of such compounds in petroleum a powerful argument indeed for an organic origin.

Oakwood (1964) studied kelp, algae, and marine bacteria and noted dextrorotatory or positive optical activity for the hydrocarbon

fractions from all three sources. He further concentrated the kelp hydrocarbons and found their molecular weight to be between 272 and 435. A comparison of the kelp hydrocarbons and those in the high molecular weight range of petroleum led Oakwood to conclude that the molecular structures were similar. Oakwood et al. (1952) summarized the characteristics of the optically active fractions in petroleum and emphasized that, (1) the optically active fractions are always in the high boiling-point range and have molecular weights of 220-400 and (2) most crude oils are dextrorotatory.

A third fruitful area of investigation for supporting an organic origin involves a comparison of specific hydrocarbons and specific parent biochemicals and proposing reaction schemes to account for the necessary alterations. Such biochemicals are called biological markers or chemical fossils by many authors and the criteria for these compounds are given by Speers and Whitehead (1969). They list the three prerequisites as: (1) a low probability for the compound to be generated abiogenically, (2) high chemical stability, and (3) the structural characteristics of the compound should be significantly related to biochemical synthesis.

Terpenoid hydrocarbons most nearly fulfill these requirements and in this respect, they have been the subject of several significant investigations (Speers and Whitehead, 1969; Meinschein, 1969; Bergmann, 1963; Mair, 1964; and others). Terpenoids are compounds which are composed of several isoprene skeletal units (figure 1). The fundamental isoprene unit may combine in a number of structural configurations to yield terpenes, sesquiterpenes, diterpenes, and triterpenes which have multiples of 2, 3, 4, and 6 isoprene units in their structures,

Figure 1. Structural formulas of the fundamental unit (isoprene) and terpenoid hydrocarbons formed by two isoprene units (lemonene) and three isoprene units (selinene).

respectively. Figure 1 shows the manner in which isoprene units may combine to yield terpenoid hydrocarbons.

The possible degradation of chlorophyll to phytol and then to pristane and phytane has been investigated in detail by Bendoraitis et al. (1963). Figure 2 is taken from Bendoraitis et al. and shows the mechanisms by which phytol may have been degraded to petroleum constituents from an original chlorophyll source.

Mair (1964) has reviewed the biological sources of many of the terpenoid hydrocarbons found in nature and has proposed degradational processes for the terpenoids with up to 40 carbon atoms. He points out that over 95 percent of the hydrocarbons which occur in petroleum have carbon numbers of less than 40. He further suggests that dehydrogenation of a terpenoid such as lemonene could yield aromatic hydrocarbons such as p-cymene. Figure 3 shows the structural similarity between the two molecules. The proposed mechanism is highly significant in that aromatic hydrocarbons are virtually absent in organisms and the genesis of this group of hydrocarbons is one of the least understood aspects of petroleum geochemistry.

Carbon isotope ratios indicate that petroleum is more nearly like lipids and terrestrial plant material rather than other reserves of carbon. Figure 4 represents data presented by Silverman (1973) and clearly shows the isotopic similarities mentioned above. Carbonate rocks and atmospheric carbon dioxide are two additional major reservoirs of carbon, but the isotopic ratios for both of these carbon sources are quite different from that of petroleum.

Almost all geologists and chemists agree that petroleum is of organic origin but Smith's (1954) discovery of hydrocarbons in

Figure 2. Possible degradational scheme for converting chlorophyll to a C₁₉ hydrocarbon (pristane) or a C₂₀ hydrocarbon (phytane). (After Bendoraitis, 1963)

Figure 3. An example of the dehydrogenation mechanism suggested by Mair (1964) which could yield aromatic hydrocarbons.

Figure 4. Range of carbon isotope ratios in naturally-occurring carbonaceous materials.
(After Silverman, 1973)

sediments which were only 12,000 to 15,000 years in age poised a question regarding the mechanisms of formation from organic precursors. He found that the acetone : benzene-soluble fraction of modern sediments cored off Grand Isle, Louisiana, comprised 0.01 to 0.45 grams of 100 grams of dried sediment. Using adsorption chromatography, he determined that the soluble organic fraction contained 7.5 to almost 31 percent hydrocarbons. Smith found hydrocarbons in a number of other modern mud samples as well as an "algal clay." He suggested that petroleum deposits represent accumulations of hydrocarbons generated by the metabolic activity of marine life. Extrapolating the Grand Isle data, he calculated that the accumulation of such hydrocarbons would be equivalent to 10.4 million barrels per cubic mile of sediment.

Shortly after Smith's work was published, Swain (1956) examined a number of fresh-water lakes for lipid and hydrocarbon content. He separated saturated, aromatic, and asphaltene material from the lipids and related the concentrations of these three fractions to biologic productivity. He postulated (p. 650) that an anhydrite-limestone sequence inundated by marine waters would produce ". . . an excellent though perhaps short-lived basin for the production of hydrocarbons. . . ."

Meinschein (1959) has considered the possibility that crude oil might represent hydrocarbons which were metabolically derived or only slightly altered forms. Meinschein analyzed soil samples, marine muds, and crude oils for n-paraffins, terpanes, sterols, and aromatic components. He concluded that the hydrocarbon extracts from various sources were qualitatively similar, the major difference being in absolute concentration levels. He postulated a dual but related

source for the hydrocarbons which comprise crude oils. First, the original lipid fraction of organic debris furnishes petroleum-like hydrocarbons to sediments. Second, compounds formed from biochemical intermediates such as sterols are the result of secondary reactions which are possibly enhanced by bacterial action.

Although metabolically-produced hydrocarbons are significant, both in the types produced and in quantitative abundance, there are some constituents of petroleum which have no counterparts in organisms or metabolic products. In this regard, there is a particular range (C_4 to C_8) of n-paraffins which may be absent or in extremely low concentrations in modern sediments. Dunton and Hunt (1962) examined sediments which ranged in age from Precambrian to Modern. Of the 21 samples analyzed, only three had total organic matter of less than one-half of one percent by weight. C_4 to C_8 paraffins were detected in all of the ancient sediments with the exception of the absence of the C_8 hydrocarbon in sediments from the Precambrian Gunflint Formation. Using a chromatographic technique capable of detecting 2 ppb, Dunton and Hunt found the concentrations of these C_4 to C_8 paraffins to range from .03 to over 280 ppm. By contrast, the Modern sediments had total organic matter concentrations of 1.2 to 3.4 percent by weight, but no C_4 - C_8 hydrocarbons were detected in any of the Modern samples. The C_4 - C_8 paraffins collectively represent a quantitatively important group of hydrocarbons in many petroleum deposits, with some of the paraffins in this range comprising over two percent of total hydrocarbons in some crude oils (Whitehead and Breger, 1963).

Certain aromatic hydrocarbons are analogous to C_4 - C_8 paraffins in being absent from modern sediments but common constituents

of petroleum. Erdman et al. (1958) analyzed modern and ancient sediments for low molecular weight aromatic hydrocarbons. These aromatic hydrocarbons, benzene through xylene, were not discovered in any of the analyzed modern sediments. As with the C_4-C_8 paraffins, these particular hydrocarbons are common components of crude oil. Benzene, toluene, and xylene are among the major aromatic constituents and each may reach concentrations of 1-2 percent in petroleum (Whitehead and Breger, 1962; Bestougeff, 1967).

The organic origin of petroleum is accepted by most petroleum geologists. Although some of the compounds which occur in petroleum occur in organisms, many do not, and must be generated from organic matter in the sediments. Hydrocarbons which appear to have their origin in the generation process include the aromatics and the C_4-C_8 n-paraffins.

Figure 5 is a flow chart taken from Welte (1965) and postulates the major steps involved in creating petroleum from organic precursors. The specific reactions and details associated with each step are not well-known but the general scheme is considered to represent the processes.

Figure 5. Simplified scheme showing the major geological and chemical processes involved in the generation and migration of oil. (Welte, 1965)

BIOGENIC COMPOUNDS IN SEDIMENTS

General Statement

Most studies on the nature, distribution, and occurrence of biochemicals in sediments are not as comprehensive as other studies which concern biochemistry. Analytical techniques such as gas chromatography and gas chromatography coupled with mass spectroscopy permit detection of many compounds in extremely low concentrations, but these tools have been in existence less than 15 years and a significant body of data has not yet been accumulated.

Most efforts to determine organic compounds in sediments, natural waters, or subsurface fluids in the study of the generation of hydrocarbons seem to follow one of two common paths. Both have been mentioned earlier in connection with the organic theory of petroleum generation and will only be briefly discussed here. The first of these consists of efforts to isolate and identify biologically significant biochemical compounds. Many geochemical studies concerning metal substitutions in pigments are of this type. For example, vanadium and nickel are thought to replace iron and magnesium in pigments and this relation has been studied by petroleum geochemists in attempts to relate biochemical precursors to the vanadium and nickel complexes found in petroleum (Hodgson and Peake, 1961; Hodgson, et al., 1967). Other investigations seek to demonstrate the successive degradation of particular organic compounds through several stages to an end product which is commonly found in ancient sediments. The degradation of

chlorophyll to phytol to isoprenoid hydrocarbons, as suggested by Bendoraitis (1962) and Bendoraitis, et al. (1963), is an example of this latter type of study.

Biochemicals observed in sediments may be grouped into the three basic classes described in introductory biochemistry texts--carbohydrates, proteins, and lipids. Below is a review of several studies concerning biochemicals in sediments. These studies are of value in helping to assess the role of the various groups in hydrocarbon generation.

Carbohydrates

This class of compounds is comprised of sugars, starches, and structural carbohydrates and their derivatives. The empirical formula $C_n(H_2O)_n$ characterizes most members of this class (Toporek, 1971). Carbohydrates are subdivided into three groups according to the number of simple molecular sugar units liberated during complete hydrolysis. These groups are monosaccharides, oligosaccharides, and polysaccharides. For example cellulose, the most common structural carbohydrate in plants, contains approximately 3000 glucose units, and is thus a polysaccharide (Toporek, 1971).

Carbohydrates are the fundamental energy source for many forms of life and can exist in various forms in organisms. Two factors which affect the utilization of carbohydrates as energy sources are their solubility and relative molecular size. Simple sugars such as glucose, fructose, and ribose are very soluble and can diffuse through membranes and enter into metabolic reactions rapidly. Molecular size likewise determines the extent to which a carbohydrate may be used directly as

an energy source. Starches are large polymers of simple sugars and cannot be utilized until enzymes break down the molecular chains into monosaccharide units. Cellulose and other structural carbohydrates are both very large and highly insoluble and therefore cannot be used as energy sources except where certain yeasts, protozoa, or bacteria can attack the cellulose unit and reduce it to simple sugars (Baker and Allen, 1964). The dominant role of structural carbohydrates is, as the name implies, to provide strength and rigidity to organisms. Because most marine organisms possess rigid skeletons of mineral matter rather than cellulose, high concentrations of cellulose are largely confined to terrestrial and shallow marine depositional settings.

Vallentyne (1963) was among the first investigators to synthesize and review the work on carbohydrates in geochemistry. He subdivided the above-mentioned types of carbohydrates into (1) low-molecular weight carbohydrates, (2) reserve or storage carbohydrates, and (3) structural carbohydrates. He also listed the characteristic carbohydrates of ten major phyla of plants. Cellulose was a structural carbohydrate for seven of the phyla.

Swain, Palkins, and Bratt (1970) analyzed freshwater algae, marine algae, and marine invertebrates for total carbohydrate content. They found that marine algae averaged over 430 milligrams glucose equivalent per gram dry weight. Invertebrates averaged about 235 milligrams per gram while the freshwater algae averaged 25 milligrams per gram. These workers also isolated and identified sugars from rocks of Precambrian Age and suggested possible relationships between fossil carbohydrates and their precursors.

The occurrence of carbohydrate materials in sediments, both in the form of simple sugar and as structural carbohydrates has been thoroughly discussed by Vallentyne (1963), Swain (1969), and Swain, Palkins, and Bratt (1970). The reader is referred to these papers for additional information on the subject.

Data on the preservation and stability of carbohydrate material in various depositional settings are scarce. Plunkett (1957) compared the free sugar content of sediments taken from anaerobic and aerobic settings and found that reducing conditions slightly enhanced the preservation of these compounds. A study by Modzeleski, et al. (1971) evaluated the total sugar content of two sediments, one of which was 50 and the other 750 years old. This study revealed that the older of the two sediments had approximately 50 percent less total sugars than did the younger sediment. No data were presented however which indicated similarities of sediment type and texture. The observed differences were not considered to be the result of lower initial concentrations or selective removal by microbes, again, however, no data were presented to support these assumptions.

Concentration-depth profiles of dissolved carbohydrates in sea water show that carbohydrate material decomposes less readily in the deeper waters than in the euphotic zone (Handa, 1970). This is interpreted as a reflection of the greater numbers of microbial populations in the upper water masses and the effectiveness of these organisms to degrade carbohydrate material.

Proteins

The fundamental building block of all proteinaceous material is the amino acid. About 20 amino acids are known to occur commonly in nature, and all protein in the plant and animal world are constructed from these. Amino acids are defined by the presence of an amino group (NH_2) and a carboxyl group (COOH) (Toporek, 1971). Amino acids may also contain iodine and sulfur groups.

Amino acids are connected by peptide bonds to form proteins. These bonds can be broken in the presence of water and hydrolysis of a protein thus liberates individual amino acids. Because a particular amino acid may be incorporated into any of the tens of thousands theoretically possible proteins, any relationships between fossil material and modern biochemical precursors would be exceedingly tenuous. For this reason, geochemical investigations have concentrated on individual amino acids, not initial proteinaceous material. Abelson (1963) has discussed a rare exception, where the amino acids were still bound by peptide linkage after 15,000 years. The preservational media was the asphalt matrix of the LaBrea, California, tar pits.

Erdman, Marlett, and Hanson (1956) conducted studies of total amino acids from sediments of Recent and Oligocene Age. Recent sediments had approximately 3.0 micromoles of amino acid material per gram of sediment whereas the Oligocene samples contained only 0.5 micromoles amino acids per gram of sediment. The types of amino acids present in the Oligocene sediments were essentially the same ones reported by Abelson (1959) in fossil fish, horse, and dinosaur bones.

Chert has been considered to be a highly protective matrix which might be capable of preserving individual amino acids intact. The

Precambrian Gunflint Chert was investigated with this possibility in mind (Schopf, et al., 1968; Abelson and Hare, 1969). These workers confirmed the presence of amino acids but the origin of the amino acids was still in doubt. The two possibilities were (1) that the dense chert matrix preserved the amino acids intact (Schopf, et al., 1968), and (2) that the amino acids were introduced post-diagenetically (Abelson and Hare, 1969). Laboratory experiments were subsequently conducted by Hare and Mitterer (1969) which proved that the amino acids in the Gunflint Chert were not indigenous to the rock but represented a later stage of contamination by proteinaceous material.

An analogous study to evaluate the protection afforded by carbonate matrix was conducted by Abelson (reported in Abelson, 1959). He analyzed modern and fossil specimens of the clam Mercenaria for amino acids. Both samples contained a number of individual amino acids but in somewhat different concentrations. Abelson concluded that the calcified structural units which comprised discreet layers in the shell served to inhibit degradation by bacteria and aqueous solutions.

Studies such as those described above indicate the relative difficulty of preserving amino acids in large concentrations for geologically significant periods of time. Apparently the ease with which proteinaceous material is broken down into its constituent amino acids by hydrolysis and microbes works against these compounds being incorporated into the stratigraphic column. The presence of an effective media emerges as the most important factor in the preservation of amino acids in sediments.

In addition to the factors of chemical stability there is another factor to be considered for biochemicals which are incorporated

into sedimentary sequences and later subjected to the processes which affect subsurface lithologies. This factor is thermal stability. Abelson (1963) and recently, Khan and Sowden (1971) have conducted research on the thermal stability of amino acids. Abelson's (1963, p. 435) investigations suggest that ". . . near room temperatures, solutions of alanine might persist for a billion years. . . ." The influence of increases in temperature are demonstrated by Abelson's calculations which indicate that this same solution would be highly degraded at 120°C in 1000 years and completely destroyed within a few hours at 250°C.

The work of Khan and Sowden (1971), although primarily concerned with the amino acids found in soils, provides additional data on the thermal stability of these compounds. The data from their research show that disappearance of amino acids is extremely rapid for about the first 100-200 hours and somewhat less rapid thereafter (figure 6). The relative stabilities of different amino acids were found to be similar to the sequence of stabilities suggested by Abelson (1963).

The above discussion of carbohydrate and proteinaceous material in sediments has been necessarily brief because of the relatively small number of investigations devoted to these compounds in sediments and, to a lesser extent, the skepticism with which carbohydrates and proteins are held as possible precursors of hydrocarbons (Hanson, 1959; Breger, 1963). Considerably more investigators have addressed themselves to an examination of the role of lipids as parent material for hydrocarbons.

Figure 6. Thermal decomposition of amino acids as a function of time at 170° C. (After Khan and Sowden, 1971)

Lipids

Lipids are biochemical constituents which are insoluble in water but soluble in non-polar organic solvents such as ether, benzene, and chloroform. This group of biochemicals includes all of the naturally-occurring fats, oils, and waxes (Hart and Schuetz, 1972). Because of the great similarities between certain members of this group and the hydrocarbons found in crude oil, lipids have emerged as the most probable source materials for hydrocarbons (Hanson, 1959; Breger, 1963; Cooper and Bray, 1963; Mair, 1964; Welte, 1965; Abelson, 1963; Elginton, 1968; and others).

Lipids are classified as simple lipids or compound lipids. Simple lipids consist of fats, fatty acids, and waxes. Compound lipids contain nitrogen and phosphate compounds and may combine with proteins and carbohydrates to form lipoproteins and glycolipids, respectively (Toporek, 1971). Most geochemical investigations have involved what Breger (1963, p. 57) calls, ". . . derived lipids such as fatty acids, sterols, or alcohols . . . inasmuch as many of the other varieties eventually break down to these simpler forms"

Many recent studies in the literature have been devoted to the lipid content, especially the fatty acids of organisms and, to a lesser extent, the lipids associated with modern depositional environments (Slowey, et al., 1962; Cooper and Bray, 1963; Yamada, 1964; Ackman and Sipos, 1965; Bradley, 1966; Colombo, 1967; Oro, et al., 1967; Elginton, 1969; Kaneda, 1968; Nissenbaum, et al., 1972; Jamieson and Reid, 1972). It is significant that studies of lipids began in earnest at approximately the same time gas chromatographs became commercially available.

Slowey, et al. (1962) analyzed waters of the Pacific Ocean and the Gulf of Mexico for their fatty acid content. These workers found saturated and unsaturated fatty acids in the C₁₂ to C₂₂ range. This range and type of fatty acids has been reported by Jamieson and Reid (1972) as occurring in marine algae. Jamieson and Reid's study also showed that the fatty acids with carbon numbers of 14, 16, 18, 20, and 22 accounted for over 70 percent of the total fatty acids for the 34 species of marine algae which they analyzed. Analyses of a marine bacterium, a fresh water blue-green algae, and an algal mat community from the Gulf of Mexico yielded fatty acids in the C₈ to C₁₈ range with a maximum abundance occurring at C₁₆ for all organisms analyzed (Oro, et al., 1967). Bradley (1966) reported C₁₂ to C₃₄ fatty acids in dried algal ooze from what he considered to be (p. 1334), ". . . a present-day analogue of a precursor of rich oil shale. . . ." He also reported a C₁₆ fatty acid to be most abundant. Yamada (1964) analyzed the fatty acids extracted from plankton taken from the Antarctic and northern Pacific oceans. The fatty acids with the highest concentrations were those in the C₁₄ to C₂₀ range. Yamada noted that over 90 percent of the dry plankton weight was acetone soluble, indicating an extremely high lipid content.

Lipid extracts from higher marine organisms were analyzed by Ackman and Sipos (1965). They concluded that most saturated normal fatty acids originate in phytoplankton and the fatty acid distributions are altered to characteristic patterns for each group of higher marine organisms.

Fatty acids from the genus Bacillus have been reported in a two-part series by Kaneda (1967, 1968). According to Kaneda, this

particular strain of bacteria can produce normal, branched, and unsaturated fatty acids in the C_{12} to C_{17} range. Examination of the data presented by Kaneda reveals considerably greater variability in fatty acid production from these bacteria than might have been anticipated for such primitive life forms.

Studies concerning the occurrence of fatty acids in sediments, although not as extensive as those for fatty acids in organisms, are rapidly progressing. Papers by Douglas, et al. (1970) and Kvenvolden (1970) on the presence of fatty acids in modern and ancient sediments will serve as summary articles for interested readers. Douglas, et al. (1970) analyzed the Eocene Green River Shale and a Scottish torbanite (algal coal) for their fatty acid content. Their data shows that the Green River Shale contains a broader range of compositions of fatty acid material than those extracted from the torbanite. The relative difference in concentration of total fatty acids for the two samples is striking, the Green River Shale containing approximately 6 times as much fatty acid material as the torbanite sample.

Table 1 is modified from Douglas, et al. (1970) and represents the results of the most significant investigations concerning fatty acids in ancient sediments.

Kvenvolden (1970) analyzed six modern unconsolidated samples for fatty acids and normal paraffins. He compared the compositional data obtained with similar data for n-paraffins and fatty acids which had been extracted from ancient sediments. Some of Kvenvolden's conclusions regarding these data are as follows:

- (1) Distributions of normal fatty acids from modern sediments are extremely uniform, having a strong even-carbon-numbered pattern.

TABLE 1
FATTY ACIDS IN ANCIENT SHALES

Age	Shale	Range of n-acids	Predominant Acid	Authors
Eocene	Green River	C ₁₂ -C ₂₀	C ₁₈	Abelson and Parker (1962)
Eocene	Green River	C ₁₀ -C ₃₅	C ₁₈	Lawler and Robinson (1965)
Eocene	Green River	C ₁₂ -C ₁₈	C ₁₆	Leo and Parker (1963)
Upper Cretaceous	Eagle Ford	C ₁₁ -C ₃₄	C ₁₆	Cooper and Bray (1963)
Upper Cretaceous	Navesink	C ₁₄ -C ₃₀	C ₁₆ , C ₁₈	Nagy and Bitz (1963)
Lower Cretaceous	Skull Creek	C ₈ -C ₃₅	C ₁₈	Cooper and Bray (1963)
Lower Cretaceous	Mowry	C ₈ -C ₃₄	C ₂₀	Cooper and Bray (1963)
Lower Cretaceous	Mowry	C ₁₃ -C ₃₄	C ₂₀	Cooper and Bray (1963)
Lower Cretaceous	Mowry	C ₁₁ -C ₃₁	C ₁₆ , C ₁₈ , C ₂₀	Kvenvolden (1966)
Lower Cretaceous	Thermopolis	C ₁₃ -C ₃₃	C ₂₀ , C ₂₂	Kvenvolden (1966)
Lower Cretaceous	Thermopolis	C ₁₂ -C ₃₅	C ₂₀ , C ₂₂	Kvenvolden (1966)
Mississippian	Chattanooga	C ₁₈ -C ₂₈	C ₁₆	Cooper and Bray (1963)
Cambrian	Alun	C ₁₂ -C ₁₈	C ₁₈	Abelson and Parker (1962)

(After Douglas, et al., 1970)

- (2) Degradational processes during sedimentation produce essentially the same fatty acid mixtures, at least for modern sediments.
- (3) Distributions of fatty acids in ancient sediments vary from those dominated by even-numbered species to those which have no even-numbered dominance.
- (4) Transformations of fatty acids are not as dependent on geologic time as they are dependent on, ". . . favorability of environment. . . ." for inducing such changes.

Table 2 contains data extracted from Kvenvolden's work showing the relative range and concentrations for fatty acids in modern sediments.

An investigation by Nissenbaum, et al. (1972) reveals that fatty acid concentrations are considerably higher for sediments from a reducing environment than those from an oxidizing environment. Nissenbaum's study, conducted on sediments from the Dead Sea, shows that fatty acids from reducing sediments and which had carbon numbers of 16, 18, 22, and 24 were approximately two times as abundant as the fatty acids extracted from oxidizing sediments.

Figure 7 is a summary chart of structural formulas for typical amino acids, carbohydrates, and lipids.

TABLE 2
FATTY ACIDS IN MODERN SEDIMENTS

Age in Years	Sample and Location	Range Found	Recovered Fatty Acids mg/g sample
22,000	San Nicolas Basin (Calif.) mud	C ₁₂ -C ₃₄	41
11,000	Tanner Basin (Calif.) mud; 10-80 cm	C ₁₄ -C ₃₂	7
30,000	Tanner Basin (Calif.) mud; 500-555 cm	C ₁₄ -C ₃₂	17
5,000	Mississippi Delta mud	C ₁₂ -C ₃₆	20
2,000	Florida Bay carbonate mud	C ₁₂ -C ₃₈	4
1,000	Mud Lake (Fla.) algal ooze	C ₁₂ -C ₃₄	570

(After Kvenvolden, 1970)

CARBOHYDRATES

PROTEINS

LIPIDS

Figure 7. Structural formulas for typical representatives of the three major biochemical groups, carbohydrates, proteins, and lipids.

KEROGEN STUDIES

General Statement

Organic matter in sediments may be divided into two fractions depending on its solubility in laboratory organic solvents. The soluble material consists mainly of paraffinic and aromatic hydrocarbons and nitrogen, sulfur, and oxygen organic compounds (hetero-compounds). These soluble materials constitute only about 5 percent of the world's organic matter. The remaining 95 percent exists as an insoluble, complex, and high molecular weight material of variable composition (kerogen) (Abelson, 1968). Various estimates (McIver, 1967; Foresman, 1963; Hoering and Abelson, 1962) for the amount of kerogen in sedimentary rocks suggest that kerogen is 1000 times as plentiful as coal and about 16,000 times as large as the ultimate petroleum reserves estimated by Weeks (1958). These figures indicate that kerogen constitutes a significant proportion of sedimentary rock components. The extremely complex chemical nature of kerogen has prevented the detailed investigation which many other sedimentary rock components have had.

Most of the significant kerogen studies (Foresman, 1963; Foresman and Hunt, 1958; McIver, 1967; Abelson, 1968; Hoering and Abelson, 1962; Hoering and Abelson, 1963; Breger and Brown, 1962; Giraud, 1970; Staplin, 1969; and Robinson, 1969) have been done only within the last 10 to 15 years. This period of investigation coincides with two factors (1) new developments and progress in analytical instruments

and (2) increased emphasis on research on the origin of petroleum by industrial laboratories and various research institutions.

Formation of Kerogen

Although biologic productivity is high in many marine environments, especially in the photic zone, only a small percentage of the biochemicals associated with this high productivity will be incorporated into bottom sediments. The processes which degrade biochemicals under oxidizing marine conditions have been described by Abelson (1963, 1967) and are briefly outlined here. While an organism is alive, metabolic pathways and membranes do not permit degradative oxidation of the biochemical components. When the organism dies, the rigid separation of biochemicals breaks down and degradational processes are set in motion. The investigations described below indicate that these processes are quite rapid. Bordovskiy (1965), in his excellent paper on organic matter in marine sediments, cites several Russian workers whose investigations relate settling velocity of marine organisms to rates of decomposition. One such study is that of Skopintsev (Bordovskiy, p. 15) and it shows that:

- (1) Organisms greater than 1 mm in size reach the deepest oceanic depths only slightly decomposed.
- (2) Organisms between 1 and 0.2 mm and 0.05 mm reach 2,000 meter depths in a highly decomposed state.
- (3) Organisms between 0.2 and 0.05 mm are almost completely decomposed within the upper 1,500 meters.

An exception to the above is when organisms are bound up in fecal pellets. Similar studies on the decomposition of soft tissue in Pteropods and Foraminifera as a function of depth also are discussed by Bordovskiy. All of the studies suggest that the primary contribution

of marine organisms to marine sediments is predominantly in the form of skeletal oozes, the body tissue being decomposed in the upper water mass.

Williams (1965) conducted a study to evaluate the decrease in fatty acid content with increasing water depth. A surface sample populated by various types of algae had a fatty acid to organic carbon ratio of 0.2. At a depth of 400 meters, the ratio had decreased to 0.003.

The carbon, nitrogen, and hydrogen content of common marine organisms does not differ drastically from that of kerogen (Table 3). The major difference is a depletion of nitrogen and hydrogen in the kerogen.

TABLE 3
CARBON, HYDROGEN, AND NITROGEN CONTENT OF
SELECTED MARINE ORGANISMS AND KEROGENS

	C	H	N
	(Weight Percent)		
Diatoms (Vinogradov <u>in</u> Bordovskiy)	45.9	9.4	9.0
Bacteria (Federov <u>in</u> Bordovskiy)	50.4	12.3	6.8
Copepods (Vinogradov <u>in</u> Bordovskiy)	45.5	10.0	7.2
Wilcox Kerogen (Foresman and Hunt, 1958)	65.6	2.5	5.0
Woodford Kerogen (Foresman and Hunt, 1958)	54.6	2.2	4.4

Biologic productivity is only the first requirement in the sequence of events which lead ultimately to kerogen formation. A low free-oxygen content of bottom water masses greatly enhances the possibility that organic matter will be preserved. Not only are the effects of chemical oxidation minimized but such settings are often barren of bottom dwelling organisms which might assimilate sedimented organic matter into their food chain. Several investigators have documented the correlation between oxygen-minimum zones and high

organic carbon content (Richards and Redfield, 1954; Stewart, et al., 1965; Redfield, 1958).

Fine-grain sediments also contribute significantly toward preservation of organic matter. Rapid accumulation of clay-size particles protects the organic matter from further chemical and biologic degradation. Such sediments also give rise to lithologies which inhibit the flow of circulating ground waters which could contribute to further chemical degradation. The relation between sediment texture and organic carbon content has been investigated in areas such as the Gulf of California (Van Andel, 1964), the East China and Yellow Seas (Niino and Emery, 1961), the southern California shelf (Revelle and Shepard, 1939), as well as southern Barataria Bay (Krumbein, 1939). All of these studies show maximum organic carbon concentrations occur in areas characterized by fine-grain sediments.

Types of Kerogen

Because of the lack of information on the structural configuration of the molecules and atoms which comprise kerogen, classification of kerogen has been largely empirical. A review of the papers which attempt to group or classify kerogens suggest good agreement for the two kerogen end members.

Foresman (1963), using elemental distributions of carbon, hydrogen, and oxygen as well as the physical appearance of demineralized, solvent-extracted kerogen, proposed two distinct groups of kerogen. These two groups were termed "coaly" and "non-coaly." Coaly kerogen closely resembles coal, both in physical appearance and in elemental composition. Coaly kerogen has approximately one half

as much hydrogen as non-coaly kerogen and often contains plant fragments. Non-coaly kerogen, according to Foresman, has higher hydrogen to carbon ratios. A third class of kerogen was suggested, but Foresman recognizes that it may represent a physical mixing of the coaly and non-coaly types.

Breger and Brown (1962) arrived at essentially the same conclusions through their study of kerogen in the Chattanooga shale. They proposed the use of the hydrogen content of extracted kerogen to determine the relative contribution of terrestrial organic matter to shales. Breger and Brown suggested that low hydrogen content in the Chattanooga shale is the result of an influx of terrestrial organic material. They further postulated that the low concentration of marine organic matter in the shale may be responsible for the lack of hydrocarbon production in the area. Although Breger and Brown call the types of kerogen humic and sapropelic, these two terms are approximately equivalent to Foresman's coaly and non-coaly types.

The data of McIver (1967) show that the hydrogen content of a single shale unit varies as a function of distance from shoreline. The kerogen extracted from the offshore facies of a Mesozoic shale contained 7 to 7.5 weight percent hydrogen whereas the bay and tidal flat environment contained about 3.5 percent. Assuming the environmental interpretations to be correct, the work of McIver supports the observations of Foresman and Breger and Brown. McIver suggests that the two broad classes of kerogen may be classified on the basis of precursors, namely carbohydrates and lipids. Thus there is good agreement on the two basic types of kerogen, the coaly kerogen of Foresman is fundamentally the same as the humic kerogen of Breger and Brown and the

carbohydrate-rich kerogen of McIver. Likewise non-coaly, sapropelic, and lipid-rich kerogens are approximately equivalent.

The types of hydrocarbons which each of these two types of kerogen may yield has been investigated by Giraud (1970).

Figure 8 shows chromatograms of hydrocarbons generated from shales which contain marine and terrestrial organic matter. All samples were pyrolyzed at 280°C for 10 minutes. The most striking feature of the chromatograms is the low yield of the terrestrial sediments. Marine shales produce hydrocarbons throughout a much broader range and in considerably higher quantities than the terrestrial shales.

Integrating the results of the pyrolysis experiments of Giraud with the attempts to classify kerogens, a working principle may be formulated which relates kerogen type to potential hydrocarbon generation. Hydrogen-rich or sapropelic kerogens are most likely to yield hydrocarbons throughout a broader range and in larger quantities than kerogens derived from hydrogen-deficient or humic depositional settings. The most extreme humic settings, however, do not yield kerogens at all but coals.

Thermal Maturity

Laboratory pyrolysis experiments of both kerogens and organic-rich shales have been conducted by several investigators in attempts to duplicate the thermal conditions necessary to initiate hydrocarbon generation in nature (Hoering and Abelson, 1963; Mitterer and Hoering, 1966; Douglas, et al., 1970; Giraud, 1970; and others). Hoering and Abelson analyzed the light hydrocarbons which were

Marine Sediments

- A) Upper Silurian, Libya; 0.64 percent carbon.
 B) Upper Silurian, Libya; 0.29 percent carbon.
 C) Triassic, Sicily; 4.81 percent carbon.

Continental Sediments

- D) Lower Carboniferous, Libya; 3.02 percent carbon.
 E) Middle Devonian, Tunisia; 0.40 percent carbon.
 F) Lower Devonian, northwestern Sahara; 0.59 percent carbon

Figure 8. Gas chromatograms of hydrocarbons generated by pyrolyzing sediments at 280° C for 10 minutes (Giraud, 1970).

generated from pyrolysis of several types of organic-rich sediments and sedimentary rocks. All samples were heated at 266°C for 100 hours. Figure 9 is constructed from the data of Hoering and Abelson and shows yields of gaseous hydrocarbons. Methane is by far the dominant generated product for all three samples. The anthraxolite sample yielded no hydrocarbon gases other than methane and ethane, however, and the yields were all less than 1 microgram per gram organic carbon. Modern marine mud and Green River shale samples yielded isobutane through n-pentane gases in quantities between 8 and 22 micrograms per gram organic carbon.

Mitterer and Hoering, in a series of experiments performed on modern organic-rich muds, investigated the C₁₇ to C₃₁ paraffins generated at 225°C in a nitrogen atmosphere for three days. Figure 10 is a comparison of the chromatograms for paraffinic hydrocarbons extracted from heated and unheated mud samples. The strong odd carbon-number dominance of the paraffins from the unheated sample is absent in the paraffins from the heated sample.

The work of Douglas, et al. (1970) involved an examination of the aromatic, unsaturated, and branched chain paraffins as well as the n-paraffins. Total hydrocarbon yield for samples of Green River shale heated to 500°C for 3 hours was 4.3 percent of the original sample weight. The hydrocarbons extracted from unheated Green River shale was only 0.5 percent of the original sample weight. The odd carbon-number dominance which is characteristic of the paraffins from the unheated material is absent in the paraffins extracted from the heated samples.

Figure 9. Yield of light hydrocarbons resulting from pyrolysis of organic-rich sediments (data from Hoering and Abelson, 1963).

Figure 10. Gas chromatograms of hydrocarbons from modern sediments.

A. Total paraffins extracted from modern marine sediments (Gulf of California).

B. Hydrocarbons extracted from same sediment after being heated for 3 days at 225° C in a nitrogen atmosphere.

(Redrawn from Mitterer and Hoering, 1966)

Thermal conditions which determine temperatures in sedimentary basins are quite variable and geothermal gradients change markedly from one geographic locality to another. Examination of a geothermal gradient map of southern Texas and southern Louisiana reveals that the area immediately west of the Sabine River has a gradient change of $2.92^{\circ}\text{C}/100$ meters to $4.01/100$ meters within a 25 to 35 mile distance. Compilations by Pusey (1973a, 1973b) and Levorsen (1959) show that thermal gradients for deep wells and productive areas range from $0.55^{\circ}\text{C}/100$ meters on Andros Island, British West Indies to almost $19.69^{\circ}\text{C}/100$ meters in Sumatra.

Variation in geothermal gradients is only one of the factors which has restricted the number of detailed investigations which identify progression from non-generating to generating thermal conditions for hydrocarbon source rocks.

Perhaps the best documented study of this kind is the work by Philippi (1968). He analyzed the normal paraffin extracts from Recent samples in the San Pedro Channel as well as samples which were taken down to depths of 11,450 feet in the Los Angeles Basin. The uppermost samples display the paraffin odd carbon-number dominance which is typical of hydrocarbons in modern sediments. The dominant paraffin peaks occur at the C_{27} , C_{29} , C_{31} , and C_{33} positions. With depth, the odd dominance disappears and the paraffin distribution more closely resembles that of the crude oils in the area. On the basis of chemical similarities of the hydrocarbons as well as geological evidence, Philippi considered the Miocene D and E shale units to be the source beds for the Los Angeles Basin crude oils. On this basis, the first appearance of Miocene D and E shale extracts which resemble crude oil

rather than modern paraffins roughly indicates a transition from non-generating to generating conditions. In the Los Angeles Basin this transition occurs below 8,000 feet. Using geothermal gradients cited by Philippi, the thermal threshold which must be exceeded for hydrocarbon generation in the Los Angeles Basin is approximately 120°C. Figure 11 is redrawn from Philippi's data and shows the distributional changes in paraffins which result from increased temperatures.

In further assessing the role of temperature in hydrocarbon generation, the "liquid-window concept" of Pusey (1973a, 1973b) is of considerable importance. Pusey's work marks the first attempt to quantify rigidly the maximum temperature to which kerogens have been subjected. He has compiled geothermal gradient data for several producing areas of the world and proposes temperature boundaries for initial liquid generation and subsequent destruction via "thermal cracking." Figure 12 is a graph showing the relation between Pusey's "liquid-window" boundaries and the temperatures employed in this study.

Another source of information regarding thermal conditions of hydrocarbon-producing areas of the world comes from a compilation by Hedberg (1967). He lists (p. 6) several productive regions where the ". . . maximum temperatures could probably have been no more than 300°F or 150°C. . . ."

Pressure conditions appear to be insignificant as related to hydrocarbon generation. Dott and Reynolds (1969) have reviewed the major studies which examined the possible relationship between pressure and hydrocarbon yield. One such study was that of Hawley. Hawley employed pressures equivalent to burial depths of 10-15 miles and could not detect any changes in the amount of "extractable matter."

Figure 11. Variation in n-paraffin concentrations as Tertiary rocks in the Los Angeles Basin experience greater depth-of-burial (temperature). (Redrawn from Philippi, 1968)

Figure 12. Depth-temperature relation of Pusey's "liquid-window" concept. Dashed lines indicate boundaries of liquid-window; solid lines indicate temperatures used in this experimental study. Temperatures of petroleum deposits vary from low temperature (biogenic) to high temperatures (thermal or cracked gas). (Modified from Pusey, 1973)

Philippi (1968) and Erdman (1967) both indicate that temperature is the controlling factor in hydrocarbon generation and consider pressure to be of minor importance.

Thermal Indicators

Several tools have been used to help assess the thermal history of sedimentary basins. Electron spin resonance (Pusey, 1973), vitrinite reflectance (Castano, 1973), miospore preservation and carbonization (Wilson, 1961, 1971; Gutjahr, 1966), and kerogen color (Staplin, 1969) have been shown to be useful maturity parameters. An early attempt to use the thermal evolution of a basin as a hydrocarbon exploration tool was made by White (1915). He observed that commercial oil fields coincided with stratigraphic sequences which contained coal seams which had approximately 60 percent fixed carbon. Using the fixed carbon indices commonly used by coal petrographers, White was among the first to propose a correlation between thermal history and hydrocarbon evolution.

Wilson (1961) correlated the degree of preservation of miospores from coals in the Arkoma basin with fixed carbon percentages. He compared the preservational features of ten common miospore genera with fixed carbon percentages and found that no identifiable miospores existed in coals with fixed carbon values greater than 70.1 percent. Wilson's 1971 paper emphasized the increase in miospore opacity with increases in temperature and suggested that localization of heat in fault zones might be detected by changes in miospore carbonization.

Gutjahr (1966) conducted a study which related light transmission through miospores to thermal conditions. He was the first to quantitatively describe the changes in carbonization as a function of temperature. Gutjahr's work will be discussed again later.

Visual examination of demineralized, solvent-extracted kerogen was proposed as a method to evaluate the thermal alteration of organic matter (Staplin, 1969). The following data (table 4) lists the five stages of thermal alteration proposed by Staplin as well as the type of hydrocarbons which may accompany each index value.

Another thermal indicator which has found wide acceptance as an operational tool is vitrinite reflectance. Vitrinite is one of the major coal macerals but differs from other macerals in that it is found in many ancient organic-rich sediments exclusive of other coal components. As with many of the bright coal macerals, the degree to which vitrinite can reflect light is dependent on the temperature to which it has been exposed. Thus greater reflectance values for vitrinite fragments extracted from an organic-rich shale implies a higher temperature history. The method commonly in practice is to extract the vitrinite by a technique similar to that for kerogen extraction, mount the vitrinite fragments in an epoxy medium, grind the epoxy and vitrinite to a flat surface, and measure light reflectance with a light sensing device.

TABLE 4
THERMAL ALTERATION INDEX SCHEME OF STAPLIN^a

Thermal Alteration Index	Organic Matter	Hydrocarbons
1. None	Fresh, yellow	Wet or dry
2. Slight	Brownish yellow	Wet or dry
3. Moderate	Brown	Wet or dry
4. Strong	Black	Dry gas
5. Severe	Black with additional evidence of metamorphism	Dry gas to barren

^a1969.

PROCEDURE

General Statement

This study was designed to evaluate the hydrocarbon-generating potential of a modern organic-rich sediment under various laboratory conditions. Investigations by the Louisiana State University Coastal Studies Institute indicated that sediments in the northern part of Barataria Bay (John-The-Fool Lake) were rich in organic matter and could serve as material for this study.

Sediments in John-The-Fool Lake and Bayou contain 20-34 percent organic carbon (Ho, 1971) and in situ Eh measurements of -200 to -250 millivolts have been observed (Ho, unpublished data). Exchange of water between the open bay area and John-The-Fool Lake is extremely poor and major flushing of the northern portion of Barataria Bay is primarily dependent upon precipitation runoff. Poor water exchange between the open Gulf and Barataria Bay waters is reflected in the total dissolved salt content of the lake and bayou water. Water samples taken at a station with open communication to the Gulf have approximately 5 times the concentration of total dissolved salts as do water samples from John-The-Fool Bayou although both are approximately the same distance inland (Ho, 1971).

Rapid accumulation of organic matter is greatly enhanced by high organic productivity, lack of freely circulating oxygen-rich waters, and slow sedimentation of only fine-grained material. Organic material either settling through or deposited in oxidizing environments

is rapidly degraded into carbon dioxide and water. Organic matter deposited with coarse sediments stands little chance of surviving the oxidizing effects of ground waters which can flow readily through such lithologies. Hanson (1959) suggests that the three conditions for producing lithologies which may ultimately serve as hydrocarbon source rocks are (1) quiet waters of deposition, (2) muddy sediments, and (3) low free oxygen content.

The sediments of John-The-Fool Lake meet all these criteria and thus may serve as a modern analog for ancient source rocks which owe their origin to similar conditions.

In addition, three modern samples from the open Gulf of Mexico were used in this study. The reasons for requesting the off-shore samples were twofold. First, a comparison of the estuarine and open-Gulf muds might yield significant results on the dilution effect of terrestrial organic matter being transported seaward. The second reason for analyzing offshore samples is to compare the types of lipids produced in a strictly marine environment with those found in estuaries. The material supplied by the University of Texas Marine Science Institute represents a split of two samples analyzed by Newman et al. (1973). They have shown that stable carbon isotopes can be used successfully to differentiate modern organic material of terrestrial and marine origin.

Sample Location and Collection

Modern Organic-Rich Sediments

John-The-Fool Lake Samples.--Figure 13 shows the location of John-The-Fool Lake and its position within the Barataria Bay complex.

Figure 13. Site of sediments collected for experimental study.

Mud samples were taken from John-The-Fool Lake with a small clam-shell type dredge. The contents of each dredge haul were emptied into a metal container until a quantity sufficient to fill one-liter sample jars was obtained. Mud was then transferred to the jars and the jars were sealed with screw-on Bakelite caps. Because of the gelatinous nature of the mud, it was difficult to retain appreciable quantities in the dredge and several dredge hauls were required to fill a single one-liter jar. The sample jars were placed in an ice-chest and covered with ice until they could be transferred to a freezing unit for storage.

Gulf of Mexico Samples.--Figure 14 is a map which shows the location of the offshore Gulf of Mexico samples used in this study. These samples were provided by the University of Texas Marine Science Institute and the Sun Oil Company Research Laboratory. The exact location of the samples furnished by Sun was not revealed for proprietary reasons related to a proposed Federal Offshore Sale. All Gulf of Mexico samples were taken with piston coring devices.

Ancient Organic-Rich Sediments

Core material of two ancient organic-rich shales was furnished by Exxon Research and Amoco Production Research. These samples consisted of two cores of Cretaceous Tuscaloosa Shale and a single core of Doig Shale of Triassic Age.

The Exxon Tuscaloosa cores were taken in the Humble-Tatum #1 in Lamar County, Mississippi, and in the Humble-Masonite #1 in Wayne County, Mississippi. The sample from the Humble-Tatum #1 was taken at 8,983 feet; the temperature at this depth was estimated to be 230°F (Kaiser, personal communication, 1972). The Humble-Masonite #1 sample

Figure 14. Location of Gulf of Mexico samples. UT designates samples obtained from the University of Texas Marine Science Institute. SRL samples are from the Sun Oil Company Research Laboratory.

was taken at 7,028 feet and the estimated temperature at this depth is 184°F (Kaiser, personal communication, 1972). Both temperatures were estimated from bottom hole temperature surveys and from reported temperatures of nearby wells and fields.

The core supplied by Amoco Production Research was taken in the Doig Shale of Triassic Age in Alberta, Canada. No details concerning well location and cored interval were supplied with the sample.

Amoco Production Research also provided a sample of an extracted kerogen and its whole-rock counterpart from south Louisiana. These samples are organic-rich Gulf Coast muds in a very early stage of diagenesis and are probably similar to John-The-Fool Lake mud samples (Harwood, personal communication, 1973).

Sample Treatment

Homogenizing the Samples

Variation in samples due to treatment is more readily apparent when samples taken from a common source have a high degree of homogeneity. Thus, if the source material is initially heterogeneous, any subtle variation which results from treatment may be difficult to detect. The preliminary extractions for John-The-Fool Lake samples resulted in a high degree of variation in concentrations of both fatty acid and hydrocarbon material. (In this study, the term extraction refers to the removal of lipids by successive treatments with a 50:50 methyl alcohol: chloroform solvent mixture; components removed in this manner are called soluble.) Visual examination of freeze-dried samples revealed a large size variation in plant debris, which were composed predominantly of Spartina alterniflora fragments. Two methods of homogenizing the samples were investigated.

The first method involved simply wet-sieving the sample and discarding all large plant fragments. Variation in the concentrations of fatty acid and hydrocarbon fractions from several wet-sieved samples was reduced but was still unacceptable for a routine analytical procedure.

The second method of homogenizing the mud sample consisted of wet-sieving followed by blending in a Waring blender for 15 minutes. This treatment yielded a sample which was uniform in texture and in extractable lipid content. A large sample of wet-sieved and blended material was divided into four equal portions and extracted. The results of these extractions are presented in Appendix I, and show that concentrations of the various extracted organic fractions do not vary greatly. Elemental analysis of a sample of the mud was performed by Amoco Production Research and data are given in Appendix II.

Mud samples used in the study were collected during two trips to John-The-Fool Lake. Samples from the first trip were stored in a freezer until they were combined with samples taken during the second trip. The combined samples were wet-sieved and blended in the manner previously described and the resulting slurry was poured into 500 ml Teflon beakers and stored in a freezing unit. The sample pre-treatment provided a uniform slurry matrix with a minimum of sample heterogeneity so that large variations in the type and amount of extractable organic fractions must be the result of subsequent treatment.

In order to minimize variation resulting from different volumes of mud subjected to treatments, a standard bomb charge (SBC) or control quantity of sample material was selected. The volume for this standard bomb charge was a 442 ml slurry. A bomb charge of

442 ml was compatible with the capacities of both the Parr bomb and the Barnes Hydrothermal System both of which are described below. In addition, the four extractions used to evaluate sample homogeneity were performed on 442 ml slurry samples and the data indicate that 442 ml is a satisfactory volume for yielding reproducible quantities of extractable fractions. The control or standard bomb charge quantities for each fraction are the numerical averages of the four extractions (see Appendix I).

Experimental

Bomb Equipment

Description.--A Parr Model 4011 bomb was used for many of the low temperature and low pressure runs. The Parr Bomb used in this study was constructed of Monel alloy and had temperature and pressure limits of 400°C and 5000 psi, respectively. A Honeywell Model R71616B Potentiometric Temperature Controller was used to control the temperature of the reaction vessel. Details on the 4000 Series Reaction Vessels are given in Parr Instrument Company Specification Number 5000, available from the manufacturer.

A Tem-Press Barnes Volumetric Hydrothermal System, Model RA-2A-1 was used for high temperature and high pressure experiments. This instrument has a temperature range of 25-600°C and a pressure range of 0-15,000 psi. The reaction vessel, fittings, tubing and hardware of the system are made of high pressure stainless steel.

Additional details can be obtained from Barnes (1963) and by contacting Tem-Press Research, State College, Pennsylvania.

The volumes of both closed systems including valving and tubing was determined by filling each with distilled water and recovering the water, taking care to displace all air in the valves and tubes. This procedure was repeated until three successive volumetric determinations varied by only 2 ml per determination. The volumes thus obtained were 1017 ml for the Parr Bomb and 540 ml for the Barnes System, both values being slightly different from those listed in the manufacturer's specifications.

Operating Conditions.--Temperature conditions for this study were chosen as 80°C, 160°C, and 240°C. The routine heating period was 50 hours. This temperature range was considered to embrace the minimum and possibly an upper limit for initiation of the reactions which serve to generate liquid hydrocarbons from organic-rich source rocks. Laboratory studies which involved the generation of hydrocarbons from organic-rich shales and kerogens have been conducted at somewhat higher temperatures (Hoering and Abelson, 1963; Giraud, 1970; Gransch and Eisma, 1970; Douglas, et al., 1970).

Pressures in the bomb experiments were subject to variation as a result of temperature variation. The Barnes System is equipped with a temperature controlling unit which "overshoots" and "undershoots" the set temperature. The amount of "overshoot" cannot be predicted consistently and, as a result, pressure variations were ± 250 psi of the desired pressure. Graphs of temperature setting versus measured temperature and temperature-pressure-fill factor curves are shown in Appendices III and IV.

After the slurry material had been placed in the reaction vessel and the vessel sealed, the void between the head of the

reaction vessel and the top of the slurry was pressurized with gas. Hydrogen, oxygen, or air was used as the atmospheric filling for different experiments.

The void was purged for 15 minutes with the pressure fitting loose to permit the displaced gases to escape. All purging was done at 10 psi with the pressure vessel in an upright position. When the purging was complete, the pressure fitting was tightened and the reaction vessel was pressurized to 100 psi. Initially, it was thought that gaseous hydrogen and oxygen might influence reactions which yielded saturated and unsaturated products respectively, but the sediments were so strongly reducing that even oxygen-pressurized experiments resulted in strongly negative Eh readings (Appendix IX). Because of the similarity of pH and Eh readings for slurry material exposed to the three atmospheres, air was used only twice at each temperature. The majority of the experiments used either pure hydrogen or pure oxygen gas.

Extraction Procedures

Lipid Extraction

The lipid extraction technique employed in this study is widely used by investigators in lipid geochemistry. Specific details and references as well as a flow-chart for the method are presented in Parker (1969). A modification of Parker's flow-chart is presented in Appendix VI. A description of the extraction scheme is presented in the following paragraphs. Identical procedures were used for untreated muds and slurry material taken from the reaction vessels.

Mud samples were washed with distilled water to remove salts and the water was filtered through a 12.5 cm diameter Buchner funnel

into a 1-liter side-arm filter flask. All filter paper used in the lipid extractions was pre-washed twice with 1:1 (by volume) mixture of distilled methyl alcohol and chloroform. All solvents were distilled in ungreased glass distillation systems. The washed sediment was dried in an oven at 50°C for 12 hours.

Two hundred ml of methyl alcohol was added to the sample which was permitted to stand 30 minutes, followed by addition of 200 ml of chloroform. The mixture was blended in a Waring blender for 15 minutes, was treated ultrasonically for another 15 minutes and then filtered through a Buchner funnel into a 1-liter filter flask under reduced pressure. The filtrate was retained and the sediment residue was subjected to one additional extraction procedure again. Samples treated in this manner are called extracted throughout the text. Distilled water was added to the extracted sediments in order to bring the total sample volume to 442 ml.

The two organic extracts were combined, evaporated with a rotary evaporator under reduced pressure at room temperature, and saponified with a 5 percent potassium hydroxide-methyl alcohol solution. The mixture was transferred into a separatory funnel and washed three times with distilled hexane. The hexane removed the hydrocarbon fraction, leaving the fatty acids in the aqueous layer.

The aqueous solution was acidified, converting the fatty acid salts into hexane-soluble fatty acids. The solution was washed three times with hexane to ascertain complete fatty acid extraction and was esterified with a 5 percent solution of boron trifluoride-methyl alcohol. Fatty acid-boron trifluoride-methyl alcohol esters were analyzed directly by gas chromatography.

Hydrocarbon Extraction

The hexane-soluble fraction of the lipid extract was comprised of several types of hydrocarbons as well as sulfur, oxygen, and nitrogen-containing organic molecules which are also soluble in a methyl alcohol-chloroform solvent system. The latter compounds are grouped under the term hetero-compounds and represent a significant portion of the total organic matter in John-The-Fool Lake sediments.

A silica gel-activated alumina adsorption chromatographic column was used to separate the hexane-soluble portion of the lipids into aromatic, paraffin, and hetero-compound fractions.

Adsorption chromatographic columns used in the analysis were 0.6 cm in diameter and 30 cm in length. The columns were pre-wetted with hexane and then packed with 60-200 mesh chromatographic grade silica gel to a height of 20 cm. The uppermost layer of packing consisted of 2-3 grams of 80-325 mesh activated alumina.

The sample was introduced into the column and n-paraffins were eluted from the column by passing hexane through the column until 30 ml of eluent had been collected. A second 30 ml of eluent was collected while the first 30 ml was evaporated to near-dryness. The second 30 ml of eluent was combined with residue of the first and again evaporated to near-dryness. The flask was placed in a dessicator for 24 hours and weighed.

In order to elute the aromatic fraction from the column, the same procedure was followed except benzene was used instead of hexane.

The final elution was made with 1:1 mixture of methyl alcohol-chloroform. This fraction invariably contained the compounds which showed dark brown color of the initial sample, the hexane and

aromatic fractions were colorless or grayish. Exceptions to the color of the aromatic fraction occurred with the offshore Mexico sample (UT-2) and the Triassic Doig Shale. Both of these samples yielded reddish-brown aromatic fractions.

The hexane eluted paraffin fraction was analyzed by gas chromatography. Paraffins with 15 to 28 carbon atoms per molecule were analyzed with a column packed with 10 percent FFAP on acid-washed Chromasorb-W. The long-chain molecules with carbon numbers of 29 to 32 were analyzed with a column packed with 3 percent Dexsil on acid-washed Chromasorb-W. The concentrations and distributions of the paraffins are discussed elsewhere in this dissertation.

The aromatic fractions were subjected to gas chromatographical analysis but the individual components in the mixture were not resolved. The column used for aromatic hydrocarbon analysis was packed with 5 percent Bentone 34 and 5 percent Dinonylphthalate on acid-washed Chromasorb-W and was capable of separating many of the aromatic hydrocarbons which commonly occur in petroleum.

ANALYTICAL TECHNIQUES

Gas Chromatography

Gas chromatography is a relatively new analytical technique which came into application in the early 1960's. It permits detection of a wide range of organic and many inorganic compounds. A voluminous literature has accumulated in the field of chromatography for both theoretical and applied aspects. For this reason, only a brief description of chromatographic systems will be discussed in this section. Interested readers may refer to Littlewood (1962), Purnell (1962), Ettre and Zlatkis (1967) and several other sources for detailed discussions on the basic principles of gas chromatography. Shorter, less detailed descriptions of principles and techniques may be found in sources such as Weiss (1970), McNair and Bonelli (1969), and Robinson (1970).

Gas chromatographic units may be resolved into four basic components; the carrier gas system, the column, the detector, and the recorder.

The carrier gas system provides the means by which a sample is transported from an injection port or inlet, through the chromatographic column, and on to the detector. Carrier gases must be inert to the sample and column packing material and should be available in a pure state. Two commonly used carrier gases are helium and nitrogen. To maintain a constant rate of elution, the flow rate of the carrier gas must be kept constant by a gas pressure regulator.

The column is the most important component in a chromatographic unit. It is this part of the system which permits the separation of individual compounds from sample mixtures. Columns are made of stainless steel, copper, aluminum, or glass and are filled or coated with various types of packing material. Packing material in columns consists of a solid support or inert material and a stationary phase. The stationary phase is made of an organic compound dissolved in a solvent such as chloroform, acetone, toluene, or benzene and is used to coat the solid support. The stationary phase material selectively collects all similar molecules in the sample until they flow through the column in distinct bands. A tabulation of materials used as stationary phases is found in Weiss (1970) and in McNair and Bonelli (1969).

After separation into single groups of molecules of the same type, the sample exits the column and enters the detector. The function of the detector is to indicate the presence and quantity of components which have been separated in the column. Two commonly-used detectors are the flame ionization detector (FID) and the thermal conductivity detector (TCD). Figure 15 illustrates an FID chromatogram.

The operating principle of the FID is described by McNair and Bonelli (1969, p. 101) as being a process whereby ". . . effluent gas from the column is mixed with hydrogen and burned in air or oxygen. Ions and electrons formed in the flame enter the electrode gap, decrease the gap resistance, thus permitting a current to flow in the external circuit. . . ." The FID is extremely sensitive to organic compounds, there are several sources of compiled tables of relative FID response to various groups of compounds (McReynolds, 1966; Lewis, 1967).

Figure 15. Typical gas chromatograms of n-paraffins and fatty acids extracted from samples.

Whereas the principle of flame ionization detector operation is such that it is specific for organic molecules, the thermal conductivity detector is governed by the principle that a hot filament will lose heat in proportion to the kind of gas flowing through the detector. Most TC cells have one filament placed in the effluent gas streams from the column and has a second filament positioned so that it is exposed only to pure carrier gas. The filaments are operated under identical thermal conditions so that the only manner by which electrical resistance may change is by a change in the composition of the gas flowing around the filament. Thermal conductivity detectors are not as sensitive as flame ionization detectors but TC detectors will analyze all components.

Table 5 was compiled from Weiss (1970) and McNair and Bonelli (1969) and represents the important characteristics of TC and flame ionization detectors.

The function of the recorder is to provide a record of electrical signal output from the detectors. The recorder used in this study was a Westronics Model LS11A and was equipped with a Disc Integrator which converts peak areas to quantities of the components being analyzed.

A brief description of the gas chromatograph used in this study and the operating conditions for each type of analyses may be found in Appendix VII.

Gas Analysis

Carbon dioxide, nitrogen, and hydrocarbon gases which evolved from the slurry material were analyzed after allowing the reaction

TABLE 5
CHARACTERISTICS OF THERMAL CONDUCTIVITY (TCD) AND FLAME
IONIZATION (FID) DETECTORS USED IN GAS CHROMATOGRAPHY

Detector	Sensitivity (gm)	Components Detected	Limitations
TCD	10^{-6}	All	Low sensitivity
FID	10^{-12}	Organics with CH bonds	Destructive

From Weiss, 1970, and McNair and Bonelli, 1969.

vessel to cool to room temperature. After the reaction vessel had cooled, the residual pressure was reduced to approximately 30 psi by opening the sampling valve on the vessel.

A short section of surgical tubing was connected to the sampling valve stem and sealed at the open end by a pinch-clamp. The sample valve was opened and the gases in the reaction vessel were permitted to flow into the surgical tubing. Atmospheric gases were flushed from the tubing by opening the pinch-clamp and bleeding the system pressure to 15 psi. One cc of sample was then withdrawn by inserting a gas-tight syringe into the tubing. The syringe was equipped with a Mini-Inert valve which prohibited contamination by atmospheric gases.

The TC detector was used for all gas analyses. A six-foot stainless steel column of $\frac{1}{4}$ " I.D. packed with Chromasorb-102 was used. Qualitative peak positions were determined by comparison with gas chromatograms obtained by analyzing natural gases of known compositions. A Scott Calibration Gas Mixture was used for quantitative standards. The results of the gas analyses are presented in Table 7.

Fatty Acid and Hydrocarbon Analysis

Fatty acids and paraffinic hydrocarbons were analyzed with the FID and a ten-foot copper column of $\frac{1}{8}$ " I.D. packed with 10 percent FFAP on Chromasorb-W. Fatty acids and hydrocarbons were separated as previously described and 1 micro-liter samples were taken from the extracts and injected into the gas chromatograph.

Fatty acids were analyzed isothermally at 100°C for 1 minute post-injection and then programmed to 240°C at a constant heating rate of 5°C/minute. Paraffins were analyzed similarly but the one minute post-injection temperature was 125°C.

The benzene-soluble fraction was injected into a $\frac{1}{4}$ " six-foot stainless steel column packed with 5 percent Bentone 34 and 5 percent Dinonylphthalate on Chromasorb-W. A standard mixture of the aromatic hydrocarbons which occur most commonly in petroleum was prepared from a Poly-Science Aromatic Standard Kit. The greatest retention time for a component in the standard mixture was slightly over 18 minutes. The aromatic component extracted from unaltered John-The-Fool Lake and from the slurry material subjected to high temperature-pressure bomb treatment had a retention time of over 32 minutes. These aromatic hydrocarbons were not identified, but their extremely long retention time suggest that they may be high molecular weight compounds.

Miospore Carbonization Measurements

In order to quantify the progressive carbonization of miospores as they are subjected to increasing temperatures, an extremely sensitive light measuring device was required. Gutjahr's (1966) pioneer work in this field was done with a photocell and provided the first quantitative measurements of pollen and spore opacity. He subjected oak pollen to various temperatures and measured the resultant changes in light absorption.

In this study pine pollen was added to the slurry material prior to sealing the reaction vessels and was recovered by standard palynological techniques after each run. Carbonization experiments were conducted under all temperature, pressure, and atmospheric gas combinations and the degree of carbonization was found to be solely a function of temperature (figure 19). Later experiments to determine fatty acid and hydrocarbon variation due to treatment were conducted without pine pollen.

The technique used to measure carbonization changes was essentially the same as that employed by Gutjahr. A Leitz Ortholux microscope was equipped with a photocell and a DC current meter and the light passing through the central body of pine pollen grains was measured. The photocell used in this work was the same one used by Martinez (1965) in his work on mineral orientation in igneous rocks.

Gutjahr's original technique was modified slightly in order to read the amperage of the DC current more conveniently. Gutjahr constructed a reverse scale for his apparatus so that increasing opacity would correspond to higher milliamp readings. No such modification was made in this study and amperage values are expressed as ratios (figure 19).

Discussion of the carbonization study appears in the section on experimental data.

Eh and pH Measurements

Eh and pH measurements were made on the aqueous solutions which were taken from the reaction vessel. Two such measurements were taken for each temperature-atmospheric filling combination except those experiments which utilized air as the atmospheric gas.

In order to prevent the aqueous solutions from coming in contact with the atmosphere and possibly altering true pH-Eh values in the reaction vessel, a device was constructed according to a verbal suggestion made by D. Langmuir in 1970. A drawing of the device and the electrode arrangement is shown in Appendix VIII. The reaction vessel was positioned so that the gas pressure inside the vessel would force fluid through the sampling valve and into the Eh-pH measuring device.

Corning electrodes and a Corning Model 12 Research pH Meter was used for the determinations. Standard pH buffer solutions were used to calibrate the instrument prior to use. Quinhydrone was used as an Eh standard. Tables which relate Eh measurements of quinhydrone to various pH levels are listed in Lange (1944). Results of Eh and pH measurements are presented in Appendix IX.

X-Ray Diffraction Patterns

A Phillips Model 3500 Automatic Powder X-ray Diffractometer was used for analysis of the clay minerals. After the slurry material had been extracted with organic solvents, the sediment residue was washed with methyl alcohol and allowed to evaporate to dryness. The samples were pulverized with a Spex Mill and separation of the <4 μ size fraction was made according to Stoke's Law. The less than 4 micron fraction was analyzed for clay minerals by x-ray diffraction using CuK_{α} radiation.

The diffraction patterns for the modern organic-rich samples and the ancient samples are shown on figures 16 and 17. All diffraction patterns except that of the Doig Shale indicate similar mineralogy. The clay minerals constitute a three-component system of a mixed-layer clay, illite, and kaolinite.

Figure 16. X-Ray diffractograms of clays in Modern samples. See Figures 13 and 14 for location of specific samples. Samples glycolated for 24 hours prior to analysis.

Figure 17. X-Ray diffractograms of clays in Ancient samples. All samples glycolated for 24 hours prior to analysis.

SAMPLE IDENTIFICATION

In discussing the experimental data obtained in this study, sample abbreviations are used to designate sediment matrix, temperature, gas filling, and system pressure combinations. Sample identification abbreviations are described below.

SBC	Standard bomb charge or control consisting of 442 ml of unaltered, homogenized John-The-Fool Lake sediment slurry.
US	Unaltered homogenized sediment matrix.
LE	Unaltered homogenized sediments which have undergone lipid extraction.
H ₂	Experiments which utilized hydrogen as a filling gas.
O ₂	Experiments which utilized oxygen as a gas filling.
A	Experiments which utilized air as a filling gas.
KS	Experiments which were conducted as a kinetics study.
TUS	Tuscaloosa Shale (Cretaceous), Southern Mississippi.
DOS	Doig Shale (Triassic), Alberta, Canada.
AM	Modern organic-rich mud supplied by Amoco Research.
EX	Sample of mineral-free, chloroform-extracted kerogen from AM sample.
UT1-UT2	Modern mud samples supplied by the University of Texas Marine Science Institute; locations shown on figure 14.
SRC	Modern mud sample furnished by Sun Research Center, location shown on figure 14.
NPC	Experiments involving lipid extract from a standard charge and a sodium-saturated montmorillonite clay.
CPC	As NPC above except the montmorillonite clay is calcium saturated.

Numbers used in sample identification indicate the temperature, in degrees centigrade, to which the sample was subjected. The last numbers of the KS sample identification represent exposure periods, in hours. LP, IP, and HP correspond to low pressure (1500-2000 psi), intermediate pressure (3000-3500 psi), and high pressure (5000-5500 psi) respectively and indicate the maximum system pressures to which samples were exposed.

STATISTICAL ANALYSIS

In order to evaluate the effects of the presence or absence of lipids, atmospheric gas filling, temperature, and pressure on the distribution and concentration of hydrocarbon compounds measured at the end of each experiment, the data for John-The-Fool Lake sediments were subjected to an analysis of variance. The specific model employed was a completely randomized design with a factorial arrangement of treatments. This design is most useful when the experimental units have a high degree of homogeneity (Steel and Torrie, 1960). In this study, the sediments were blended to a homogeneous material so that the initial sample matrix had little variation in extract yield (Appendix I).

In factorial experiments, several factors are included and combinations of levels of the factors provide the treatments (Steel and Torrie, 1960). Two types of sediments were used (those extracted or unextracted with chloroform-methyl alcohol) and two levels of atmospheric gas fillings (oxygen and hydrogen). Air was not used for all temperature-pressure combinations. Samples were exposed to three levels of both temperature and pressure. Thus, the factorial arrangement of treatments constituted a $2 \times 2 \times 3 \times 3$ factorial arrangement.

The source table for the ANOVA conducted is given in table 6. In the ANOVA, the main effects are those due to extraction, gas filling, temperature, and pressure. The two factor interactions are also included in the analysis. A two factor interaction measures the failure of one factor to produce the same response at various levels of a

TABLE 6
MODEL FOR ANALYSIS OF VARIANCE

Source of Variation	Degrees of Freedom
Extractions	1
Gas Filling	1
Temperature	2
Pressure	2
Extractions x Atmospheric Filling	1
Extractions x Temperature	2
Extractions x Pressure	2
Atmospheric Filling x Temperature	2
Atmospheric Filling x Pressure	2
Temperature x Pressure	4
Error (Residual)	16

second factor (Steel and Torrie, 1969). The three factor and four factor interactions have been pooled to provide an error term for evaluating main effects and two factor interactions (Cochran and Cox, 1957).

For every species of fatty acid, extraction and temperature were responsible for significant variations ($P < .05$) in concentrations. In addition, the extraction x temperature interaction was significant ($P < .05$) for fatty acids with carbon numbers of 12, 15, 16, 23, 25, 27, 28, and 30. Figure 18 is a graph of concentration versus temperature for extracted and unextracted sediments for a case where the extraction x temperature interaction is significant ($P < .05$) (anteiso- C_{15} fatty acid) and a case where the interaction is not significant ($P > .05$) (iso- C_{14}).

For every species of n-paraffin and aliphatic fatty acid as well as the gaseous products, lipids, fatty acids, aromatics, and hetero-compounds, the only factors which were statistically significant ($P < .05$) were temperature, extractions, and the temperature x extraction interaction. Table 7 lists the components and groups of compounds which were quantitatively determined at the conclusion of each experiment and indicates which factors had a statistically significant influence on the variation of each one ($P < .05$). Table 7 shows that fatty acid concentrations are extremely sensitive to temperature and extraction conditions whereas the concentrations of intermediate length n-paraffins are most affected by temperature. Extractions begin to affect the n-paraffin concentrations at carbon numbers of 26-28 and greater.

ANTEISO - C₁₅ FATTY ACID

n-C₁₅ FATTY ACID

Figure 18. Graphs showing variation in concentrations of fatty acids when statistical interaction is significant (A) and when interaction is not significant (B). T₁, T₂, and T₃ are 80°, 160°, and 240° C, respectively.

TABLE 7

INDIVIDUAL N-PARAFFINS AND FATTY ACIDS AND GROUPS OF COMPOUNDS
WHOSE CONCENTRATIONS WERE SIGNIFICANTLY AFFECTED
BY TEMPERATURE, EXTRACTIONS, AND TEMPERATURE
x EXTRACTION INTERACTION

Component	Temperature	Extraction	Temperature x Extraction
<u>Fatty Acids</u>			
C ₁₂	x	x	x
iso-C ₁₄	x	x	
C ₁₄	x	x	
anteiso-C ₁₅	x	x	x
C ₁₅	x	x	
iso-C ₁₆	x	x	x
C ₁₆	x	x	
C ₁₈	x	x	
C ₁₉	x	x	x
C ₂₀	x	x	
C ₂₁	x	x	
C ₂₂	x	x	
C ₂₃	x	x	x
C ₂₄	x	x	
C ₂₅	x	x	x

TABLE 7 -- (Continued)

Component .	Temperature	Extraction	Temperature x Extraction
<u>Fatty Acids</u> - Continued			
C ₂₆	x	x	
C ₂₇	x	x	x
C ₂₈	x	x	x
C ₂₉	x	x	
C ₃₀	x	x	x
<u>n-paraffins</u>			
C ₁₅	x		x
C ₁₆	x		x
C ₁₇		x	
C ₁₈	x		x
C ₁₉	x		x
C ₂₀	x		x
C ₂₁	x		x
C ₂₂	x		x
C ₂₃	x		x
C ₂₄	x		x
C ₂₅	x		
C ₂₆	x	x	x

TABLE 7--(Continued)

Component	Temperature	Extraction	Temperature x Extraction
<u>n-paraffins</u> - (Continued)			
C ₂₇	x		x
C ₂₈	x	x	x
C ₂₉	x	x	x
C ₃₀	x	x	x
C ₃₁	x	x	x
C ₃₂	x	x	x
<u>Gases</u>			
CO ₂	x	x	x
N ₂	x	x	x
CH ₄	x	x	x
<u>Organic Fractions</u>			
Lipids	x	x	x
Soluble Fatty Acids	x	x	x
Hexane-soluble	x		x
Paraffins	x	x	x
Aromatics	x		x
Hetero-Compounds	x	x	x

x indicates statistical significance (P < .05).

The concentrations of all gaseous products were significantly affected by temperature, extraction, and temperature-extraction interaction; concentrations of lipid, fatty acid (soluble in a methyl alcohol-chloroform mixture), paraffinic, and hetero-compound fractions were also significantly affected by these three factors. The yield of aromatic components was most affected by temperature and the temperature-extraction interaction.

The nature of the variation of particular species and groups of compounds for specific experimental conditions are discussed in the following sections.

GENERAL DISCUSSION OF EXPERIMENTAL DATA

Carbonization

The objective of carbonization studies is to evaluate temperature history for sedimentary basins. Temperature history, in turn, can be used to make predictions regarding oil and gas potential in various basinal settings. Using figure 19 as an approximate guide for sacculate miospore carbonization versus temperature, it is apparent that more confidence may be placed in that part of the curve between 25-160°C than at higher temperatures. Rapid carbonization occurs between 160°C and 240°C and the carbonization temperature curve is much steeper than at lower temperatures.

Gaseous Products

Carbon Dioxide

Carbon dioxide (CO_2) was by far the most abundant gaseous product generated in the bomb experiments. Although there is a general pattern of increasing CO_2 yield with higher temperature conditions, some experiments had higher CO_2 concentrations than similar experiments conducted at higher temperatures (see table 8). For example, sediments with the lipids extracted, run at 160°C and 3000-3500 psi (160 LEO₂-IP) yielded a P_{CO_2} of 29.93 atm., whereas an unaltered sample run at 240°C and 3000-3500 psi (240 USH₂-IP) yielded a P_{CO_2} of only 15.88 atm. (table 8).

Figure 19. Effect of temperature on carbonization of Pinus spp.

TABLE 8

MAXIMUM SYSTEM PRESSURE AND PARTIAL PRESSURES OF CARBON DIOXIDE,
NITROGEN, AND METHANE AFTER ALLOWING REACTION
VESSEL TO COOL TO AMBIENT TEMPERATURE
(In Atmospheres)

Sample	Maximum Pressure	CO ₂	N ₂	C ₁
80 USH ₂ -LP	125.12	0.02	6.10	0.00
80 USH ₂ -IP	220.12	0.06	6.06	0.00
80 USH ₂ -HP	354.96	0.05	6.07	0.00
80 LEH ₂ -LP	123.76	1.79	4.18	0.15
80 LEH ₂ -IP	233.92	1.93	3.96	0.23
80 LEH ₂ -HP	352.24	1.84	4.02	0.26
80 USO ₂ -LP	106.08	0.22	5.90	0.00
80 USO ₂ -IP	235.28	0.25	5.87	0.00
80 USO ₂ -HP	368.56	0.29	5.83	0.00
80 LEO ₂ -LP	121.04	2.16	3.68	0.28
80 LEO ₂ -IP	206.72	1.71	4.20	0.21
80 LEO ₂ -HP	352.24	1.94	3.96	0.22
80 USA-LP	100.64	0.14	5.98	0.00
80 LEA-HP	350.88	2.05	3.85	0.26
160 USH ₂ -LP*	114.24	5.13	0.88	0.11
160 USH ₂ -IP	228.48	4.98	0.02	0.13
160 USH ₂ -HP	369.92	5.16	0.80	0.16
160 LEH ₂ -LP	134.64	21.27	10.86	11.31
160 LEH ₂ -IP	239.36	19.62	12.88	13.09

TABLE 8--(Continued)

Sample	Maximum Pressure	CO ₂	N ₂	C ₁
160 LEH ₂ -HP	345.44	20.31	11.14	12.27
160 USO ₂ -LP	82.96	4.67	1.42	0.03
160 USO ₂ -IP	233.92	4.59	1.51	0.02
160 USO ₂ -HP	361.76	4.85	1.27	0.00
160 LEO ₂ -LP	125.12	27.84	11.41	10.72
160 LEO ₂ -IP	221.69	29.93	10.20	11.69
160 LEO ₂ -HP	359.04	24.44	12.63	13.37
160 USA-LP	111.52	1.18	4.84	0.10
160 LEA-LP	121.04	16.50	7.15	7.63
240 USH ₂ -LP	127.84	35.79	1.80	2.33
240 USH ₂ -IP	225.76	15.88	2.05	1.12
240 USH ₂ -HP	361.76	23.40	3.34	1.82
240 LEH ₂ -LP	137.36	71.60	5.83	8.24
240 LEH ₂ -IP	209.44	76.72	7.06	8.70
240 LEH ₂ -HP	350.88	92.08	10.44	9.00
240 USO ₂ -LP	163.88	15.50	2.50	0.11
240 USO ₂ -IP	227.12	21.27	3.79	0.06
240 USO ₂ -HP	350.88	19.37	2.68	0.07
240 LEO ₂ -LP	137.36	49.40	4.11	3.61
240 LEO ₂ -IP	232.516	52.19	5.37	3.64
240 LEO ₂ -HP	371.28	105.96	10.72	7.08
240 USA-LP	131.91	5.29	0.67	0.16

TABLE 8--(Continued)

Sample	Maximum Pressure	CO ₂	N ₂	C ₁
240 LEA-LP	126.48	55.93	5.90	4.81
KS 160H ₂ -1	6.80	5.31	0.82	0.00
KS 160H ₂ -3	6.80	5.17	0.96	0.00
KS 160H ₂ -10	31.28	5.17	0.94	0.01
KS 160H ₂ -30	126.48	5.31	0.75	0.06
KS 160H ₂ -100	110.16	5.00	0.97	0.15
KS 160H ₂ -300	69.36	4.90	0.98	0.24
160 TUS-H ₂	77.52	4.93	1.14	0.05
160 TUS-O ₂	125.12	4.52	1.52	0.08
240 TUS-H ₂	130.56	4.34	1.60	0.18
160 DOS-H ₂	140.08	0.75	5.37	0.00
300 AM-H ₂	59.84	12.86	3.27	2.91
300 EK-H ₂	6.80	3.25	2.21	0.62
160 UT1-H ₂	108.80	4.49	1.63	0.00
160 UT2-H ₂	125.12	4.42	1.54	0.16
160 SRL-H ₂	137.36	4.81	1.31	0.00
80 NPC-H ₂	57.12	1.64	4.48	0.00
160 NPC-H ₂	80.24	2.02	3.99	0.11
240 NPC-H ₂	85.68	2.12	3.87	0.12
160 CPC-H ₂	72.08	2.22	3.85	0.05

The effect of extractable organic matter on CO₂ yield was pronounced. Samples which had the soluble lipids removed by methyl alcohol-chloroform extraction invariably yielded several times as much CO₂ as samples which were not so treated. Because the lipid-free samples yielded high CO₂ concentrations, it is assumed that this increase is due to the insoluble organic fraction or kerogen. Thus, it appears that the presence of soluble organic material inhibits the decarboxylation of the kerogen.

Figure 20 shows the structure suggested by Burlingame, et al. (1969) for kerogen. There are several sources in the proposed structure which could contribute CO₂ as a product of thermal degradation.

The kinetics study was conducted in order to evaluate the effects of longer exposure periods at constant temperature. Samples were heated for 1, 3, 10, 30, 100 and 300 hours at 160°C. All of the samples used in the kinetics study had similar CO₂ concentrations suggesting that the yield is not time dependent, at least for exposure periods up to several days.

Tuscaloosa Shale samples, as well as the mud samples from the open Gulf of Mexico, had about the same CO₂ yield as did John-The-Fool Lake samples. The Triassic Doig Shale had a partial pressure of CO₂ of less than one atmosphere and had the lowest yield of any sample subjected to 160°C.

The extracted kerogen and its whole rock equivalent provided by Amoco Production Research did not follow the pattern shown by John-The-Fool Lake sediments. For the latter, lipid free samples yielded higher CO₂ concentrations as a function of temperature (table 8). The

Possible sources of CO_2 as kerogen experiences increasing diagenesis.

Figure 20. The substituent structure suggested for kerogen
(After Burlingame, et al., 1970).

untreated mud supplied by Amoco yielded four times as much CO_2 as its equivalent kerogen.

It should be noted that the AM and EK samples were subjected to the highest temperatures of any samples in this study. The higher temperatures may have been adequate to initiate CO_2 generation from the soluble lipid material. Alternatively, the initial composition of the mud may have been significantly different from John-The-Fool Lake mud.

The pure clay samples (designated NPC and CPC) consisted of the lipids extracted from a standard quantity of control material and combined with 64 grams of clay material. These experiments were conducted to evaluate the catalytic effects of pure clay material on decarboxylation reactions of the extractable lipid material. The NPC samples showed an increase in CO_2 yield with increased temperatures, although the increase between 160°C and 240°C was small compared with the 80°C and 160°C change. The CO_2 concentration for the single CPC sample was similar to the NPC sample subjected to the same temperature.

Nitrogen

Nitrogen concentrations, like CO_2 , were affected by the presence of soluble organic matter, especially at 160°C (table 8). Nitrogen yields for all of the 80°C experiments were fairly consistent, ranging between about 4 to 6 atmospheres. The unextracted samples had slightly higher concentrations of nitrogen than did samples which had undergone lipid extraction.

At 160°C , the effects of the lipid extractions became quite pronounced. Lipid-free samples, except for the one run in air, had

nitrogen concentrations approximately two orders of magnitude greater than the unextracted samples. Analyses of nitrogenous compounds in sediments were not included in this study, and it is difficult to assess the behavior of various nitrogen components which could have influenced gaseous nitrogen yield. The data obtained for these experiments, however, suggest that 160°C is a temperature which greatly effects reactions related to nitrogen yield. At this temperature, it appears that either constituents of the soluble organic fraction do not yield significant quantities of nitrogen or any nitrogen which might result from the reactions is retained in the sample.

The samples treated at 240°C had a slight increase in nitrogen content as a result of lipid removal but not as large as the samples treated at 160°C (table 8).

The samples of the kinetics study (designated KS in table 8) were uniform in nitrogen concentration for all exposure periods.

Nitrogen concentrations also were similar for all experiments involving the Tuscaloosa Shale samples. The Doig Shale sample had a fairly high nitrogen yield and was comparable to the 80°C unextracted samples, not only in nitrogen content, but in total gas yield as well.

All open Gulf of Mexico samples had similar nitrogen yields. Likewise, "the pure clay experiments," NPC and CPC, had approximately the same nitrogen concentrations. The lipid extract in the presence of the pure clay minerals yielded nitrogen in considerably larger quantities than any of the corresponding unextracted samples treated at 160°C.

Methane

Methane is a minor gas component for all experiments at 80°C as well as for the unextracted samples at 160°C and 240°C (table 8). The distribution pattern of methane is analogous to nitrogen in that maximum yields were obtained for samples which were free of soluble organic matter. Unlike nitrogen, however, methane concentrations of the 240°C experiments are enhanced by prior lipid removal from the samples (for example, see 240 LEH₂ samples, table 8). Another pattern common to both methane and nitrogen partial pressures is the fact that both of these gases achieve maximum yields at 160°C.

The kinetics study, which was conducted on whole rock samples only, shows that the quantity of methane increased with increased exposure periods (table 8). The sample which was heated for 100 hours (KS 160H₂-100), however, had a methane concentration similar to those of the unextracted samples heated at 160°C in a hydrogen atmosphere.

The ancient shale had methane yields of less than 0.2 atmospheres at all temperatures.

The Amoco mud, although unextracted of the soluble lipid fraction, yielded nearly 3 atmospheres of methane. The increased methane of the AM sample may simply be due to the fact that the Amoco samples (300 AM-H₂ and 300 EK-H₂) were heated at 300°C whereas other samples were heated at a maximum of 240°C.

Samples furnished by the University of Texas and the Sun Research Laboratory, as well as the experiments involving lipid extracts and clays, had low or absent methane yields. The absence of methane in the pure clay-lipid extract experiment at 80°C and its appearance in 160°C and 240°C runs of the same mixture indicate that temperatures

below 160°C are not sufficient to generate appreciable quantities of methane from lipids. It must be remembered, however, that reactions such as those which generate methane above 160°C may be quite important at 80°C during geologically significant periods of time.

Extractable Lipid, Fatty Acid, and
Hexane-Soluble Fractions

Extractable Lipids

Experiments conducted at 80°C showed the greatest variation in extractable lipid content (table 9). The unextracted samples had 5 to 6 mg extractable lipid material per gram of dry sediment, whereas the equivalent samples which were lipid-free had less than 1.5 mg lipid material.

Samples subjected to 160°C had three to four times as much extractable lipid content as did the 80°C samples.

The effects of lipid extraction prior to thermal treatment on the total amount of lipids recovered at the end of a bomb run diminished for the 160°C experiments so that no consistent pattern of final lipid concentration could be related to the presence or absence of indigenous lipid material. Almost all experiments at 160°C which utilized hydrogen as an atmospheric gas had higher extractable lipid concentrations than did experiments involving oxygen. However, these increased yields of lipid material are not reflected in the hexane-soluble fractions. Appendix X shows that the 160°C unaltered samples in an oxygen atmosphere have a marked increase in the hetero-compound fraction relative to the same samples in a hydrogen atmosphere. Thus, the increased lipid concentration in the H₂ atmosphere may be due in part to an increase in the hetero-compound fraction.

TABLE 9
ABSOLUTE CONCENTRATIONS OF EXTRACTABLE LIPID,
FATTY ACID, AND HEXANE-SOLUBLE FRACTIONS
(expressed as mg/gm dry sediment)

Sample	Extractable Lipids	Fatty Acids	Hexane- Soluble
SBC	6.31	2.77	1.68
80 USH ₂ -LP	6.19	1.78	2.36
80 USH ₂ -IP	6.75	1.70	2.34
80 USH ₂ -HP	6.50	1.30	2.35
80 LEH ₂ -LP	1.06	0.21	0.64
80 LEH ₂ -IP	0.92	0.19	0.72
80 LEH ₂ -HP	0.96	0.16	0.63
80 USO ₂ -LP	6.39	1.63	2.30
80 USO ₂ -IP	6.50	1.72	2.36
80 USO ₂ -HP	5.88	1.55	2.31
80 LEO ₂ -LP	1.43	0.18	0.60
80 LEO ₂ -IP	1.21	0.20	0.63
80 LEO ₂ -HP	1.06	0.17	0.61
80 USA-LP	9.02	1.51	2.83
80 LEA-HP	0.93	0.19	0.74
160 USH ₂ -LP	21.99	5.40	4.91
160 USH ₂ -IP	25.38	5.12	4.91
160 USH ₂ -HP	22.49	5.63	5.27
160 LEH ₂ -LP	19.13	1.36	6.75
160 LEH ₂ -IP	22.24	1.41	7.29
160 LEH ₂ -HP	23.99	1.46	6.88

TABLE 9--Continued

Sample	Extractable Lipids	Fatty Acids	Hexane- Soluble
160 USO ₂ -LP	18.32	4.46	5.99
160 USO ₂ -IP	14.43	4.52	4.57
160 USO ₂ -HP	15.68	4.25	5.09
160 LEO ₂ -LP	20.75	1.36	6.82
160 LEO ₂ -IP	19.44	1.42	7.34
160 LEO ₂ -HP	19.88	1.46	6.39
160 USA-LP	21.03	3.35	6.45
160 LEA-LP	21.19	0.16	6.89
240 USH ₂ -LP	33.97	4.88	8.97
240 USH ₂ -IP	30.36	4.40	8.14
240 USH ₂ -HP	28.25	4.57	7.81
240 LEH ₂ -LP	24.58	1.74	9.00
240 LEH ₂ -IP	23.92	1.07	7.64
240 LEH ₂ -HP	26.88	1.50	8.12
240 USO ₂ -LP	31.70	4.21	8.96
240 USO ₂ -IP	36.12	3.86	8.50
240 USO ₂ -HP	30.70	3.70	8.38
240 LEO ₂ -LP	24.17	1.48	8.15
240 LEO ₂ -IP	22.68	1.42	7.99
240 LEO ₂ -HP	21.03	1.38	7.63
240 USA-LP	30.86	4.46	8.73
240 LEA-LP	23.08	1.42	8.71
KS 160H ₂ -1	7.19	2.71	1.55

TABLE 9--Continued

Sample	Extractable Lipids	Fatty Acids	Hexane- Soluble
KS 160H ₂ -3	10.05	2.61	1.74
KS 160H ₂ -10	9.21	2.83	2.56
KS 160H ₂ -30	18.26	2.98	3.79
KS 160H ₂ -100	21.84	2.71	4.56
KS 160H ₂ -300	21.53	4.17	4.78
TUS-US	1.68	0.64	0.79
160 TUS-H ₂	3.08	1.72	0.90
240 TUS-H ₂	2.92	0.80	0.72
160 TUS-O ₂	2.46	2.35	0.59
DOS-US	1.93	0.77	1.81
160 DOS-H ₂	2.08	0.18	0.19
300 AM-H ₂	8.09	0.71	2.02
300 EK-H ₂	3.89	0.40	0.89
UT1-US	0.25	0.38	0.82
160 UT1-H ₂	0.72	0.45	0.30
UT2-US	9.61	1.95	0.30
160 UT2-H ₂	5.48	0.74	0.39
SRL-US	0.12	0.09	0.37
160 SRL-H ₂	3.92	0.41	1.98
80 NPC-H ₂	2.77	2.09	1.43
160 HPC-H ₂	1.93	1.70	2.08
240 NPC-H ₂	2.30	1.54	2.25
160 CPC-H ₂	2.80	1.41	1.52

Samples heated at 240°C show a slight increase in extractable lipid material relative to the 160°C experiments. At 240°C, the unextracted samples have a greater lipid concentration than do the extracted samples. The magnitude of these differences are comparable to the differences shown by the 80°C samples and probably reflect the initial differences in lipid concentration.

The kinetics study shows that extractable lipid content generally increases with increasing exposure periods up to 100 hours (table 9 and Appendix XI). There is no appreciable difference in the extractable lipid content between the sample subjected to 100 hours and the sample subjected to 300 hours.

The ancient shales contained considerably less extractable lipid material than the modern muds. The Tuscaloosa Shale (160 TUS) heated to 160°C yielded about twice as much lipid material as its unheated equivalent (US TUS). The Doig Shale showed little change in extractable lipid content after treatment at 160°C (160 DOS).

The lipid material which has not yet been incorporated into kerogen influences the amount of extractable lipids as shown by the AM and EK samples. After subjecting both the unextracted mud and the isolated kerogen to 300°C, the mud yielded over twice as much lipid material as did the kerogen alone. The increased lipid yield in the mud must be due to the lipid fraction which has not yet been converted to kerogen.

The samples furnished by the University of Texas showed interesting relations between the amount of extractable lipids and temperature. UT1, which contains organic matter derived predominately

from marine sources, showed an increase in extractable lipids when heated at 160°C. UT2, in which the organic material is mostly of terrestrial origin, showed the inverse relation and nearly one-half of the lipid material extractable at room temperature was destroyed by heating the sample to 160°C.

The sample supplied by the Sun Research Laboratory was similar to one of the University of Texas samples (UT1) in that extractable lipid content for both samples increased (relative to unheated samples) after heating at 160°C. The magnitude of the lipid increase for the Sun sample heated at 160°C was thirty-fold, relative to the unheated sample.

Experiments involving pure clay material and lipid extracts showed little change in the amount of extractable lipid material.

Fatty Acids

The most striking observation regarding the fatty acid concentrations is the fact that samples subjected to temperatures of 160°C and higher, yielded considerably larger quantities of fatty acids than did the original muds without heat treatment. It is possible that the fatty acids are bound either to the mineral matrix or the kerogen and require thermal treatment to be liberated as free fatty acids. The role of soluble organic fraction is also important. Samples which did not undergo prior lipid extraction yielded about three to five times as much more fatty acids than did their extracted equivalents.

The fatty acid content of the kinetics study samples was fairly constant for the exposure periods of 1 to 100 hours. Between

100 and 300 hours, however, the fatty acid concentration increased from 2.7 to over 4 mg/gm dry sediment weight.

The Tuscaloosa Shales had a maximum fatty acid concentration at 160°C, further increase in temperature obviously reduced the yield of fatty acid material (table 9). The Doig Shale showed a lower fatty acid content after being heated at 160°C than in its unheated state, possibly reflecting a paleotemperature condition unlike that of the present.

One of the University of Texas samples (UT1) and the Sun Research samples have the same general pattern: increased fatty acid yield with exposure to 160°C, while the other University of Texas sample (UT2) showed the opposite effect and its fatty acid concentration was reduced by thermal treatment. The reason for the fatty acid depletion in the UT2 sample is not apparent. This behavior may be related to the type of organic matter present in each of the UT samples (i.e., marine organic matter in UT1 and terrestrial organic matter in UT2).

Hexane-Soluble Fraction

The concentration of the hexane-soluble portion of the organic matter, with the exception of the 80°C experiments, increases with temperature in both extracted and non-extracted samples (table 9).

At 80°C, the unextracted specimen yielded about three or four times as much hexane-soluble material as did the unextracted samples.

At 160°C, the samples subjected to lipid extraction before heating yielded 1-2 mg/g more hexane-soluble material than did unextracted samples. All samples heated at 240°C yielded similar

quantities of hexane-soluble material (table 9). The variation in quantities of hexane-soluble fractions appears to be related to the presence/absence of soluble lipid components but the relation is not obvious.

The kinetics study samples all show an increase in the quantity of hexane-soluble material as exposure time increases.

Ancient shales did not show a pattern which related yield of hexane-soluble fraction to changes in temperature. Tuscaloosa samples heated to 160°C had a slight increase in hexane-soluble material compared with the unheated sample. Other Tuscaloosa samples showed a decrease with respect to the unheated sample. The 160°C treatment of the Doig Shale virtually destroyed the hexane-soluble material which was present in the unheated sample.

The Amoco mud showed that the abundant material derived from exposing the sample to 300°C was approximately 25 percent hexane-soluble. The demineralized kerogen yielded less than 50 percent of the hexane-soluble material which the original mud (sample AM) contained.

The University of Texas samples, both from the open Gulf of Mexico, showed little variation in hexane-soluble material as a result of thermal treatment. The Sun Research samples, however, displayed a four-fold increase in the quantity of hexane-soluble material as a result of heating the sample to 160°C. This may reflect greater contribution of terrestrial lipids via Mississippi River discharge.

Pure clay and lipid extract combinations all show an increase in the quantity of the hexane-soluble fraction with increases in temperature.

Paraffinic, Aromatic, and Hetero-Compound Components.--Because the paraffins, aromatics, and hetero-compounds are normalized to 100 percent of the hexane-soluble fraction, an increase in the concentration of one component must be accompanied by a decrease in one of the other two components. For this reason, the discussion of these three components will be conducted in a single section. Discussion of paraffins, aromatics, and hetero-compounds is facilitated by reference to the ternary diagrams of figures 20-26. Concentrations of paraffinic, aromatic, and hetero-compounds are individually listed in Appendix X.

Hetero-compounds are oxygen-, nitrogen-, and sulfur-containing components. They are common in immature crude oils but as oils mature and as the process of petroleum generation enters its final phases, the generated products contain progressively less hetero-compound components (Andreev et al., 1968; Welte, 1965; Dott and Reynolds, 1969). Welte's sequence of processes of oil genesis proposes that the loss of hetero-compounds occurs between "moderately deeply buried sediments" and "deeply buried sediments" (figure 5).

Unaltered John-The-Fool Lake sediments (SBC) are extremely rich in hetero-compounds (Appendices I and II), accounting for approximately 2/3 of the hexane-soluble fraction. The effects of lipid extraction are quite pronounced as there is almost an exact reversal of the relative concentrations of the paraffinic and hetero-compound components. Data in Appendix X for the unextracted and lipid extracted 80°C samples illustrate the above relation. Concentrations of aromatic components vary from 15-16 percent to 25 percent for all 80°C experiments. At higher temperatures the aromatic concentrations vary considerably and the variations are greater at 160°C than at 240°C.

Two distinct patterns of the PAH (paraffin-aromatic-hetero-compound) concentrations are present and are dependent on the presence of the soluble lipid fraction.

Samples containing soluble lipids always had the highest paraffin fraction at 240°C. The paraffin concentrations at 80°C and 160°C are not so clearly defined but there is a tendency for the PAH data to be grouped near the hetero-compound corner of the diagram at both temperatures (figures 21 A-B, 22 A, 23 A-B). Although the unextracted samples heated to 160°C were fairly high in hetero-compound components for all of the 50-hour standard runs, the results of the kinetics study indicate that the PAH distribution may be partially time-dependent. Figure 24 shows that the 100 and 300 hours exposure times are sufficient to change the percentage of hetero-compounds from 65-73 percent to 44-51 percent. The effect of temperature is important in PAH distribution; however, the data from the kinetics study show that time of exposure at a given temperature may also be important.

The PAH values from lipid free (LE) samples reflects the composition of products which are derived from the kerogen fraction. The PAH pattern shown by lipid free samples consists of a large increase in the paraffinic fraction obtained at all temperatures. None of the samples contained less than 50 percent paraffinic material. Spartina alterniflora, the major producer in the study area, yields significant quantities of both paraffin hydrocarbons and aliphatic fatty acids. These compounds are relatively stable and probably become concentrated with respect to organic components which are more prone to degradation. The paraffins and fatty acids may have been

Figure 21. Ternary diagrams showing variation (in weight percent) in paraffinic, aromatic, and hetero-compound components as a function of temperature. A, unextracted sediment in a hydrogen atmosphere at a bomb pressure of 1500-2000 psi. B, unextracted sediment in a hydrogen atmosphere at a bomb pressure of 3000-3500 psi.

Figure 22. Ternary diagrams showing the variation (in weight percent) in paraffinic, aromatic, and hetero-compound components as a function of temperature. A, unextracted sediment in a hydrogen atmosphere at a bomb pressure of 5000-5500 psi. B, lipid-free sediment in a hydrogen atmosphere at a bomb pressure of 1500-2000 psi.

Figure 23. Ternary diagrams showing variation (in weight percent) in paraffinic, aromatic, and hetero-compound components as a function of temperature. A, unextracted sediment in an oxygen atmosphere at a bomb pressure of 1500-2000 psi. B, unextracted sediment in an oxygen atmosphere at a bomb pressure of 3000-3500 psi.

Figure 24. Ternary diagram showing variation (in weight percent) in paraffinic, aromatic, and hetero-compound components as a function of time. The sample is unextracted control material in a hydrogen atmosphere; temperature is 160° C.

incorporated into the kerogen fraction (figure 20) and are liberated by thermal treatment. Thus, for the sediments of this study, the high paraffin content shown by PAH data is probably a function of the original organic productivity of the area.

With the exception of the lipid extracted samples treated at 5000-5500 psi in an oxygen atmosphere, specimens heated at 160°C yielded products which were more paraffinic than those heated at 80°C and 240°C. This pattern also was shown by unextracted Tuscaloosa Shales, and, to a lesser extent, the unextracted Doig Shales.

A comparison of PAH values for the Amoco mud and its "extracted kerogen" counterpart reveals that the "kerogen" was richer in paraffinic compounds than the whole-rock sample, when both samples were subjected to 300°C treatment (figure 26 A).

The sodium-saturated "pure clay" plus lipid extract experiment (160 NPC) also had a higher paraffin yield than did its 80°C or 240°C counterpart (Appendix X).

Distribution of Fatty Acid and Paraffinic Components

In addition to the general groups of organic compounds presented in the previous section, distribution of specific fatty acids and paraffinic components were analyzed separately at the end of each experiment.

Figure 27 shows changes in the fatty acid distribution and concentration obtained by treating the control material at 80°C, 160°C, and 240°C temperatures in an atmosphere of hydrogen. The strong even-number predominance reflects the original biochemistry of the organisms which contribute organic matter to the sediments. At

Figure 25. Ternary diagrams showing variation (in weight percent) in paraffinic, aromatic, and hetero-compound components as a function of temperature. A, changes in Tuscaloosa Shale extract in hydrogen and oxygen atmospheres. B, changes in Doig Shale extracts in a hydrogen atmosphere.

Figure 26. Ternary diagrams showing variation (in weight percent) in aromatic, paraffinic, and hetero-compound components as a function of temperature.

Figure 27. Distribution and concentration of fatty acids from unextracted sediments in a hydrogen atmosphere. Numbers at upper right of histograms refer to total fatty acid concentrations relative to the control (standard bomb charge).

80°C, the even-number predominance is eliminated for fatty acids in the C_{20} - C_{25} range but persists for C_{16} , C_{18} , C_{26} , and C_{28} . Total fatty acid yield is only 70 percent of the control sample and suggests that fatty acids are being destroyed, possibly by decarboxylation even under relatively mild thermal conditions. Alternatively, the loss of free fatty acids may be due to polymerization of fatty acids to a complexed form such as kerogen. At 160°C, C_{23} becomes most abundant but the C_{16} , C_{18} , C_{26} , and C_{28} fatty acids are in concentrations great enough to give an overall pattern of even-number dominance. The most significant feature of the 160°C thermal treatment is that the total yield of fatty acids is nearly twice the concentration of the control. The same general pattern also exists at 240°C with the exception that the C_{23} fatty acid is no longer the most abundant component. The total yield at 240°C is slightly lower than for treatment at 160°C. The sharp increase in fatty acids yield above 80°C must result from thermally-controlled cleavage of fatty acids from the complexed (kerogen) fraction. Of the temperatures employed in this study, 160°C appears to provide an optimum condition for fatty acid cleavage; degradation may take place at 240°C.

Figure 28 shows the distribution and yield of n-paraffins for unextracted experiments in hydrogen atmospheres. The odd-carbon predominance of the control is typical of modern sediments. At 80°C, C_{27} , C_{29} , and C_{31} n-paraffins were predominant, but the predominance was not apparent for other carbon members. The total n-paraffin yield at 80°C is nearly one and one half times that of the control.

The sample subjected to 160°C treatment showed only two predominant odd-number components (C_{19} , C_{21}). The total yield is

Figure 28. Distribution and concentration of n-paraffins from unextracted sediments in a hydrogen atmosphere. Numbers at upper right of histograms refer to total n-paraffin yield relative to the control (standard bomb charge).

twice that obtained at 80°C further demonstrating how readily some of the organic fractions may contribute to this particular group of hydrocarbons under thermal treatment.

The experiment at 240°C resulted in an n-paraffin distribution which had no odd carbon number predominance and which is similar to the distribution of n-paraffins of crude oil (see figure 11). Also, the n-paraffin distribution is comparable to that obtained by Cummins, et al., (1974) for 200-250°C thermal treatment of Green River kerogen. The total n-paraffin yield at 240°C was nearly double that obtained at 160°C, and gave a four-fold increase as compared to the control. Thus the total n-paraffin yield is a function of temperature at least in the temperature range used in this study.

Lipid free samples in hydrogen atmospheres showed no significant change in fatty acid distributions throughout the entire temperature range tested (figure 29). This suggests that prior lipid removal from a sample is an important factor in subsequent total fatty acid yield. Concentrations of fatty acids greater than those for the control are not obtained for any of the lipid free specimens in a hydrogen atmosphere. At 80°C, the total yield is only 8 percent of the control and only 50 and 60 percent of the control at 160°C and 240°C, respectively. In spite of the reduction in fatty acid yield due to removal of the lipid fraction prior to thermal treatments, the ratios of fatty acid components remain unchanged as compared to that in the control. Therefore the fatty acids from the lipid-free sediments must be derived from the kerogen inasmuch as the soluble fatty acids were extracted prior to thermal treatment. The total fatty acid yield for the natural samples treated at 240°C and in a

Figure 29. Distribution and concentration of fatty acids from lipid-free sediments in a hydrogen atmosphere. Numbers at upper right of histograms refer to total fatty acid yield relative to the control (standard bomb charge).

hydrogen atmosphere is lower than that of the same samples heated to 160°C.

Figure 30 shows the concentrations of n-paraffins from heated lipid free sediments relative to the control. The odd-number predominance of the n-paraffins shown in the control is not present in the lipid free sample treated under hydrogen and 80°C temperature. The total n-paraffin yield at 240°C is the same for both extracted and unextracted samples in hydrogen atmospheres. However, at 160°C, the lipid extracted samples in an H atmosphere had about 400 percent of the n-paraffin yield from the control. The unextracted hydrogen-charged 160°C sample had 290 percent of the n-paraffin yield from standard material. In contrast to the 80°C hydrogen-charged unextracted sample, the extracted counterpart had a very low n-paraffin yield compared with that of the standard. The distribution pattern of all hydrogen-charged extracted samples is characterized by relatively high concentrations of $C_{25}-C_{30}$ n-paraffins. This is not the pattern observed in thermally mature shale extracts or in crude oil. The distribution pattern of the n-paraffins from hydrogen-charged extracted experiments suggests that the data of this laboratory work is in agreement with Welte's generalized reaction scheme (figure 5). Welte suggests that moderately deeply buried sediments would yield heavy oils rich in hetero-compounds. Lipid free samples treated under hydrogen all yielded heavy paraffin products but the hetero-compounds were low (Appendix X). In this study, the hetero-compounds were removed by the extractions and thus the heavy oils were developed without an accompanying increase in nitrogen-, oxygen-, and sulfur-containing compounds.

Figure 30. Distribution and concentration of n-paraffins from lipid-free sediments in a hydrogen atmosphere. Numbers at upper right of histograms refer to total n-paraffin yield relative to the control (standard bomb charge).

The control material served as reference concentrations for fatty acids and n-paraffins. Both fatty acids and n-paraffins were extracted from the sediment slurry at the conclusion of each experiment and concentrations were compared to control concentrations. In this manner, the changes due to treatment could be assessed. Absolute concentrations for each sample are presented in tables 10 and 11, respectively.

The relative concentration of each species of fatty acid and n-paraffin was divided by the relative concentration of the same species in control material. The quotient was plotted on a vertical logarithmic scale as "Normalized Weight Percent." The carbon number of each species of fatty acid and n-paraffin was used as the horizontal scale and the resultant semi-log histograms (figures 31-35) show enrichments and/or depletions for each species relative to control concentrations.

One of the objectives of this study was to examine the quantitative changes that occur in specific hydrocarbons as hydrocarbon mixtures are generated under varying conditions. Thus, component A with a relative concentration of 10 percent in a sample can be compared with component A in control material. If A is only 5 percent in the control mixture, then the one-fold increase is shown as an enrichment and the conditions responsible for the enrichment are due to treatment effects.

The analyses of variance conducted for this study indicated that pressure and atmospheric gas filling did not have a statistically significant effect ($p > 0.05$) on the yields of n-paraffins and aliphatic fatty acids. Thus, the specific examples discussed in this

TABLE 10

**ABSOLUTE CONCENTRATIONS OF FATTY ACIDS EXTRACTED FROM THE SEDIMENTS
AND FLUID AT THE CONCLUSION OF EACH EXPERIMENT
(in mg/442 ml slurry)**

Sample	Fatty							Acid		Carbon		Number							29	30
	12	14	14	A15	15	I16	16	18	19	20	21	22	23	24	25	26	27	28		
SBC	2.51	4.66	9.48	7.68	6.40	6.31	33.89	7.36	1.62	7.13	5.53	8.40	4.06	13.68	4.41	20.88	8.45	21.42	1.24	3.98
80 USH ₂ -LP	2.11	1.54	4.91	6.10	4.28	1.39	14.31	8.22	1.86	4.51	6.15	7.21	9.08	9.79	2.72	7.42	4.37	13.34	2.09	2.39
80 USH ₂ -IP	1.67	1.04	4.34	5.39	2.60	1.71	14.58	8.79	2.21	4.56	6.75	6.45	7.32	10.65	1.84	7.63	2.28	13.73	1.39	4.70
80 USH ₂ -HP	1.45	0.97	3.56	4.41	2.33	1.16	8.62	6.50	1.62	3.55	4.81	5.15	6.45	7.88	1.82	5.92	2.34	10.55	1.23	3.31
80 LEH ₂ -LP	0.09	0.19	0.84	0.25	0.28	0.23	2.78	1.41	0.22	1.01	0.28	1.04	0.31	0.95	0.25	0.79	0.33	1.68	0.35	0.26
80 LEH ₂ -IP	0.11	0.18	0.74	0.16	0.23	0.16	2.70	1.36	0.13	0.96	0.28	0.97	0.43	0.83	0.17	0.74	0.21	1.11	0.19	0.14
80 LEH ₂ -HP	0.09	0.18	0.81	0.22	0.18	0.16	2.25	1.29	0.15	0.84	0.26	0.98	0.30	0.78	0.22	0.53	0.13	1.23	0.08	0.11
80 USC ₂ -LP	2.16	1.69	5.50	6.05	2.54	0.99	14.56	6.85	1.33	4.86	4.64	7.14	7.31	7.72	3.22	7.62	1.39	13.46	2.82	3.05
80 USC ₂ -IP	2.07	1.90	5.36	6.46	3.44	1.49	16.38	8.22	2.50	5.87	5.46	7.72	8.01	8.69	2.62	8.56	1.47	12.04	0.73	1.33
80 USC ₂ -HP	1.92	1.86	5.76	5.97	2.83	1.17	14.21	7.25	1.69	4.83	4.63	7.02	7.15	7.57	2.63	8.36	1.21	11.25	1.24	1.35
80 LEO ₂ -LP	0.10	0.15	0.67	0.20	0.22	0.23	2.16	1.07	0.21	0.76	0.21	0.83	0.23	0.84	0.11	0.72	0.20	1.47	0.50	0.51
80 LEO ₂ -IP	0.12	0.16	0.70	0.20	0.23	0.29	2.35	1.16	0.25	0.83	0.21	0.89	0.30	1.00	0.11	0.83	0.47	1.69	0.35	0.67
80 LEO ₂ -HP	0.09	0.14	0.58	0.18	0.19	0.25	2.00	0.99	0.26	0.68	0.15	0.71	0.28	0.88	0.14	0.72	0.29	1.55	0.22	0.69
80 USA-LP	1.88	1.52	4.78	5.84	3.18	1.41	13.36	6.73	1.50	4.32	4.95	6.93	7.25	8.12	2.90	6.69	1.69	11.80	0.82	1.56
80 LEA-HP	0.11	0.21	0.72	0.16	0.24	0.25	2.40	1.39	0.17	1.01	0.14	0.89	0.33	0.71	0.11	0.78	0.33	1.72	0.32	0.37
160 USH ₂ -LP	8.53	5.48	12.56	14.43	8.08	3.26	34.55	22.13	9.19	12.56	15.51	22.96	59.18	24.28	11.62	32.30	11.17	29.17	5.69	4.23
160 USH ₂ -IP	7.11	5.69	12.97	15.70	7.11	3.65	34.30	22.62	8.06	12.81	12.24	23.64	55.07	24.76	10.47	33.35	2.83	28.94	4.35	3.52
160 USH ₂ -HP	8.22	5.94	13.47	16.62	7.39	4.31	40.08	23.35	9.70	14.16	14.12	26.29	61.05	26.91	11.70	36.06	2.32	32.37	3.40	4.63
160 LEH ₂ -LP	1.33	1.43	6.06	2.09	3.29	2.53	15.82	9.67	0.85	6.99	0.93	9.10	1.53	6.52	2.30	4.51	2.07	8.63	1.11	0.95
160 LEH ₂ -IP	1.49	1.63	6.53	1.93	2.96	2.35	17.84	11.29	1.01	7.85	0.80	8.66	1.26	8.01	0.31	3.70	0.66	10.61	1.14	0.85
160 LEH ₂ -HP	1.53	1.77	6.88	2.53	3.24	2.60	16.84	11.25	0.99	7.64	0.91	9.24	1.38	7.68	1.61	4.56	0.98	9.96	1.15	1.15
160 USC ₂ -LP	4.93	2.12	18.66	29.67	10.87	2.12	29.41	17.09	5.07	7.74	9.55	20.44	27.84	18.00	28.78	7.48	5.91	27.90	6.85	6.25
160 USC ₂ -IP	5.61	2.62	17.12	28.34	11.86	2.94	31.22	14.27	6.45	9.01	7.96	20.03	29.10	16.51	33.05	5.61	5.41	23.95	9.91	9.71
160 USC ₂ -HP	5.08	3.03	17.23	27.47	10.81	2.43	30.89	14.34	5.24	7.76	8.54	18.95	28.18	16.08	31.02	6.34	3.17	25.32	6.42	4.78
160 LEO ₂ -LP	1.19	1.35	6.01	1.51	3.18	2.50	15.47	10.15	0.79	6.76	0.90	9.10	0.82	8.14	1.86	3.29	1.23	9.13	1.47	2.44
160 LEO ₂ -IP	1.35	1.34	6.03	1.47	3.61	2.67	15.08	9.55	1.30	7.03	1.31	8.99	0.97	8.02	2.95	3.49	2.31	8.59	3.36	2.18

TABLE 10- - (Continued)

	Fatty Acid Carbon Number																			
Sample	12	14	14	15	15	16	16	18	19	20	21	22	23	24	25	26	27	28	29	30
160 LEO ₂ -HP	1.32	1.39	6.59	1.33	2.68	1.94	15.86	10.65	1.61	6.41	1.18	9.15	1.32	8.35	2.59	4.11	1.63	8.10	5.46	2.18
160 USA-LP	4.46	2.72	9.46	18.39	7.18	2.61	21.17	12.20	5.52	6.70	8.71	14.94	17.64	14.14	20.93	10.09	12.14	19.23	9.21	12.29
160 LEA-LP	0.16	0.18	0.75	0.20	0.37	0.28	2.15	1.14	0.12	0.74	0.09	1.05	0.14	0.92	0.26	0.50	0.20	0.98	0.16	0.21
240 USH ₂ -LP	7.59	6.02	14.52	6.08	17.52	10.13	60.50	28.65	10.13	24.04	11.13	17.21	13.17	11.94	6.77	23.10	6.46	27.30	3.54	7.68
240 USH ₂ -IP	6.73	6.13	13.65	5.28	16.84	10.77	52.79	27.61	7.46	23.48	9.49	15.57	10.57	8.36	8.28	20.26	4.13	23.88	4.89	6.70
240 USH ₂ -HP	5.49	6.93	15.74	5.99	18.65	12.45	53.10	30.63	6.64	24.82	9.13	16.36	7.75	7.14	10.90	21.23	5.93	22.58	7.66	4.55
240 LEH ₂ -LP	1.38	1.71	7.49	2.19	3.12	2.26	22.21	12.95	1.07	8.78	1.51	10.97	0.93	8.29	0.85	4.85	2.42	16.56	0.96	1.18
240 LEH ₂ -IP	1.09	1.01	4.25	1.38	1.64	1.33	13.44	7.49	0.83	5.47	0.87	7.02	0.64	5.07	1.01	4.05	1.16	10.01	0.81	1.31
240 LEH ₂ -HP	1.64	1.37	5.46	2.05	1.88	1.77	18.07	9.83	1.31	7.86	0.94	9.94	1.12	6.55	2.22	4.08	2.76	13.31	2.08	1.99
240 USO ₂ -LP	7.96	3.90	16.20	7.48	11.95	5.07	34.21	15.96	11.70	12.75	16.44	19.10	22.92	19.94	22.40	13.17	13.71	11.70	14.74	9.51
240 USO ₂ -IP	5.75	2.87	15.54	8.06	11.18	4.11	31.78	15.72	9.57	10.78	9.47	20.23	21.79	15.99	22.14	10.86	5.35	11.70	4.24	10.76
240 USO ₂ -HP	6.49	3.14	14.67	7.32	10.39	4.59	31.21	14.78	9.94	11.05	13.81	18.56	20.49	16.53	20.85	11.08	8.72	4.83	4.09	5.13
240 LEO ₂ -LP	1.10	1.27	6.59	1.65	2.17	1.97	19.35	10.23	0.94	7.69	0.78	7.87	0.82	6.33	1.12	3.87	2.21	12.65	2.97	1.89
240 LEO ₂ -IP	1.17	1.19	6.29	1.34	2.22	1.77	18.03	8.97	0.86	7.21	0.60	7.99	0.83	5.47	0.77	4.59	1.89	11.20	1.94	7.16
240 LEO ₂ -HP	1.16	1.31	6.00	0.92	1.99	1.56	17.59	9.29	0.73	7.25	0.82	7.08	1.08	5.74	0.82	4.23	1.70	11.66	2.98	4.84
240 USA-LP	7.66	4.96	14.11	6.97	13.82	6.19	30.51	18.21	10.73	12.13	16.89	19.42	21.16	19.96	18.27	16.72	11.87	18.21	10.55	8.43
240 LEA-LP	1.21	1.29	6.23	1.84	2.41	2.15	15.53	10.20	0.78	7.52	1.11	8.54	0.93	6.35	0.84	3.86	2.07	12.76	2.52	3.14
KS 16OH ₂ -1	4.72	2.84	9.09	12.16	6.22	3.41	36.15	23.94	4.58	11.93	3.59	9.56	6.69	7.37	5.77	6.04	3.85	10.21	1.86	4.21
KS 16OH ₂ -3	4.26	2.64	8.36	11.45	6.06	2.89	43.12	19.97	4.62	10.46	3.91	9.00	6.56	6.36	6.31	5.46	3.12	7.76	2.20	3.39
KS 16OH ₂ -10	5.32	3.51	9.76	12.95	5.85	4.41	41.61	23.11	5.55	12.40	4.99	8.96	6.86	7.57	7.48	5.41	2.80	8.85	1.60	3.15
KS 16OH ₂ -30	5.42	3.43	10.46	14.06	6.36	3.87	47.53	23.36	6.88	10.31	4.52	9.33	6.88	7.51	7.38	4.66	2.64	10.75	1.84	4.37
KS 16OH ₂ -100	3.93	2.70	8.47	11.76	6.59	3.79	35.84	26.80	3.53	14.27	3.25	11.33	7.86	7.59	3.81	6.45	4.18	11.19	3.15	3.88
KS 16OH ₂ -300	8.37	4.42	11.11	16.00	9.34	5.07	44.37	43.13	4.78	20.64	3.11	17.12	10.36	10.49	6.38	11.67	5.74	19.81	6.07	10.41
TUS-US	0.69	0.00	1.66	0.38	0.61	0.00	5.41	8.77	0.00	1.27	0.00	2.42	9.50	0.74	9.44	0.00	0.00	0.00	0.00	0.00
160 TUS-H ₂	0.94	0.00	7.86	2.13	6.23	0.00	21.65	26.70	0.00	8.19	0.00	10.32	11.79	2.22	12.85	0.00	0.00	0.00	0.00	0.00
160 TUS-O ₂	3.68	0.00	10.47	3.06	6.70	0.00	32.70	33.45	0.00	13.38	0.00	16.70	12.30	4.32	14.12	0.00	0.00	0.00	0.00	0.00

TABLE 10 - - (Continued)

	Fatty				Acid				Carbon				Number						
Sample	12	14	15	16	18	19	20	21	22	23	24	25	26	27	28	29	30		
240 TUS-H ₂	0.00	0.00	2.98	1.32	1.71	0.00	10.99	6.16	0.00	3.94	0.00	4.82	6.43	3.92	9.44	0.00	0.00	0.00	0.00
DOS-US	5.29	0.00	8.90	0.00	6.40	0.00	6.21	9.99	0.00	5.25	0.00	7.35	0.00	0.00	0.00	0.00	0.00	0.00	0.00
160 DOS-H ₂	0.05	0.00	0.76	0.00	0.55	0.00	2.99	3.52	0.00	0.78	0.00	0.74	0.87	0.53	0.40	0.22	0.00	0.00	0.00
300 EK-H ₂	0.29	0.17	0.76	0.31	0.82	0.39	2.27	1.92	0.93	2.49	1.18	3.49	3.99	2.35	1.19	1.63	0.31	1.05	0.00
300 AM-H ₂	0.20	0.43	1.67	1.99	1.35	0.77	7.41	6.51	2.29	4.51	1.99	4.03	4.33	2.53	1.39	0.97	0.38	1.97	0.33
UT1-US	0.29	0.28	1.56	1.67	0.99	0.37	1.04	4.31	1.23	3.98	0.77	1.27	1.83	1.99	1.46	0.53	0.00	0.61	0.00
160 UT1-H ₂	0.35	0.34	2.20	0.94	0.99	0.76	5.44	4.10	0.75	2.04	0.74	2.22	1.85	2.77	0.89	2.08	0.32	0.00	0.00
UT2-US	0.58	1.45	2.17	3.56	2.90	1.39	23.37	24.10	3.27	9.32	1.47	14.24	5.33	8.49	2.96	12.74	4.30	3.18	0.00
160 UT2-H ₂	0.37	0.39	2.92	1.47	1.48	0.67	10.63	10.38	1.03	3.63	0.63	4.40	3.50	1.87	1.56	2.07	0.59	0.00	0.00
SRL-US	0.02	0.02	0.21	0.09	0.16	0.08	0.28	0.45	0.15	0.65	0.62	0.71	0.36	0.74	0.34	0.53	0.09	0.20	0.00
160 SRL-H ₂	0.09	0.09	0.16	0.17	0.19	0.13	0.77	0.78	1.22	1.63	2.87	12.96	0.44	4.70	0.00	0.00	0.00	0.00	0.00
80 NPC-H ₂	1.21	1.18	2.40	3.54	1.38	1.31	12.42	11.81	2.56	8.89	1.21	13.96	21.56	10.82	9.53	11.02	5.42	11.25	4.80
160 NPC-H ₂	0.89	0.67	1.62	2.29	1.66	0.90	9.00	8.10	2.20	6.37	1.75	12.85	20.67	10.06	7.47	7.72	2.97	5.14	3.99
160 CPC-H ₂	0.17	1.22	1.25	1.73	1.12	0.74	8.55	7.54	3.29	4.94	2.41	9.37	15.30	8.27	5.87	7.84	2.99	3.75	3.03
240 NPC-H ₂	0.91	0.70	2.73	2.78	2.04	1.41	9.66	8.15	4.26	6.75	2.41	13.31	14.75	11.49	7.61	3.99	4.86	3.72	3.48

TABLE 11

**ABSOLUTE CONCENTRATIONS OF n-PARAFFINS EXTRACTED FROM THE SEDIMENTS
AND FLUID AT THE CONCLUSION OF EACH EXPERIMENT
(in mg/442 ml slurry)**

Sample	n-Paraffin									Carbon		Number							
	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	
SBC	0.07	0.05	0.18	0.08	0.26	0.10	0.32	0.18	0.49	0.32	0.41	0.41	0.81	8.43	1.44	0.16	1.31	0.20	
80 USH ₂ -LP	0.04	0.04	0.06	0.03	0.19	0.07	0.15	0.22	0.19	0.24	0.30	0.26	0.54	0.41	0.90	0.08	0.87	0.17	
80 USH ₂ -IP	0.07	0.06	0.10	0.07	0.33	0.06	0.18	0.33	0.23	0.33	0.43	0.41	0.74	0.39	1.24	0.07	1.00	0.15	
80 USH ₂ -HP	0.10	0.11	0.13	0.08	0.45	0.12	0.31	0.48	0.37	0.42	0.76	0.59	1.19	0.74	1.88	0.17	1.64	0.14	
80 LEH ₂ -LP	0.10	0.20	0.40	0.67	0.46	0.86	0.56	2.50	0.98	1.56	0.96	3.32	2.28	2.62	3.13	0.63	0.85	0.94	
80 LEH ₂ -IP	0.16	0.28	0.33	0.73	0.40	1.01	0.76	2.59	1.28	1.42	0.92	3.67	2.09	2.91	3.14	0.59	0.34	1.47	
80 LEH ₂ -HP	0.23	0.22	0.55	0.68	0.46	0.97	0.71	1.96	1.17	1.53	1.00	3.92	1.54	2.93	2.72	0.85	0.51	1.05	
80 USO ₂ -LP	0.16	0.04	0.42	0.24	0.76	0.49	0.97	1.28	1.36	1.17	1.00	1.87	2.19	1.63	3.40	0.27	3.16	0.48	
80 USO ₂ -IP	0.19	0.10	0.39	0.26	0.79	0.40	0.94	1.21	1.24	1.23	1.15	1.94	2.20	1.54	3.57	0.27	3.49	0.27	
80 USO ₂ -HP	0.17	0.07	0.38	0.27	0.65	0.48	1.03	1.29	1.27	1.15	1.07	1.90	2.21	1.51	3.47	0.26	2.61	0.21	
80 LEO ₂ -LP	0.12	0.17	0.35	0.65	0.37	0.76	0.46	1.99	0.94	1.56	0.81	2.84	1.84	2.16	2.73	1.57	1.07	1.03	
80 LEO ₂ -IP	0.14	0.15	0.34	0.75	0.37	0.77	0.51	2.04	1.01	1.65	0.81	2.89	0.96	2.21	2.64	1.43	1.60	1.94	
80 LEO ₂ -HP	0.16	0.10	0.29	0.75	0.28	0.65	0.49	1.79	0.96	1.55	0.75	2.57	1.23	2.32	2.31	1.16	1.38	1.27	
80 USA-LP	0.36	0.29	0.76	0.43	1.63	0.86	1.68	2.49	2.30	2.43	2.55	3.48	4.66	3.55	7.57	0.75	7.51	0.60	
80 LEA-HP	0.17	0.32	0.50	0.75	0.45	1.06	0.73	2.96	0.86	1.58	1.19	4.06	2.20	3.22	2.77	0.96	0.52	1.79	
160 USH ₂ -LP	0.15	0.23	0.84	1.46	5.20	0.92	2.49	1.09	1.25	1.71	2.23	2.49	3.72	2.34	0.81	1.27	1.09	0.51	
160 USH ₂ -IP	0.20	0.27	0.82	1.65	5.49	0.95	2.40	1.00	1.27	1.93	2.27	2.69	3.74	2.81	1.06	1.40	1.37	1.27	
160 USH ₂ -HP	0.12	0.19	0.55	1.03	3.58	0.60	1.63	0.71	0.83	1.27	1.49	1.82	2.35	1.56	0.71	0.92	0.89	0.65	
160 LEH ₂ -LP	2.47	5.20	6.13	4.00	11.49	9.53	6.34	26.01	12.81	15.49	11.07	51.30	24.42	28.45	29.74	21.11	19.27	15.88	
160 LEH ₂ -IP	2.46	5.10	6.94	6.04	11.06	10.16	5.28	35.18	11.43	15.44	13.78	61.33	27.05	36.41	41.69	32.76	31.31	8.17	
160 LEH ₂ -HP	2.62	5.44	7.44	5.69	9.93	11.17	6.82	35.19	13.93	16.37	12.48	61.94	22.27	28.75	31.92	24.65	29.06	18.92	
160 USO ₂ -LP	0.09	0.13	0.57	0.70	2.28	0.41	0.95	0.84	0.94	0.93	1.13	0.80	0.96	0.35	0.28	0.14	1.49	0.14	
160 USO ₂ -IP	0.19	0.21	0.92	1.20	3.95	0.61	1.58	1.47	1.81	1.87	1.92	1.38	1.41	0.58	0.46	0.50	2.60	0.61	
160 USO ₂ -HP	0.14	0.19	0.79	1.01	3.20	0.57	1.32	1.26	1.45	1.51	1.61	1.21	1.29	0.55	0.63	0.47	1.94	0.08	
160 LEO ₂ -LP	3.95	3.46	7.31	4.63	9.47	10.15	3.20	28.56	9.69	11.88	13.90	49.91	20.01	33.91	39.49	37.11	27.91	11.84	
160 LEO ₂ -IP	4.28	3.83	6.09	4.91	9.22	8.56	4.13	22.97	9.49	9.83	13.05	49.34	19.99	31.56	34.99	25.44	25.41	18.33	

TABLE 11 - - (Continued)

Sample	n-Paraffin										Carbon		Number							
	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32		
160 LEO ₂ -HP	3.95	2.52	4.63	3.41	6.36	6.43	2.52	15.79	6.69	7.36	9.69	34.30	13.97	21.37	22.65	20.89	20.16	15.46		
160 USA-LF	0.41	0.64	2.34	2.47	7.91	1.97	3.35	2.80	3.82	4.02	3.77	1.72	4.33	1.30	0.63	1.05	5.08	0.71		
160 LEA-LF	1.27	5.18	7.36	5.39	12.44	9.95	3.85	31.46	12.00	16.12	13.43	56.69	25.70	35.01	38.66	30.99	17.76	15.61		
240 USH ₂ -LF	3.00	4.15	24.72	31.65	27.99	21.44	28.38	31.77	15.05	9.21	10.57	24.44	20.78	12.60	10.21	14.11	5.48	0.00		
240 USH ₂ -IF	4.00	4.46	24.55	29.83	23.09	21.37	26.62	29.06	15.99	14.75	18.67	25.18	23.63	20.26	8.93	9.51	10.30	6.74		
240 USH ₂ -HF	5.10	3.56	20.51	26.81	17.84	17.42	20.18	22.39	13.42	16.59	20.23	22.45	23.08	20.32	5.99	4.86	10.05	5.22		
240 LEH ₂ -LF	1.47	5.35	5.89	3.25	7.50	7.39	2.79	32.56	7.10	10.66	10.49	50.47	24.37	32.73	37.24	6.09	26.56	15.43		
240 LEH ₂ -IF	2.42	6.41	7.23	4.58	10.25	10.25	3.35	42.45	8.09	14.42	13.12	64.33	30.41	40.74	46.47	23.96	32.87	11.89		
240 LEH ₂ -HF	2.57	5.77	7.13	5.51	10.67	8.15	4.18	43.21	7.20	16.03	14.25	62.86	29.68	40.84	42.39	29.22	32.02	15.08		
240 USO ₂ -LF	6.75	4.15	14.56	20.69	15.09	13.17	14.88	16.44	18.45	19.24	31.41	10.07	25.73	29.29	11.96	5.69	30.09	6.81		
240 USO ₂ -IF	1.39	5.51	15.88	20.43	16.30	16.27	17.84	15.15	20.97	18.56	27.84	8.35	23.71	27.39	11.33	6.06	28.59	14.49		
240 USO ₂ -HF	6.78	5.55	16.59	22.59	17.24	16.78	18.34	17.63	21.23	20.90	35.19	12.92	26.39	30.71	12.76	22.10	14.05	6.85		
240 LEO ₂ -LF	1.03	4.31	5.97	2.41	5.00	7.22	1.88	23.95	6.11	10.10	6.03	41.60	18.16	24.93	27.66	31.33	23.61	22.00		
240 LEO ₂ -IF	2.77	6.50	6.24	4.00	6.71	6.92	2.74	26.38	6.50	13.38	7.73	43.53	15.91	25.36	29.27	37.96	35.70	21.81		
240 LEO ₂ -HF	2.32	5.10	6.49	2.35	5.13	7.02	2.14	23.82	5.72	13.65	7.53	40.12	15.33	23.69	27.03	34.62	25.13	19.97		
240 USA-LF	4.69	3.77	20.59	25.58	21.93	16.61	21.84	20.23	17.41	16.99	38.55	12.00	23.71	22.16	15.78	15.18	6.00	4.07		
240 LEA-LF	1.31	5.11	6.42	2.47	6.66	7.01	4.19	31.67	5.76	11.44	9.68	50.09	22.07	31.70	34.73	27.39	22.96	16.40		
KS 160H ₂ -1	0.03	0.06	0.11	0.12	0.48	0.13	0.30	0.32	0.47	0.90	0.42	0.53	0.50	0.94	0.11	0.18	0.32	0.19		
KS 160H ₂ -3	0.03	0.10	0.11	0.16	0.63	0.16	0.38	0.41	0.56	1.14	0.56	0.68	0.68	1.22	0.13	0.38	0.44	0.33		
KS 160H ₂ -10	0.11	0.36	0.42	0.47	2.61	0.60	1.58	1.80	2.25	4.28	2.26	2.83	2.58	5.10	0.48	1.18	1.45	0.52		
KS 160H ₂ -30	0.16	0.51	0.56	0.78	3.36	0.90	2.18	2.27	3.07	5.87	2.88	3.83	3.34	7.09	0.58	0.71	1.72	1.08		
KS 160H ₂ -100	0.57	0.30	1.46	3.01	7.61	2.98	4.96	7.75	3.73	7.23	2.71	4.01	5.36	6.87	3.09	3.11	5.93	2.11		
KS 160H ₂ -300	0.72	0.55	1.52	4.30	8.08	3.15	5.15	8.34	3.56	8.68	3.18	4.23	6.68	8.66	4.46	4.19	2.17	2.85		
TUS-US	0.00	0.32	1.07	2.75	3.40	1.49	2.46	2.33	2.14	1.56	3.95	3.95	2.14	2.22	0.00	0.00	0.00	0.00		
160 TUS-H ₂	0.10	1.35	4.17	5.91	2.26	2.11	2.48	5.37	5.43	2.80	3.80	4.63	1.79	0.79	0.00	0.00	0.00	0.00		
160 TUS-O ₂	0.09	0.39	1.13	2.34	1.69	1.35	0.97	3.84	3.45	2.71	1.48	2.23	1.65	0.52	0.00	0.00	0.00	0.00		

TABLE 11 - - (Continued)

Sample	n-Paraffin										Carbon		Number							
	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32		
240 TUS-H ₂	0.00	0.00	0.02	0.24	0.34	0.46	1.20	0.85	0.45	1.41	2.03	2.21	10.53	2.07	0.00	0.00	0.00	0.00		
DOS-US	1.14	2.69	4.41	3.64	3.52	3.05	4.37	3.34	2.71	2.89	1.93	3.03	4.57	5.15	1.17	1.61	0.00	0.00		
160 DOS-H ₂	0.22	1.38	2.56	3.92	3.38	3.57	3.28	4.27	5.23	3.59	20.85	3.89	4.08	3.44	0.00	0.00	0.00	0.00		
300 EK-H ₂	0.21	0.25	1.40	2.85	2.55	1.68	2.82	2.51	4.22	1.93	2.55	1.36	0.96	2.15	2.04	0.28	0.98	0.27		
300 AK-H ₂	0.03	0.33	0.87	1.22	2.60	0.84	1.89	2.17	1.14	1.76	2.12	3.01	4.25	4.57	1.27	0.56	0.64	0.14		
UT1-US	0.00	0.58	0.42	1.25	2.25	1.44	1.41	1.66	1.98	4.22	3.82	2.25	0.90	0.30	0.00	0.00	0.00	0.00		
160 UT1-H ₂	0.50	0.20	0.56	0.32	0.64	0.66	0.93	1.62	0.50	1.13	2.87	2.25	0.69	2.14	0.00	0.00	0.00	0.00		
UT2-US	0.00	0.04	0.11	0.21	0.34	0.25	0.48	0.91	0.73	0.99	0.73	0.60	1.02	0.94	0.60	0.30	0.02	0.00		
160 UT2-H ₂	0.00	0.06	0.18	0.17	0.39	0.28	0.48	0.84	0.78	1.07	0.97	0.53	0.84	1.07	0.71	0.11	0.00	0.00		
SRL-US	0.09	0.08	0.16	0.26	0.31	0.26	0.57	0.59	0.63	0.96	0.99	0.67	0.00	1.19	0.11	0.00	0.00	0.00		
160 SRL-H ₂	0.00	0.05	0.17	0.07	0.09	0.13	0.25	0.20	0.19	0.45	0.39	0.64	0.36	0.79	0.19	0.30	0.00	0.00		
60 NFO-H ₂	0.07	0.10	0.45	0.62	1.43	1.79	2.03	2.58	2.07	2.40	2.16	1.80	2.85	2.14	1.65	0.36	0.53	0.44		
150 NFO-H ₂	0.06	0.09	0.54	0.79	1.53	2.77	2.95	3.36	3.24	2.73	3.52	3.20	3.75	2.82	3.11	0.33	0.46	0.64		
160 CPC-H ₂	0.05	0.12	0.86	1.35	2.65	4.31	3.64	5.10	4.92	4.13	4.56	3.30	3.96	3.27	3.19	0.58	1.02	0.86		
240 NFO-H ₂	0.13	0.19	0.52	1.23	1.59	3.23	3.51	3.94	3.84	3.52	3.35	3.21	3.50	2.45	2.10	1.15	0.50	2.25

Figure 31. Semi-log histograms showing distribution of fatty acids and n-paraffins for unextracted sediments heated at 80° C in an oxygen atmosphere; pressure conditions 1500-2000 psi.

Figure 32. Semi-log histograms showing distribution of fatty acids and n-paraffins for lipid-free sediments heated at 80° C in a hydrogen atmosphere; pressure conditions 1500-2000 psi.

Figure 33. Semi-log histograms showing distribution of fatty acids and n-paraffins for unextracted sediments heated at 160° C in a hydrogen atmosphere; pressure conditions 1500-2000 psi.

Figure 34. Semi-log histograms showing distribution of fatty acids and n-paraffins for lipid-free sediments heated at 160° C in an oxygen atmosphere; pressure conditions 1500-2000 psi.

Figure 35. Semi-log histograms showing distribution of fatty acids and n-paraffins for unextracted sediments heated at 240° C in an oxygen atmosphere; pressure conditions 1500-2000 psi.

section are samples subjected to various atmospheric gas fillings and pressure conditions and are considered representative of each temperature-extraction combination.

Characteristic n-paraffin and fatty acid distribution profiles for unextracted and extracted sediments subjected to 80°C are shown in figures 31 and 32. Fatty acids extracted from unaltered samples show increased concentrations, relative to control concentrations, e.g., fatty acids of carbon numbers of 12, 14, and 15, 18-25, and 28-30 are all greater than those in control material. The distribution of the n-paraffins for unextracted samples shows a strong even-number dominance (figure 31).

The unextracted sediments subjected to 160°C yielded greater amounts of C_{12} , C_{19} , and C_{23} fatty acids than did the same samples heated to 80°C. The n-paraffin even-carbon number predominance of 80°C unextracted samples is almost completely absent in 160°C unextracted samples (figure 33).

The 160°C lipid-free samples yielded fatty acids which were qualitatively similar to fatty acids from 80°C lipid-free samples. Figure 34 shows fatty acids from a 160°C lipid-free sample. The distribution pattern for the n-paraffins is similar for the 80 LE samples also. Comparison of the n-paraffin data displayed in figure 32 (80 lipid-free) and figure 34 (160 lipid-free) reveals that very few differences exist between the two. The 160°C lipid-free samples have a less pronounced even-numbered ratio predominance for n-paraffins in the C_{15} - C_{19} range than do the 80°C lipid-free samples. The 160°C lipid-free samples had considerably lower concentrations of the C_{21} n-paraffin than the 80°C lipid-free samples. The 160°C experiments did,

however, yield greater quantities of C_{30} and C_{31} n-paraffins than any of the 80°C experiments.

The 240°C unextracted samples had greater concentrations of all fatty acids, except anteiso- C_{15} and C_{24} , than any of the lower temperature experiments. Distribution patterns for 240°C unextracted n-paraffins show a slight even-numbered ratio dominance, although this is restricted to the C_{18} , C_{20} , C_{22} , and C_{28} components (figure 35). The overall pattern is one of increased n-paraffin concentrations in the C_{15} - C_{24} range with respect to the standard material. The n-paraffins in the C_{26} - C_{31} range show slight depletions with respect to standard material yields.

POSSIBLE ROLE OF DECARBOXYLATION

Previous discussion has pointed out the possible role of decarboxylation in a fatty acid to n-paraffin conversion. In dealing with modern organic-rich whole rock sediments, two possibilities for decarboxylation reactions must be considered. The first possibility is that only the soluble or free fatty acid material may decarboxylate. The second possibility is that fatty acids may lose a carboxyl group even though they are bound in kerogen. Figure 20 shows that fatty acids probably exist on kerogen. Decarboxylation could occur in such acids. Unfortunately, fatty acid decarboxylation reactions which involve the kerogen fraction cannot be predicted by assuming that the products will be free n-paraffins and carbon dioxide. Such a reaction would probably yield the carbon dioxide as a free detectable product; however, the n-paraffin might be incorporated into the kerogen.

Evaluation of possible fatty acid decarboxylation reaction is much more feasible for the soluble fatty acids. The approach used in this study was to mix the lipid extract with pure clays, subject the mixture to various temperature conditions, and analyze the products by gas chromatography. Decarboxylation of any fatty acid should yield n-paraffins with one less carbon atom than the original fatty acid carbon dioxide. Thus, a C_{18} fatty acid would yield carbon dioxide and a C_{17} n-paraffin.

The fatty acids, n-paraffins, and the carbon dioxide concentrations were determined at the conclusion of each NPC

experiment. All three fractions were converted to mg of carbon and the concentrations were plotted against temperature (figure 36).

If the major source of carbon dioxide is due to decarboxylation of fatty acids then carbon dioxide and fatty acid content should be inversely related. Also, the total n-paraffin yield should increase. Figure 36 shows exactly such a relationship except for the 240°C experiment. At 240°C, the carbon contribution from carbon dioxide increases markedly, whereas the carbon contribution from both the paraffins and fatty acids are essentially unchanged. The data support the hypothesis that at 80°C and 160°C, fatty acid decarboxylation is a very probable reaction. At 240°C, the non-fatty acid organic compounds in the lipid fraction become major contributing sources of CO₂.

Figure 36. Carbon content of fatty acid, paraffin, and CO₂ fractions for decarboxylation (pure clay) experiments.

SUMMARY AND CONCLUSIONS

The three-fold objectives of this study were to: (1) determine the approximate conditions required to initiate significant hydrocarbon generation from a uniform mud matrix, (2) examine the n-paraffin and aliphatic fatty acid variation which results from various types of thermal treatment, and (3) evaluate the relative potential of both the soluble and insoluble fractions of the sediment for generating hydrocarbons. These three objectives may be combined into a major generalized objective of examining the "evolutionary series" of crude oils which Welte (1965) suggests should come from a single hydrocarbon source rock. By utilizing a homogenous organic-rich modern mud as material for the laboratory work, the requirement of a common source material has been satisfied. Experiments on open marine muds and ancient organic-rich shales were conducted mainly for comparative purposes.

The 80°C temperature increments used in this study prohibited a detailed examination of changes in hydrocarbon yield which result from small changes in temperature. Thus, no definitive statements regarding the lowest temperature at which products can be formed can be made on the basis of this study. It is evident that treatment for 50 hours at 80°C produces an appreciable increase in the total quantity of hexane-soluble components (Appendix X). Data in Appendix X also show that the aromatic and hetero-compound components for unextracted samples heated to 80°C are almost twice that of standard

starting or control material. However, the ratios of paraffins, aromatics, and hetero-compounds are not markedly different. At 160°C, the product mixture for the unextracted samples is enriched in aromatics; total hexane yield is twice that of their 80°C counterparts. At 240°C, the generated products from unextracted samples are strongly paraffinic while the total hexane-soluble fraction is almost double that of the unextracted 160°C samples (table 9).

A comparison of figures 21 A-B, 22 A-B, and 23 A-B (which represent paraffin-aromatic-hetero-compound distributions from the present study) with published diagrams (figure 37) reveals a common feature. Figure 37A shows that crude oils are richer in the n-heptane fraction (paraffins) than marine muds. The diagrams of figures 21 A-B, 22 A-B, and 23 A-B all show an enrichment in paraffinic products with increasing temperatures. Figure 37B, although having a naphthene fraction instead of a hetero-compound or methanol-soluble fractions, shows the same general paraffinic enrichment for crude oils of increasing geologic age. Diagrams of paraffin, aromatic, and naphthene distributions plotted with geologic age must be interpreted with caution because crude oil which has migrated and collected in reservoirs does not necessarily have its origin in rocks of the same geologic age as the rocks in which it is found. If increasing the temperature of the laboratory experiments is assumed to produce variations in crude oils similar to the changes displayed in figure 37, mainly increasing paraffin content, then the results of this study would appear to parallel naturally-occurring changes.

Thus, the products generated at the three temperatures employed in this study might be considered as three separate

Figure 37. Ternary diagrams showing increasing paraffinic fractions (in weight percent) with increasing maturity levels.

A after Stevens *et al.*, (1956); B after Kartsev (1964).

evolutionary stages of product formation. Products generated from the extracted sediments represent the minimum hydrocarbon yield inasmuch as some of the soluble material will be transformed into stable forms and probably increase the capacity of kerogen to produce hydrocarbons. The general characteristics of the generated products for the extracted samples are summarized as follows. These probably reflect the yields of an organic-rich shale deposited under near-ideal conditions for preserving deposited organic matter, e.g., the conditions of modern northern Barataria Bay.

- (1) CO_2 and nitrogen were more abundant products for lipid extracted samples than for unextracted samples. Although much of the organic matter has converted to the insoluble form (kerogen), the continued presence of these two non-hydrocarbon gases indicates that petroleum source rocks will yield significant quantities of noncommercial gaseous products during early diagenesis.
- (2) Methane yields were also greater for lipid extracted samples than for unextracted samples but never became a dominant gaseous product. The kinetics study samples indicate that methane concentration increased with increased exposure periods; thus, laboratory studies may not be of sufficient duration to yield reliable data on methane generation.
- (3) Total lipid yield was strongly temperature-dependent and at 160°C , yields for lipid extracted samples were similar to those for unextracted 80°C samples. Generated lipid products from the insoluble kerogen are of such quantity at elevated temperatures that the amount of indigenous lipid material is

not of importance. As noted earlier, however, the initial presence of soluble lipids does affect the distribution of generated products.

- (4) Lipid extracted samples had considerably lower free fatty acid yields than unextracted samples. Total fatty acid yields generally increased with temperature.
- (5) The hexane-soluble or hydrocarbon fraction increased with temperature regardless of prior lipid extraction so that the yield for 240°C lipid-extracted samples was essentially the same as for 240°C unextracted samples.
- (6) Paraffinic products increased markedly for lipid-extracted samples through all temperature ranges. The n-paraffins in the C_{25} - C_{30} range were relatively high for all lipid-free hydrogen atmosphere experiments.

REFERENCES

- Abelson, P. H., 1959, Geochemistry of organic substances, in *Researches in Geochemistry* (P. H. Abelson, ed.), John Wiley and Sons, New York.
- Abelson, P. H., 1963, Geochemistry of amino acids, in *Organic Geochemistry* (I. Breger, ed.), Macmillan Company, New York.
- Abelson, P. H., 1963, Organic geochemistry and the formation of petroleum: Proceedings of the sixth world petroleum congress, Frankfurt, Germany, Verein Zur Forderung Des 6, Welt-Erdol-Kongresses, Hamburg.
- Abelson, P. H., 1968, Conversion of biochemical to kerogen and n-paraffins in *Researches in Geochemistry*, vol. 2 (P. H. Abelson, ed.): Wiley and Sons, New York.
- Abelson, P. H. and Hare, P. E., 1969, Recent amino acids in the Gunflint chert: *Carnegie Inst. Washington Year Book*, 66, p. 208-210.
- Ackman, R. G. and Sipos, J. C., 1965, Isolation of the saturated fatty acids of some marine lipids with particular reference to normal odd-numbered fatty acids and branched-chain fatty acids: *Comparative Biochem. Physiol.*, vol. 15, p. 445-456.
- Andreev, P. F., 1962, Geochemical transformations of petroleum in the lithosphere: *Geochemistry*, vol. 10, p. 1005-1014.
- Baker, J. J. W. and Allen, G. E., 1964, *Matter, Energy, and Life*: Addison-Wesley Publishing Company, Inc., Massachusetts.
- Baker, E. W., 1969, Porphyrins in *Organic Geochemistry: Methods and Results* (G. Eglinton and M. T. J. Murphy, eds.), Springer-Verlag, Berlin, p. 464-497.
- Baker, D. R. and Claypool, G. E., 1970, Effects of incipient metamorphism on organic matter in mudrock: *Bulletin of The American Association of Petroleum Geologists*, vol. 54, no. 3, p. 456-468.
- Barnes, H. L., 1963, Ore solution chemistry. I Experimental determinations of mineral solubilities: *Econ. Geol.*, vol. 58, no. 7, p. 1054-1060.
- Barry, J. M. and Barry, E. M., 1969, *An Introduction to the Structure of Biologic Molecules*, Prentice-Hall, Inc., Englewood Cliffs, New Jersey.

- Bendoraitis, J. G., Brown, B. L., and Hepner, L. S., 1962, Isoprenoid hydrocarbons: *Petroleum Anal. Chem.*, vol. 34, no. 1, p. 49-53.
- Bendoraitis, J. G., Brown, B. L., and Hepner, L. S., 1963, Isolation and identification of isoprenoids in petroleum: *Proceedings of the sixth world petroleum congress, Frankfurt, Germany, Verein Zur Forderung Des 6, Welt-Erdol-Kongresses, Hamburg.*
- Bergmann, Werner, 1963, Geochemistry of Lipids *in Organic Chemistry* (I. Breger, ed.), Macmillan Company, New York, p. 503-542.
- Bestougeff, M. A., 1967, Petroleum hydrocarbons *in Fundamental Aspects of Petroleum Geochemistry* (B. Nagy and U. Colombo, eds.), Elsevier Publishing Company, Amsterdam, p. 77-108.
- Bordovskiy, O. K., 1965, Accumulation and transformation of organic substances in marine sediments: *Marine Geology*, vol. 3, no. $\frac{1}{2}$, p. 3-114.
- Bradley, W. H., 1966, Tropical lakes, copropel, and oil shale: *Geol. Soc. America Bull.*, vol. 77, no. 12, p. 1333-1338.
- Bray, E. E. and Evans, E. D., 1965, Hydrocarbons in non-reservoir source beds: *Bulletin of the American Association of Petroleum Geologists*, vol. 49, p. 248-257.
- Breger, I. A., and Brown, A., 1962, Kerogen in the Chattanooga shale: *Science*, vol. 137, p. 221-224.
- Breger, I. A., 1963, Classification of naturally-occurring carbonaceous substances *in Organic Geochemistry* (I. Breger, ed.), Macmillan Company, New York, p. 503-542.
- Burlingame, A. L., Haug, Patricia A., Schnoes, Heinrich K., and Simoneit, Bernd R., 1969, Fatty acids derived from the Green River formation oil shale by extractions and oxidations - a review *in Advances in Organic Geochemistry, 1968* (P. A. Schenck and I. Havenaar, eds.), Pergamon Press, Braunschweig, p. 85-130.
- Burnham, C. W., Holloway, J. R., and Davis, N. F., 1969, Thermodynamic properties of water to 1,000°C and 10,000 bars: *Geological Society of America Special Paper No. 132, Boulder, Colorado.*
- Castrano, J. R. and Sparks, D. M., 1973, Interpretation of vitrinite reflectance measurements in sedimentary rocks and determination of burial history using vitrinite reflectance. *Geol. Soc. Amer. Spec. Pap.* 153, p. 31-52.
- Clark, R. C. and Blumer, M., 1967, Distribution of n-paraffins in marine organisms and sediment: *Limnology and Oceanography*, vol. 12, no. 1, p. 79-87.
- Cochran, W. G. and Cox, G. M., 1957. *Experimental Designs*, 2nd ed. John Wiley and Sons, New York.

- Colombo, U., 1967, Origin and evolution of petroleum in Fundamental Aspects of Petroleum Geochemistry, Amsterdam, Elsevier, Chap. 8, p. 331-370.
- Cooper, J. E. and Bray, E. E., 1963, A postulated role of fatty acids in petroleum formation: *Geochem. et Cosmochim. Acta*, vol. 27, p. 1113-1127.
- Cordell, R. J., 1973, Colloidal soap as proposed primary migration medium for hydrocarbons: *Bulletin of the American Association of Petroleum Geologists*, vol. 57, no. 9, p. 1618-1643.
- Cummins, J. J., Doolittle, F. G., and Robinson, W. E., 1974, Thermal degradation of Green River kerogen at 150°C to 350°C - composition of products: U. S. Bureau of Mines Report of Investigations 7924, 18 pp.
- Douglas, A. G., Eglinton, G., and Henderson, W., 1970, Thermal alteration of the organic matter in sediments in *Advances in Organic Geochemistry*, Braunschweig, p. 369-388.
- Dott, R. H. and Reynolds, M. J., 1969, Sourcebook for petroleum geology: American Association of Petroleum Geologists, Memoir No. 5, Tulsa, Oklahoma.
- Dunning, H. N., 1963, Geochemistry of organic pigments in *Organic Geochemistry* (I. Breger, ed.), Macmillan Company, New York, p. 367-430.
- Dunton, M. L. and Hunt, J. M., 1962, Distribution of low molecular weight hydrocarbons in Recent and ancient sediments: *Bulletin of The American Association of Petroleum Geologists*, vol. 46, no. 12, p. 2246-2248.
- Eglinton, G., 1969, Organic geochemistry: the organic chemist's approach in *Organic Geochemistry: Methods and Results* (G. Eglinton and M. T. J. Murphy, eds.), Springer-Verlag, Berlin, p. 20-73.
- Erdman, J. G., Marlett, E. M., and Hanson, W. E., 1956, Survival of amino acids in marine sediments: *Science*, vol. 124, no. 3230, p. 1026.
- Erdman, J. G., Marlett, E. M., and Hanson, W. E., 1958, The occurrence and distribution of low molecular weight aromatic hydrocarbons in Recent and ancient carbonaceous sediments: *Am. Chem. Soc.*, 134th Meeting, Chicago, Preprints, C-39 - C-49.
- Erdman, J. G., 1967, Geochemical origins of the low molecular weight hydrocarbon constituents of petroleum and natural gases: *Proceedings of the seventh world petroleum congress*, vol. 2, Barking, Essex, Elsevier Publishing Company, Ltd., p. 13-24.
- Ettre, L. S. and Zlatkis, A., 1967, *The Practice of Gas Chromatography*, Interscience, New York.

- Evans, W. D., Morton, R. D., and Cooper, B. S., 1964, Primary investigation of the oleiferous dolerite of dyvika in *Advances in Organic Geochemistry* (U. Colombo and G. D. Hobson, eds.), Macmillan Company, New York, p. 141-148.
- Foresman, J. P. and Hunt, J. M., 1958, Insoluble organic matter (kerogen) in sedimentary rocks of marine origin in *Habitat of Oil* (L. G. Weeks, ed.), American Association of Petroleum Geologists, p. 747-778.
- Foresman, J. P., 1963, Geochemistry of kerogen in *Organic Geochemistry* (I. A. Breger, ed.): Macmillan Co., New York, Chap. 5, p. 148-182.
- Garner, F. H., Green, S. J., Harper, F. D., and Pegg, R. E., 1953, Metallic elements in residual fuel oils: *Jour. Institute of Petroleum*, vol. 39, p. 278-293.
- Giraud, A., 1970, Application of pyrolysis and gas chromatography to geochemical characterization of kerogen in sedimentary rock: *Bulletin of the American Association of Petroleum Geologists*, vol. 54, no. 3, p. 439-455.
- Gransch, J. A., and Eisma, E., 1970, Characterization of the nsoluble organic matter of sediments by pyrolysis in *Advances in Organic Geochemistry*, 1966 (G. D. Hobson and G. C. Spears, eds.), Pergamon Press, Braunschweig, p. 407-426.
- Gutjahr, C. C. M., 1966, Carbonization measurements of pollen-grains and spores and their application: *Leidse Geologische Mededelingen*, vol. 36, p. 1-29.
- Handa, N., 1970, Dissolved and particulate carbohydrates in *Symposium on Organic Matter in Natural Waters* (D. W. Hood, ed.), University of Alaska Institute of Marine Science, Occasional Publication No. 1, p. 129-148.
- Hanson, W. E., 1959, Some chemical aspects of petroleum genesis in *Researches in Geochemistry* (P. H. Abelson, ed). Wiley and Sons, p. 104-117.
- Hare, P. E., and Mitterer, R. M., 1969, Laboratory simulation of amino acid diagenesis in fossils: *Carnegie Institute Washington Yearbook* 67, p. 205-208.
- Hart, H. and Schuetz, R. D., 1972, *Organic Chemistry: A Short Course*. Houghton Mifflin Company, Boston.
- Harwood, R., 1973, Amoco Production Research Corporation, P. O. Box 591, Tulsa, OK 74102.
- Hedberg, H. D., 1964, Geologic aspects of the origin of petroleum: *Bulletin of American Association of Petroleum Geologists*, vol. 48, no. 11, p. 1755-1803.

- Hedberg, H. D., 1967, Geologic controls on petroleum genesis: Seventh world petroleum congress, Mexico, Proceedings, vol. 2, p.3-11, Elsevier Publishing Co.
- Ho, Clara, 1971, Seasonal changes in sediment and water chemistry in Baratoria Bay: Coastal Studies Bulletin No. 6, Special Sea Grant Issue, p. 16-25.
- Hodgson, G. W., Baker, B. L., and Peake, E., 1967, Geochemistry of porphyrins in Fundamental Aspects of Petroleum Geochemistry (B. Nagy and U. Colombo, eds.), Elsevier, New York.
- Hoering, T. C. and Abelson, P. H., 1963, Hydrocarbons from the low-temperature heating of kerogen: Carnegie Institute of Washington Yearbook 1963, p. 256-258.
- Hunt, J. M., 1961, How gas and oil form and migrate: World Oil, October, 140-150.
- Jamieson, G. R. and Reid, E. H., 1972, The component fatty acids of some marine algal lipids: Phytochemistry, vol. II, p. 1423-1432.
- Kaiser, A., 1972, Exxon Production Research, P. O. Box 2189, Houston, Texas 77001.
- Kaneda, T., 1967, Fatty acids in the genus Bacillus. I. Iso- and anteiso-fatty acids as characteristic constituents of lipids in 10 species: Jour. Bacteriol., vol. 93, p. 894-903.
- Kaneda, T., 1968, Fatty acids in the genus Bacillus. II. Similarities in the fatty acid compositions of Bacillus thuringiensis, Bacillus anthracis, and Bacillus cereus: Jour. Bacteriol., vol. 95, p. 2210-2216.
- Kartsev, A. A., 1964, Geochemical transformation of petroleum in Advances in Organic Geochemistry (U. Colombo and G. D. Hobson, eds.), Pergamon Press, p. 11-14.
- Khan, S. U. and Sowden, F. J., 1971, Thermal stabilities of amino acid components of humic acids under oxidative conditions: Beochim. et Cosmochim. Acta, vol. 35, p. 854-858.
- Krumbein, W. C., 1939, Tidal lagoon sediments on the Mississippi Delta in Recent Marine Sediments (P. D. Trask, ed.), American Association of Petroleum Geologists, p. 178-194.
- Kvenvolden, Keith A., 1970, Evidence for transformations of normal fatty acids in sediments in Advances in Organic Geochemistry, 1966 (G. D. Hobson and G. C. Speers, eds.), Pergamon Press, p. 335-366.
- Landmuir, D., 1970, Pennsylvania State University, University Park, Pennsylvania 16802.

- Lange, N. A., 1944, Handbook of Chemistry, Fifth Edition, Handbook Publishers, Inc., Sandusky, Ohio.
- Levorsen, A. I., 1959, Geology of Petroleum: W. H. Freeman and Company, San Francisco.
- Lewis, J. S., 1967, Compilation of gas chromatographic data: ASTM Special Publication No. 343, American Society for Testing and Materials, Philadelphia.
- Littlewood, A. B., 1962, Gas Chromatography, Principles, Techniques, and Applications. Academic Press, New York.
- Mair, B. J., 1964, Terpenoids, fatty acids, and alcohols as source materials for petroleum hydrocarbons: Geochim. et Cosmochim. Acta, vol. 28, p. 1301-1321.
- Martinez, J. D., 1965, Photometric determination of preferred orientation of feldspars in fine-grained igneous rocks: Tulane Studies in Geology, vol. 3, no. 3, p. 165-174.
- McIver, R. D., 1967, Composition of kerogen - clue to its role in the origin of petroleum in 7th world petroleum cong. proc., vol. 2: Barking, Essex, Elsevier Publishing Co., Ltd., p. 25-36.
- McKinney, J. W., and Masters, J. A., 1968, Dineh-Bi-Keyah Field, Apache County, Arizona: Bulletin of the American Association of Petroleum Geologists, vol. 52, no. 10, p. 2045-2057.
- McNair, H. M. and Bonelli, E. J., 1969, Basic Gas Chromatography: Consolidated Printers, Berkeley, California.
- McReynolds, W. O., 1966, Gas Chromatographic Retention Data: Preston Technical Abstracts Co., Evanston, Illinois.
- Meinschein, W. G., 1959, Origin of Petroleum: Bulletin of The American Association of Petroleum Geologists, vol. 43, no. 5, p. 925-943.
- Meinschein, W. G., 1969, Hydrocarbons - saturated, unsaturated, and aromatic in Organic Geochemistry: Methods and Results (G. Eglinton and M. T. J. Murphy, eds.), Springer-Verlag, Berlin, p. 330-356.
- Mitterer, R. M. and Hoering, T. D., 1966, Production of hydrocarbons from the organic matter in a Recent sediment: Carnegie Institute of Washington Yearbook, 1966, Garamond/Pridemark Press, Baltimore, Maryland, p. 510-514.
- Modzeleski, J. E., Laurie, W. A., and Nagy, B., 1971, Carbohydrates from Santa Barbara Basin sediments: gas chromatographic - mass spectrometric analysis of trimethylsilyl derivatives. Geochim. et Cosmochim. Acta, vol. 35, p. 825-838.

- Mulik, J. D. and Erdman, J. G., 1963, Genesis of hydrocarbons of low molecular weight in organic-rich aquatic systems: *Science*, vol. 141, p. 806-807.
- Newman, J. W., Parker, P. L., and Behrens, E. W., 1973, Organic carbon isotope ratios in Quaternary cores from the Gulf of Mexico: *Geochimica et Cosmochimica Acta*, vol. 37, p. 225-238.
- Niino, H. and Emery, K. O., 1961, Sediments of shallow portions of East China Sea and South China Sea: *Bull. Geol. Soc. Am.*, vol. 72, p. 731-762.
- Nissenbaum, A., Baedeker, M. J., and Kaplan, I. R., 1972, Organic geochemistry of Dead Sea sediments: *Geochim. et Cosmochim. Acta*, vol. 36, p. 709-727.
- Oakwood, T. S., 1946, Transformation of organic materials into petroleum - chemical and biochemical phases: Review of API Research Project 43B - Fundamental research on occurrence and recovery of petroleum, p. 99-102.
- Oakwood, T. S., Schriver, D. S., Fall, H. H., McAleer, W. J., and Wuntz, P. R., 1952, The optical activity of petroleum: *Ind. and Eng. Chem.*, vol. 44, no. II, p. 2568-2570.
- Oro, J., Tornabene, T. G., Noonan, D. W., and Gelpi, E., 1967, Aliphatic hydrocarbons and fatty acids of some marine and fresh-water microorganisms: *Jour. of Bacteriology*, vol. 93, no. 6, p. 1811-1818.
- Parker, P. L., 1969, Fatty acids and alcohols in *Organic Geochemistry: Methods and Results*, (G. Eglinton and M. T. J. Murphy, eds.), Springer-Verlag, Berlin, p. 357-373.
- Philippi, G. T., 1965, On the depth, time, and mechanisms of petroleum generation: *Geochim. et Cosmochim. Acta*, vol. 29, p. 1021-1049.
- Philippi, G. T., 1968, Essentials of the petroleum formation process are organic source material and a subsurface temperature controlled chemical reaction mechanism in *Advances in Organic Geochemistry 1968*, (P. A. Schenck and I. Havenaar, eds.) Pergamon Press, p. 25-46.
- Plunkett, M. A., 1957, The qualitative determination of some organic compounds in marine sediments: *Deep-Sea Research*, vol. 5, no. 4, p. 259-262.
- Porfir'ev, V. B., 1974, Inorganic origin of petroleum: *Bulletin of the American Association of Petroleum Geologists*, vol. 58, no. 1, p. 3-33.

- Price, L. C., 1971, The aqueous solubility of petroleum and petroleum forming hydrocarbons as applied to the origin and primary migration of petroleum: Unpublished Ph.D. Dissertation, University of California at Riverside.
- Purnell, J. H., 1962, Gas Chromatography: Wiley and Son, New York.
- Pusey, W. C., III, 1973a, How to evaluate potential gas and oil source rocks: World Oil (April), p. 71-75.
- Pusey, W. C., III, 1973b, Paleotemperatures in the Gulf Coast using the ESR-kerogen method: Transactions of the Gulf Coast Association of Geological Societies, p. 195-202.
- Redfield, A. C., 1958, Precludes to the entrapment of organic matter in the sediments of Lake Maracaibo in Habitat of Oil (L. G. Weeks, ed.), American Association of Petroleum Geologists, p. 968-981.
- Revelle, R. and Shepard, F. P., 1939, Sediments off the California Coast in Recent Marine Sediments (P. D. Trask, ed.), American Association of Petroleum Geologists, p. 245-282.
- Richards, F. A. and Redfield, A. C., 1954, A correlation between oxygen content of sea water and the organic content of marine sediments: Deep-Sea Research, vol. 1, p. 279-281.
- Robinson, J. W., 1970, Undergraduate Instrumental Analysis, Marcel Dekker, Inc., New York, Chap. 12, p. 237-273.
- Robinson, W. E., 1969, Kerogen of the Green River Formation in Organic Geochemistry: Methods and Results (G. Eglinton and M. T. J. Murphy, eds.), Chap. 26, p. 619-637, Springer-Verlag, Berlin.
- Sackett, W. M., 1966, Carbon isotope effects in methane production by thermal cracking in Advances in Organic Geochemistry (G. D. Hobson, ed.), Pergamon Press, Hungary, p. 37-54.
- Sackett, W. M., 1968, The carbon isotope composition of natural methane occurrences: Bulletin of the American Association of Petroleum Geologists, vol. 52, no. 5, p. 852-857.
- Schopf, J. W., Kvenvolden, K. A., and Barghoorn, E. S., 1968, Amino acids in Precambrian sediments: An essay, Proc. Nat. Acad. Sci., 59, no. 2, p. 639-648.
- Silverman, S. R., 1973, Diagenesis in organic sediments: Supplementary syllabus for the AAPG meeting, Anaheim, California.
- Slowey, J. F., Jeffrey, L. M., and Hood, D. W., 1962, The fatty acid content of ocean water: Geochim. et Cosmochim. Acta, vol. 26, p. 607-616.

- Smith, P. V., 1954, Studies on origin of petroleum: occurrence of hydrocarbons in Recent sediments. Bulletin of The American Association of Petroleum Geologists, vol. 38, no. 3, p. 377-404.
- Staplin, F. L., 1969, Sedimentary organic matter, organic metamorphism, and oil and gas occurrence: Canadian Petroleum Geology, vol. 17, p. 47-66.
- Steel, R. G. D., and Torrie, J. H., 1960, Principles and Procedures of Statistics, McGraw-Hill, New York.
- Stevens, Nelson P., Bray, Ellis E., and Evans, Ernest D., 1956, Hydrocarbons in sediments of Gulf of Mexico: Bulletin of the American Association of Petroleum Geologists, vol. 40, no. 5, p. 975-983.
- Stewart, R. A., Pilkey, O. H., and Nelson, B. W., 1965, Sediments of the northern Arabian Sea: Marine Geology, vol. 3, p. 411-427.
- Swain, F. M., 1956, Stratigraphy of lake deposits in central and northern Minnesota: Bulletin of The American Association of Petroleum Geologists, vol. 40, no. 4, p. 600-653.
- Swain, F. M., 1969, Fossil carbohydrates in Organic Geochemistry: Methods and Results (G. Eglinton and M. T. J. Murphy, eds.) Springer-Verlag, Berlin, p. 374-399.
- Swain, F. M., Palkins, G. V., and Bratt, J. G., 1970, Possible taxonomic interpretation of some Paleozoic and Precambrian carbohydrate residues in Advances in Organic Geochemistry, 1966, (G. D. Hobson and G. C. Speers, eds.), Pergamon Press, Hungary, p. 469-492.
- Speers, G. C. and Whitehead, E. V., 1969, Crude petroleum in Advances in Organic Geochemistry: Methods and Results, (G. Eglinton and M. T. J. Murphy, eds.) Springer-Verlag, Berlin, p. 638-675.
- Toporek, M., 1971 Essentials of Biochemistry: Appleton-Century-Crofts, New York.
- Trieb, Alfred, 1934, Chlorophyll und Haminderivate in bituminosen gesteinen, erdolen, erdwachsen und asphalten: Annalen Der Chemie, vol. 510, p. 42-62.
- Vallentyne, J. R., 1963, Geochemistry of carbohydrates in Organic Geochemistry (I. A. Breger, ed.) Macmillan Company, New York.
- Van Andel, T. H., 1964, Recent marine sediments of the Gulf of California: Memoir No. 3, American Association of Petroleum Geologists, p. 216-310.

- Walford, L. A., 1958, Living Resources of the Sea: Opportunities for Research and Expansion. Ronald Press, New York.
- Weeks, L. G., 1958, Habitat of oil and some factors that control it in Habitat of Oil (L. G. Weeks, ed.), American Association of Petroleum Geologists.
- Weete, J. D., 1972, Aliphatic hydrocarbons of the fungi: *Phytochemistry*, vol. 11, p. 1201-1205.
- Welte, D. H., 1965, Relationship between petroleum and source rocks: *Bulletin of The American Association of Petroleum Geologists*, vol. 49, no. 12, p. 2246-2268.
- Weismann, T. J., 1971, Stable carbon isotope investigation of possible igneous origin of natural gases in Sacramento Valley and Delaware-Val Verde basins: Paper presented at the fifty-sixth annual AAPG meeting, Houston.
- Weiss, F. T., 1970, Determination of Organic Compounds: Methods and Procedures, Chapter 21, p. 369-416, Wiley Interscience, New York.
- White, D. C., 1915, Some relations in origin between coal and petroleum: *Washington Academy of Science Journal*, vol. 5, no. 6, p. 189-212.
- Whitehead, W. L. and Breger, I. A., 1963, Geochemistry of petroleum in *Organic Geochemistry* (I. A. Breger, ed.), p. 248-332, Macmillan Company, New York, Chap. 7, p. 248-232.
- Williams, P. M., 1965, Fatty acids derived from lipids of marine origin: *Journal of Fisheries Research Board of Canada*, 22 (5), p. 1107-1122.
- Wilson, L. R., 1961, Palynological fossil response to low-grade metamorphism in the Arkoma Basin: *Tulsa Geological Society*, vol. 29, p. 131-140.
- Wilson, L. R., 1971, Palynological techniques in deep-basin stratigraphy; *Oklahoma City Geological Society Shale Shaker*, vol. 21, p. 124-139.
- Winters, K., Parker, P. L., and Van Baalen, C., 1969, Hydrocarbons of blue-green algae: geochemical significance. *Science*, vol. 163, p. 467-468.
- Wollrab, V. and Streibl, M., 1963, Earth waxes, peat, montan wax, and other organic brown coal constituents in *Organic Geochemistry: Methods and Results* (G. Eglinton and M. T. J. Murphy, eds.), Springer-Verlag, Berlin, p. 576-598.
- Yamada, M., 1964, Lipids of plankton: *Bulletin of the Japanese Society of Scientific Fisheries*, vol. 30, no. 8.

APPENDIX I

EXTRACTION DATA FOR FOUR SAMPLES OF JOHN-THE-FOOL LAKE MUD

Component	Extraction				
	1	2	3	4	SBC
Dry Sediment Wt. (gm)	63.662	64.850	63.621	65.031	64.291
Total Extractable Lipid (mg)	771.3	814.8	737.1	842.8	791.5
Total Extractable Fatty Acids (mg)	179.3	180.6	175.2	176.4	177.8
Total C ₆ -Soluble (mg)	116.7	112.1	104.3	87.5	108.1
Paraffinic Hydrocarbons (mg)	6.3	8.1	7.8	6.9	7.3
Aromatic Hydrocarbons (mg)	13.4	11.5	9.1	10.6	11.15
Hetero-Compounds (mg)	38.6	41.4	43.7	35.3	37.0
Fatty Acid (Rel. %)					
C ₁₂	1.43	1.26	1.62	1.32	1.41
I-C ₁₄	2.57	2.83	2.46	2.63	2.62
C ₁₄	5.33	4.96	5.87	5.17	5.33
A-C ₁₅	4.63	4.06	4.26	4.35	4.32
C ₁₅	3.22	3.56	3.92	3.72	3.60
I-C ₁₆	3.64	3.72	3.31	3.55	3.55
C ₁₆	19.06	19.32	18.71	19.13	4.14
C ₁₈	3.39	4.62	4.06	4.49	19.05
C ₁₉	1.31	0.48	0.87	0.97	0.91
C ₂₀	4.11	3.77	4.21	3.97	4.01
C ₂₁	4.73	2.33	2.49	2.88	3.11
C ₂₂	7.25	4.09	3.73	3.81	4.72

Note: Average values for extractions represent standard bomb charge (SBC) or control qualities.

APPENDIX I--Continued

Component	Extraction				
	1	2	3	4	SBC
C ₂₃	2.10	2.37	2.39	2.26	2.28
C ₂₄	6.34	7.64	8.61	8.16	7.69
C ₂₅	1.06	3.21	2.71	2.94	2.48
C ₂₆	10.96	11.61	12.22	12.17	11.74
C ₂₇	4.78	5.66	3.87	4.71	4.75
C ₂₈	11.97	12.82	11.46	11.89	12.04
C ₂₉	0.96	0.64	1.07	0.13	0.70
C ₃₀	11.16	3.88	2.16	1.76	2.24
Paraffinic Hydrocarbons (Rel. %)					
C ₁₅	0.92	1.13	0.74	0.86	0.91
C ₁₆	0.79	0.86	0.41	0.65	0.68
C ₁₇	2.44	2.79	2.13	2.53	2.47
C ₁₈	1.06	1.21	0.96	1.11	1.08
C ₁₉	3.58	3.42	3.72	3.66	3.59
C ₂₀	1.39	1.71	1.15	1.42	1.42
C ₂₁	4.56	4.86	4.06	4.35	4.46
C ₂₂	2.36	2.73	2.23	2.43	2.44
C ₂₃	6.73	6.96	6.55	6.82	6.76
C ₂₄	4.31	4.16	4.62	4.54	4.41
C ₂₅	5.94	5.32	5.27	5.76	5.57
C ₂₆	5.65	5.06	6.18	5.76	5.66
C ₂₇	11.13	11.62	10.41	11.21	11.09
C ₂₈	5.82	6.65	5.37	5.97	5.95
C ₂₉	20.58	20.21	21.06	21.62	19.77
C ₃₀	2.07	2.17	2.26	2.38	2.22
C ₃₁	19.24	18.43	19.56	19.07	17.96
C ₃₂	3.50	2.88	2.27	2.25	2.72

APPENDIX II

ELEMENTAL ANALYSIS OF JOHN-THE-FOOL LAKE KEROGEN
(After Demineralization)

Element	Weight Percent
Carbon	62.3
Hydrogen	5.4
Oxygen	29.6
Nitrogen	2.8

Analyses by Amoco Production Research, Tulsa,
Oklahoma.

APPENDIX III

Temperature controller settings versus measured temperature for the Barnes Hydrothermal System

Relation between occupied vessel volume (fill factor), temperature, and pressure.

APPENDIX V

LIPID EXTRACTION SCHEME¹

1. Frozen modern sediment
2.
 - a. Treat with dilute HCl to remove carbonate
 - b. Wash with distilled water to remove salts
 - c. Recover sediment by filtration
3.
 - a. Add methyl alcohol to moist sediment, then place mixture in blender for 15 minutes and treat ultrasonically for 15 minutes
 - b. Add chloroform and repeat 3a
4. Filter, retain both fractions
5. Repeat 3a-b, and 4
6. Combine lipid fraction and reduce volume on rotary evaporator
7. Add 3% KOH-methyl alcohol to reduced volume of lipid extract and place on steam bath for 1 hour
8. Place mixture in separatory funnel, add distilled hexane, and shake well.
9. Recover hexane from step 8; this fraction contains the hydrocarbons
10. Acidify KOH-methyl alcohol mixture with HCl and extract fatty acids with distilled hexane.
11. Add BF₃-methyl alcohol to the hexane fraction of step 10 and place on steam bath for 10 minutes. This fraction contains the fatty acids.

¹Modified from Parker, 1968.

APPENDIX VI

Frozen Sediment

Flow chart of lipid extraction scheme used in this study.

APPENDIX VII

DESCRIPTION OF GAS CHROMATOGRAPH AND OPERATING CONDITIONS

Gas Chromatograph

Micro-Tek, Model 220, equipped with flame ionization and thermal conductivity detectors

Operating Conditions

Gas Analysis

Detector - Thermal Conductivity
Column - 5' x $\frac{1}{4}$ ", stainless steel, packed with chromosorb
102 (80/100 mesh)
Oven Temperature - 27°C
Detector Amperage - 250 mA
Sample Size - 1 cc

Paraffin Analysis

Detector - Flame Ionization
Column - 10' x 1/8", stainless steel, packed with:
1. 10% FFAP on chromosorb W
2. 3%DEXSIL on chromosorb W
Oven Temperature - 100°C isothermally for 1 minute
post-injection, then temperature-programmed
to 240°C at 5°C/minute
Sample Size - 1 microliter

Fatty Acid Analysis

Detector - Flame Ionization
Column - As for paraffins
Oven Temperatures - 125°C isothermally for 1 minute
post-injection, then temperature-programmed
to 240°C at 5°C/minute
Sample Size - 1 microliter

APPENDIX VII--Continued

Aromatic Analysis

Detector - Flame Ionization

Column - 6' x $\frac{1}{4}$ " stainless steel packed with 5% bentone 34
and 5% dinonylphthalate on chromosorb W

Oven Temperature - Isothermal at 125°C

Sample Size - 1 microliter

APPENDIX VIII

Drawing of Eh-pH measuring device

Fluid is drawn through plastic cyclinders in direction of arrows until all three electrodes are immersed. Measurements are made on pH meter.

APPENDIX IX

Eh AND pH VALUES

Sample	Eh (in millivolts)	pH
80 USH ₂ -IP	-212	5.2
80 LEH ₂ -IP	-188	5.8
80 USO ₂ -LP	-147	6.0
80 USO ₂ -LP	-158	5.5
160 USH ₂ -IP	-177	6.3
160 LEH ₂ -IP	-169	5.6
160 USO ₂ -HP	-171	6.1
160 LEO ₂ -IP	-143	6.0
240 LEH ₂ -HP	-196	6.2
240 LEH ₂ -IP	-265	5.7
240 USO ₂ -LP	-148	6.1
240 HEO ₂ -LP	-159	5.9

Eh and pH values of various samples of slurry material withdrawn from reaction vessels.

APPENDIX X

CONCENTRATION OF PARAFFINIC AND AROMATIC HYDROCARBON
AND HETERO-COMPOUND FRACTIONS
(As Normalized Weight Percent)

Sample	Paraffins	Aromatics	Hetero-Compounds
SBC	13.15	20.18	66.67
80 USH ₂ -LP	14.07	19.93	66.00
80 USH ₂ -IP	15.16	20.59	64.29
80 USH ₂ -HP	16.78	25.23	57.99
80 LEH ₂ -LP	61.01	18.04	20.95
80 LEH ₂ -IP	58.31	18.55	23.14
80 LEH ₂ -HP	60.00	19.50	21.50
80 USO ₂ -LP	25.39	16.04	58.57
80 USO ₂ -IP	15.99	16.06	67.95
80 USO ₂ -HP	15.56	15.40	69.04
80 LEO ₂ -LP	58.79	16.21	25.00
80 LEO ₂ -IP	57.51	20.21	22.28
80 LEO ₂ -HP	59.70	18.81	21.49
80 USA-LP	26.05	12.76	61.19
80 LEA-HP	57.11	17.72	25.16
160 USH ₂ -LP	9.62	32.04	58.34
160 USH ₂ -IP	11.23	21.19	67.59
160 USH ₂ -HP	6.85	24.04	69.10
160 LEH ₂ -LP	75.92	5.88	18.20
160 LEH ₂ -IP	78.10	2.20	19.70
160 LEH ₂ -HP	78.95	2.24	18.80

APPENDIX X --Continued

Sample	Paraffins	Aromatics	Hetero-Compounds
160 USO ₂ -LP	3.42	17.19	79.39
160 USO ₂ -IP	8.06	14.63	77.32
160 USO ₂ -HP	6.04	16.39	77.57
160 LEO ₂ -LP	76.33	2.13	21.54
160 LEO ₂ -IP	64.79	4.60	30.61
160 LEO ₂ -HP	53.39	21.12	25.49
160 USA-LP	13.05	36.10	50.85
160 LEA-LP	77.20	3.03	19.77
240 USH ₂ -LP	57.93	12.20	29.87
240 USH ₂ -IP	63.14	14.67	22.19
240 USH ₂ -HP	58.41	5.67	35.92
240 LEH ₂ -LP	50.08	14.60	35.32
240 LEH ₂ -IP	76.09	2.55	21.36
240 LEH ₂ -HP	73.38	6.26	20.36
240 USO ₂ -LP	57.28	12.13	30.59
240 USO ₂ -IP	56.54	16.66	26.80
240 USO ₂ -HP	62.27	15.46	22.37
240 LEO ₂ -LP	50.72	8.73	40.55
240 LEO ₂ -IP	59.42	6.58	34.00
240 LEO ₂ -HP	54.76	4.16	41.08
240 USA-LP	53.02	15.26	31.72
240 LEA-LP	53.03	15.26	31.71
KS 160H ₂ -1	10.39	23.51	66.10

APPENDIX X--Continued

Sample	Paraffins	Aromatics	Hetero-Compounds
KS 160H ₂ -3	8.46	17.87	73.67
KS 160H ₂ -10	18.82	16.19	64.99
KS 160H ₂ -30	17.81	18.33	63.86
KS 160H ₂ -100	25.39	30.37	44.24
KS 160H ₂ -300	26.18	22.53	51.29
TUS-US	64.92	13.51	21.57
160 TUS-H ₂	69.35	9.68	20.97
240 TUS-H ₂	32.61	28.02	39.37
160 TUS-O ₂	68.19	10.03	21.78
DOS-US	48.52	28.40	23.08
160 DOS-H ₂	55.36	25.02	19.62
300 AM-H ₂	34.15	27.64	38.21
300 EK-H ₂	56.26	15.97	27.77
UT1-US	47.10	14.19	38.71
160 UT1-H ₂	79.79	9.57	10.64
UT2-US	49.40	7.14	43.46
160 UT2-H ₂	40.28	13.27	46.45
SRL-US	44.23	15.38	40.39
160 SRL-H ₂	3.42	80.41	16.17
80 NPC-H ₂	28.62	12.01	59.37
160 NPC-H ₂	34.12	17.11	48.77
240 NPC-H ₂	27.23	27.94	44.83
160 CPC-H ₂	50.75	17.69	31.56

APPENDIX XI

Graph showing increased total lipid yield as a function of exposure time at 160° C.

VITA

William E. Harrison was born in Galveston, Texas, on April 7, 1942, to Macie and Thomas Harrison. He was educated in the Texas City, Texas, public school system where he graduated from Texas City High School in 1960. From 1960 to 1964 he attended junior colleges in the Houston and Baytown (Texas) school districts and worked as a seaman in the Merchant Marine. In 1964 he entered Lamar State College of Technology, where he received a B.S. degree in Geology in August, 1966. He entered the University of Oklahoma and received his M.S. in Geology in 1968. He joined Shell Oil Company in 1968 as an exploration geologist in the Houston Division and remained with that organization until 1971 when he enrolled at Louisiana State University. He left Baton Rouge in 1973 and joined the Atlantic Richfield Geoscience Research Group as a Senior Research Geochemist. In October of 1974, he joined the Oklahoma Geological Survey at the University of Oklahoma where he is currently employed. He received his Ph.D. in geology from Louisiana State University in December, 1976.

EXAMINATION AND THESIS REPORT

Candidate: William E. Harrison

Major Field: Geology

Title of Thesis: Experimental Diagenetic Study of a Modern Lipid-Rich Sediment.

Approved:

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

Date of Examination:

December 2, 1976