In memory of

Wolfgang Klaus Seifert

1931–1985

for his pioneering work in this field
This page intentionally left blank
CONTENTS

Preface xi

BIOLOGICAL MARKERS IN GRAHAMITES AND PYROBITUMENS 1
   J. A. Curiale

BIOMARKERS AS SOURCE INPUT INDICATORS IN SOURCE ROCKS OF SEVERAL TERRESTRIAL BASINS OF CHINA 25
   X. Zeng, S. Liu and S. Ma

A NEW TECHNIQUE FOR OIL/SOURCE-ROCK AND OIL/OIL CORRELATION 51
   F. Behar and R. Pelet

CORRELATION OF OIL-SOURCE BIOMARKERS IN RENQIU OILFIELD, NORTH CHINA 71
   B. Liu, X. Zeng and S. Liu

DETERMINATION OF THE MINERAL-FREE NICKEL AND VANADIUM CONTENTS OF GREEN RIVER OIL SHALE KEROGEN 89
   G. J. Van Berkel and R. H. Filby

ISOLATION, IDENTIFICATION AND CORRELATION OF PORPHYRINS FROM SOME CONTINENTAL CRUDE OILS, SOURCE ROCKS, OIL SHALES AND COALS OF CHINA 115
   Z. Yang and Z. Cheng

STUDIES ON THE STRUCTURE OF THE TERPENOID SULFIDE TYPE BIOLOGICAL MARKERS IN PETROLEUM 133
   J. D. Payzant, T. D. Cyr, D. S. Montgomery and O. P. Strausz

PORPHYRIN TYPES AND EPIMERS OF TRITERPANES AND STERANES IN COALS OF DIFFERENT RANKS IN SOUTHEASTERN UINTA REGION 149
   Y.-D. Gu, Y. Wang and T. F. Yen

BIOMARKER COMPARISONS OF MICHIGAN BASIN OILS 181
   K. W. Dunham, P. A. Meyers and J. Rullkötter
# CONTENTS

<table>
<thead>
<tr>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>RETENE AND PIMANTHRENE FROM CONTINENTAL SOURCE ROCKS IN CHINA</td>
<td>203</td>
</tr>
<tr>
<td>Z. D. Cheng</td>
<td></td>
</tr>
<tr>
<td>SEPARATION OF VANADIUM AND NICKEL COMPLEXES FROM THE ATHABASCA OIL SAND ASPHALTENES</td>
<td>221</td>
</tr>
<tr>
<td>D. Toulakou and R. H. Filby</td>
<td></td>
</tr>
<tr>
<td>USING MEAN SQUARE DIFFERENCE OF STERANES AND TRITERPANES TO CORRELATE CRUDE OILS AND SOURCE ROCKS FROM WESTERN-LIAOHE DEPRESSION</td>
<td>241</td>
</tr>
<tr>
<td>N. Jiang</td>
<td></td>
</tr>
<tr>
<td>DETERMINATION OF BIOMARKERS IN GEOLOGICAL SAMPLES BY TANDEM MASS SPECTROMETRY</td>
<td>253</td>
</tr>
<tr>
<td>R. P. Philp and M. Johnston</td>
<td></td>
</tr>
<tr>
<td>SOME FEATURES OF PORPHYRINS AND OTHER BIOMARKERS IN CRUDE OIL AND SOURCE ROCK FROM CONTINENTAL SALT-LAKE SEDIMENTS IN CHINA</td>
<td>275</td>
</tr>
<tr>
<td>Z. Yang, Y. Tong and Z. Fan</td>
<td></td>
</tr>
<tr>
<td>ANALYSIS OF CHLOROPHYLL DIAGENESIS III. THE EFFECT OF METALS ON THE PHORBIDE TO PORPHYRIN TRANSITION</td>
<td>293</td>
</tr>
<tr>
<td>P. P. Zelmer, J. B. Salimon and E. H. Man</td>
<td></td>
</tr>
<tr>
<td>SOME FEATURES OF PYROLYSIS-GAS CHROMATOGRAPHY-MASS SPECTROMETRY OF KEROGENS FROM CONTINENTAL SOURCE ROCKS IN CHINA</td>
<td>317</td>
</tr>
<tr>
<td>T. Tong and F. Jia</td>
<td></td>
</tr>
<tr>
<td>PRESENCE OF BENZOHOPANES, MONOAROMATIC SECOHOPANES, AND SATURATED HEXACYCLIC HYDROCARBONS IN PETROLEUMS FROM CARBONATE ENVIRONMENTS</td>
<td>331</td>
</tr>
<tr>
<td>G. G. L. Rinaldi, V. M. Leopold and C. B. Koons</td>
<td></td>
</tr>
<tr>
<td>TANDEM MASS SPECTROMETRIC ANALYSES OF GEOPORPHYRINS</td>
<td>355</td>
</tr>
<tr>
<td>J. M. E. Quirke, M. Perez, E. D. Britton and R. A. Yost</td>
<td></td>
</tr>
</tbody>
</table>
CONTENTS

INCORPORATION OF PETROPORPHYRINS INTO GEOCHEMICAL CORRELATION PROBLEMS 373
   P. Sundararaman, J. M. Moldowan and W. K. Seifert

A BIOLOGICAL MARKER STUDY OF A TERTIARY SPHAGNUM COAL FROM YUNAN PROVINCE, PRC 383
   J. Fu, G. Sheng, S. C. Brassell, G. Eglinton, A. P. Gower,
   D. Chen and D. Liu

APPLICATION OF BIOMARKERS FOR CHARACTERIZATION OF NATURAL WATERS: BLACK TRONA WATER 409
   Y. Wang, L.-S. Wang and T. F. Yen

Subject Index 437
PREFACE

There are several ways to assess the paleodepositional environment and diagenetic past of sedimentary rocks. When we concentrate our attention on the organic matter within those rocks, we are engaged in the science of organic geochemistry. This organic matter may be studied on several different levels. Its gross fossil or preserved structure is assessed through micropaleontology, and classical organic geochemistry deals with bulk properties of the organic matter. High resolution chromatographic methods often coupled with mass spectral analysis allow us to separate and analyze the organic components to the extent that they may be studied on the molecular level.

Thus another area of organic geochemistry has opened up in recent years which concentrates on the study of molecular fossils, or as they are sometimes called, geochemical biomarkers. These are complex organic molecules found in the geosphere which have survived or retained enough chemical structural information to be recognizable as having a biochemical origin.

Certain molecular structural features may be directly linked to a given type of biotic input. Acid catalyzed, photochemically or enzymatically induced alterations in biomarker structure generally reflect early diagenetic processes while higher energy, free radical and acid catalyzed, transformations reflect later diagenesis and catagenesis of the organic matter. In fact, the progress of these later reactions can be used to monitor the thermal history of a given sediment.

An economically important aspect of biomarker chemistry is that the same biomarkers and their transformations can be measured in crude oils as in sedimentary rock extracts, including crude oil source rocks. Thus biomarkers can be used to obtain many kinds of information useful in petroleum exploration such as maturity of potential source rocks and relative maturities among oils and rocks, aspects of environment of deposition of an oil source rock, including the types of organisms contributing to the lipids and the strength of anoxicity at the sediment water interface during deposition.

In this volume, the authors address a number of recent advances in the fundamental knowledge and applications of biological markers. These advances cover a wide spectrum of interests within the field ranging from the property exhibited by the natural asphalts and bitumen systems to its formation of different ranks of coals, from the diagenetic fate of biological compounds in natural waters and aerosols to the recognition of maturation effects in ancient sediments, and from the characterization of depositional environments of petroleum source rocks to the classification of precursor organisms by their molecular fossil remnants.

As a point of interest, this volume contains the most extensive collection of
chapters on geochemical markers of the continental basins of China yet to appear in the western literature. These Chinese basins provide a unique laboratory for geochemical research on paleo-lacustrine systems having diverse depositional environments.

Most chapters in this volume were originated initially from a Symposium entitled "Geochemical Biomarkers," sponsored by the Geochemistry Division of the American Chemical Society, at which, the present editors served as co-chairmen.

The authors would like to thank Seon-Hwa (Deseree) Moon, Nancy Yan and Linda Raftree for their editing assistance.

T. F. Yen
University of Southern California
Los Angeles, California

J. M. Moldowan
Chevron Oil Field Research Co.
Richmond, California
Grahamites and pyrobitumens are solid bitumens traditionally distinguished on the basis of their solubilities; pyrobitumens exhibit low solubility in carbon disulfide. In this paper biomarker analyses were used to examine grahamites from Oklahoma, Pennsylvania and Spain, albertites from Utah and Canada, imponite from Oklahoma, and ingramite from Utah. Although both grahamites and pyrobitumens contain a suite of biomarkers commonly associated with petroleum, including steranes, diasteranes and terpanes, relative concentrations of steroidal hydrocarbons vs terpanes are generally very low in comparison with crude oils. As with conventional crude oils, biomarker distributions of the extractable organic matter of solid bitumens are useful for bitumen-bitumen and oil-bitumen correlations, and assessment of source type and thermal maturation. Both 20S/20R- and 14β,17β(H)/14α,17α(H)-ethylcholestane ratios are useful in assessing solid bitumen maturation. Results suggest that biomarker analyses of grahamite and pyrobitumen extracts can assist the petroleum explorationist in assessing basinal prospects.
1. **INTRODUCTION**

Solid bitumens are defined, for the purposes of this paper, as non-coaly, allochthonous, solid, localized organic matter found in, or associated with, rocks. These materials are found throughout the stratigraphic section in sedimentary basins from around the world. The implications associated with their occurrence have often puzzled the petroleum explorationist: is the presence of solid bitumen noteworthy when exploring for oil and gas? What is the origin of this material? Can knowledge of the chemical composition of solid bitumens be applied to the search for petroleum? It is this last question that this paper addresses. More specifically, I will discuss the characteristics of certain common biological markers found in the solvent extractable fraction of two particular kinds of solid bitumens. Our knowledge concerning applications of biomarker technology to petroleum exploration can be expanded by studying the cyclic hydrocarbons in solid bitumens.

Solid bitumens have been traditionally classified in a generic fashion, utilizing carbon disulfide solubility, flame fusibility and hydrogen/carbon atomic ratios as classification criteria. Thus, "grahamite" is the name applied to a solid bitumen which is relatively soluble in carbon disulfide, yet fusible only with difficulty, whereas "albertite" is applied to those solids which are relatively insoluble in carbon disulfide, having H/C ratios greater than 1.0. As a class, solid bitumens having very low carbon disulfide solubilities are referred to as pyrobitumens, and include albertite, imposnite
BIOLOGICAL MARKERS IN GRAHAMITES AND PYROBITUMENS

and ingramite. A generic classification scheme such as this, while useful to those interested in the technological utility of solid bitumens, is of little use to the petroleum explorationist. Rather, the explorationist is concerned with the origin of the material. For this reason, a genetic classification scheme, based on organic geochemical criteria, is the classification method of choice for solid bitumens.

As part of a continuing effort to define the origin of various solid bitumens, the biomarker distributions of two generic classes of these materials, grahamites and pyrobitumens, have been examined. Previous work has suggested that, despite the largely insoluble nature of many of the samples involved, sufficient material can be extracted for geochemical analysis. Terpanes and steroid hydrocarbons, including steranes, diasteranes and aromatized steroids, were examined.

2. ANALYTICAL METHODS

A total of thirteen samples (Table I) were studied, including grahamites, albertites, ingramites and impsonites. Sample preparation methods are the same as those described for rock samples by Curiale; extractions were accomplished with a ternary solvent, having 70% toluene, 15% methanol and 15% acetone. Biological markers were analyzed in the total gas oil hydrocarbon fraction (with prior removal of n-paraffins), rather than as separate aliphatic and aromatic hydrocarbon fractions, in order to directly compare steranes and terpanes with aromatized
steroid hydrocarbons. Analyses were conducted on a Finnigan MAT Triple Stage Quadrupole. Instrument conditions are as in Curiale, excepting that analyses for solid bitumen hydrocarbon fractions were carried out using the MID mode, monitoring

TABLE I. Sample Identification

<table>
<thead>
<tr>
<th>Sample</th>
<th>Location</th>
<th>Age</th>
<th>Generic Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>AK7429</td>
<td>Sardis Mine east, OK</td>
<td>Miss</td>
<td>grahamite</td>
</tr>
<tr>
<td>AK7430</td>
<td>Jumbo Mine, OK</td>
<td>Miss</td>
<td>grahamite</td>
</tr>
<tr>
<td>AK7431</td>
<td>Sardis Mine west, OK</td>
<td>Miss</td>
<td>grahamite</td>
</tr>
<tr>
<td>AK7432</td>
<td>Pumroy Mine, OK</td>
<td>Miss</td>
<td>grahamite</td>
</tr>
<tr>
<td>AK7433</td>
<td>South Bald Pit, OK</td>
<td>Miss</td>
<td>grahamite</td>
</tr>
<tr>
<td>AK7434</td>
<td>Page Mine, OK</td>
<td>Miss</td>
<td>impsonite</td>
</tr>
<tr>
<td>AK7442</td>
<td>Washington County, Penn.</td>
<td>---</td>
<td>grahamite</td>
</tr>
<tr>
<td>AK7443</td>
<td>Page Mine, OK</td>
<td>Miss</td>
<td>impsonite</td>
</tr>
<tr>
<td>AK7444</td>
<td>Wasatch County, Utah</td>
<td>Eocene</td>
<td>albertite</td>
</tr>
<tr>
<td>AK7445</td>
<td>Wasatch County, Utah</td>
<td>Eocene</td>
<td>ingramite</td>
</tr>
<tr>
<td>AK7446</td>
<td>New Brunswick, Canada</td>
<td>Devonian</td>
<td>albertite</td>
</tr>
<tr>
<td>AK7452</td>
<td>Northern Spain</td>
<td>---</td>
<td>graham/imps</td>
</tr>
<tr>
<td>AK7453</td>
<td>Jumbo Mine, OK</td>
<td>Miss</td>
<td>grahamite</td>
</tr>
</tbody>
</table>

a Mississippian

parents and major fragments of the common biomarkers (a total of 23 ions). Relative distributions of biological markers discussed herein are based on area integrations of major fragment peaks. Comparisons of biomarkers are
based on the relationship between integrated areas taken from several chromatograms, and are uncorrected for relative fragment intensities for separate compound types.

A total of fifty-eight cyclic hydrocarbons were monitored. These include the 13β,17α-diasteranes having 27-29 carbon atoms; five regular steranes of each carbon number from C₂₇ through C₂₉ (5α,14α,17α(H),20S&R; 5α,14β,17β(H),20S&R; and 5β,14α,17α(H),20R); major monoaromatic and triaromatic steroid hydrocarbons; and tricyclic and pentacyclic terpanes, through the bis­homo­hopane epimers. This 58-compound distribution is histogram-formed, for the purposes of this paper, as shown in Figure 1: from left to right, diasteranes, steranes, monoaromatic steroids, triaromatic steroids, tricyclic terpanes, and pentacyclic terpanes. Specific compound identifications are presented elsewhere.

3. RESULTS

Biological marker concentrations in the grahamites and pyrobitumens vary with the content of extractable organic matter (EOM) in each sample. Percentage EOM values, and two distinctive biomarker ratios are shown in Table II. The values indicate an EOM range for grahamites and pyrobitumens of 12.4-25.8% and 0.5-7.1%, respectively. Note that, based on EOM yields, the sample having an unclear generic designation, AK7452 (Table I), is probably the pyrobitumen impsonite.
FIGURE 1 Distribution of fifty-eight (58) biological markers in sample AK7432, an Oklahoma grahamite.
TABLE II Numerical Data

<table>
<thead>
<tr>
<th>Sample</th>
<th>EOM(%)</th>
<th>a</th>
<th>b</th>
</tr>
</thead>
<tbody>
<tr>
<td>AK7429</td>
<td>16.0</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>AK7430</td>
<td>22.9</td>
<td>0.50</td>
<td>0.35</td>
</tr>
<tr>
<td>AK7431</td>
<td>16.9</td>
<td>0.48</td>
<td>0.29</td>
</tr>
<tr>
<td>AK7432</td>
<td>25.8</td>
<td>0.55</td>
<td>0.52</td>
</tr>
<tr>
<td>AK7433</td>
<td>23.7</td>
<td>0.45</td>
<td>0.37</td>
</tr>
<tr>
<td>AK7434</td>
<td>0.5</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>AK7442</td>
<td>12.4</td>
<td>0.61</td>
<td>0.30</td>
</tr>
<tr>
<td>AK7443</td>
<td>1.2</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>AK7444</td>
<td>7.1</td>
<td>--</td>
<td>0.83</td>
</tr>
<tr>
<td>AK7445</td>
<td>6.8</td>
<td>--</td>
<td>0.77</td>
</tr>
<tr>
<td>AK7446</td>
<td>2.8</td>
<td>0.39</td>
<td>0.19</td>
</tr>
<tr>
<td>AK7452</td>
<td>2.7</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>AK7453</td>
<td>13.2</td>
<td>0.46</td>
<td>0.34</td>
</tr>
</tbody>
</table>

a. \((5a,14B,17B,20R&S/5a,14B,17B,20R&S+5a,14a,17a,20R&S)\)

b. tricyclic terpanes/pentacyclic terpanes

Despite the fact that the grahamites and pyrobitumens examined represent a wide range of biomarker characteristics, certain common features are present in some samples. For example, concentrations of pentacyclic terpanes are equal to or greater than those of tricyclic terpanes in all samples except the Oklahoma impsonites (containing only diasteranes) and the Utah

pyrobitumens (AK7444, AK7445) (Table II). Monoaromatic and triaromatic steroid hydrocarbons are either absent or in extremely low concentration in all grahamites and pyrobitumens examined. In the single sample containing both monoaromatic and triaromatic steroid hydrocarbons (AK7446), the triaromatic compounds dominate.

These characteristic features are shown together in Figure 2, for six solid bitumens. The distributions in Figure 2 appear to be controlled by at least two processes, namely source input and subsequent organic matter alteration. For example, the similarities in the bio-
Biological markers have found recent applications in several aspects of petroleum geochemistry. They are most commonly used as source organic matter indicators, in an oil-oil or oil-source rock correlation fashion.\(^6,24,26\) In addition, their uses as maturation parameters\(^5\) and indicators of biodegradation\(^2,23,25\) are now commonplace. The results of the present study of biomarkers in solid
FIGURE 3 Ternary diagram showing the distribution of $5\alpha,14\alpha,17\alpha,20R$ steranes by carbon number ($C_{27}, C_{23}, C_{29}$), for seven grahamites and pyrobitumens.

bitumens show that these common uses in petroleum and source rock extracts are immediately extendable to the extractable organic matter content of grahamites and pyrobitumens. Consequently, biological markers can be utilized for bitumen-bitumen correlations, estimates of thermal maturity of solid bitumens, and determination of
the post-expulsion effects of biodegradation on these materials. Taken together, knowledge of the biological marker distribution in the EOM of grahamites and pyrobitumens provides a powerful tool for elucidating the genesis of these solids in sedimentary basins.

4.1 Correlation Applications

Recent work involving sterols in recent sediments has suggested that the distribution of sterol carbon number in sediments is indicative of depositional environment. This work has been extended to steranes found in ancient organic matter, in an effort to deduce source rock depositional environment, and concurrently provide a correlation tool (presumably) independent of subsequent changes due to thermal maturation or other types of alteration. Figure 3 shows the sterane carbon number distributions for the 5α,14α,17α,20R steranes, for five grahamites and two pyrobitumens. The separation of the three sample groups suggests differing source controls for the Canadian albertite, Utah ingramite and Oklahoma grahamites. Further, the similar sterane carbon number distributions for the Oklahoma grahamites implies a common source for these samples, a conclusion previously reached using bulk geochemical parameters such as elemental concentrations and stable isotope ratios, as well as pyrolysis-GCMS data. The similarities among the Oklahoma grahamites based upon 5α,14α,17α,20R sterane carbon numbers are clearly seen in the entire sterane distribution as well. M/z 217 mass chromatograms for four of these bitumens are
FIGURE 4  M/z 217 mass chromatograms for four Oklahoma grahamites.

shown in Figure 4. Note that the distributions of regular and rearranged steranes are extremely similar from sample to sample, regardless of the fact that solubilities of these solid bitumens range from 13% to 26%. The distributions of terpanes in these four solid bitumens (Fig. 5) are not quite as similar as those of
FIGURE 5 M/z 191 mass chromatograms for the same samples shown in Figure 4.
the steranes, although common characteristics are certainly present. One unusual difference among the samples is the variability in the relative concentration of the \( \text{C}_{28} \) and \( \text{C}_{29} \) tricyclic terpanes (Fig. 5). This variability tends to coincide with solubility trends of the grahamites: the most soluble samples appear to contain the highest relative amounts of the higher carbon number tricyclic terpanes (Table II). Another component which appears to co-vary with tricyclic terpane content, one which is clearly visible in Figure 5, is the relative concentration of 28,30-bisnorhopanes. These compounds, at least two isomers of which are apparent in these chromatograms\textsuperscript{22}, are in highest concentration in AK7432, also the most soluble of the Oklahoma grahamites. Further examination of this sample, and subsequent examination of the other Oklahoma grahamite extracts, revealed the presence of the unusual compound 25,28,30-trisnorhopane. This compound (Fig. 6) has been noted in several California Monterey oils, and well as extracts from North Sea rock samples and recent sediments in the Norwegian Sea\textsuperscript{12}. Nevertheless, its occurrence is generally regarded as unusual\textsuperscript{6}. In addition to bitumen-bitumen correlation utilizing extractable biomarkers, it would also be useful if these compounds could be used for oil-solid bitumen correlation efforts. That this is feasible is shown by the close correlation between the Oklahoma grahamites and an oil produced from similar age rocks nearby. This oil (Oil #45 of ref. 7) has been shown previously, using bulk geochemical parameters, to be commonly sourced with these Oklahoma grahamites\textsuperscript{10}. The ability to geochemically
FIGURE 6  M/z 163, 177 and 191 mass chromatograms for sample AK7432, an Oklahoma grahamite exhibiting the highest relative concentration of 28,30-bisnorhopanes.
correlate a solid bitumen with a crude oil using biological marker data provides a specific method for assessing the origin of solid bitumens encountered during the exploration process. Continuing efforts in this area include attempts to correlate the pyrobitumens of this study with crude oils from similar locations.

4.2 Thermal Maturity of Solid Bitumens

One of the earliest uses of biological marker geochemistry, the determination of the so-called thermal maturity of organic matter, has recently become one of the most fruitful aspects of biomarker research\(^5,19\). The nature of the two major origins of solid bitumens (i.e., altered petroleum vs immature petroleum) makes the determination of the thermal maturity of solid bitumens of critical importance. The maturity question is of particular interest for pyrobitumens such as impsonite, insomuch as the insolubility of these materials is traditionally viewed as the result of extensive thermal alteration\(^16\). Consequently, the common biomarker thermal maturity parameters, such as epimer ratios, have been calculated for the solid bitumen extracts, for the purpose of determining the maturity of these samples and the genetic connotation, if any, of the term "pyrobitumen". Although the biochemical stereoisomeric configuration of steranes at the 14 and 17 positions is \(\alpha\alpha\), empirical observations have shown that this isomer converts to the \(\beta\beta\) configuration with increasing thermal input\(^17,24\). While this isomerization is not as chemically straightforward as the
more classical 20R\rightarrow 20R+20S sterane or 22R\rightarrow 22R+22S hopane epimerization, it can be used as a general indicator of thermal maturity ranking. For this reason, the 
\[ \frac{\text{14B,17B}}{\text{14B,17B} + \text{14a,17a}} \] 
ratio of the ethylcholestanes has been calculated (where data are available) for the grahamites and pyrobitumens of the present study (Table II). Results indicate that, while the \( \frac{\text{8B/8B+8a}}{\text{66/66+aa}} \) ratios of the grahamites range from 0.45-0.61, and suggest marginal to full thermal maturity, the single pyrobitumen for which data are available (AK7446) has a \( \frac{\text{8B/8B+8a}}{\text{66/66+aa}} \) ratio of only 0.39, suggesting immaturity. The immature appearance of the sterane distribution of this Canadian pyrobitumen can be seen in the top m/z 217 chromatogram of Figure 7.

Using a second sterane isomer ratio, namely the 20S/20R ethylcholestane epimer ratio, another pyrobitumen can be shown to be even more immature than AK7446. The m/z 217 mass chromatogram for sample AK7445, the Utah ingramite, is shown at the bottom of Figure 7.

Here, the \( \frac{\text{8B/8B+8a}}{\text{66/66+aa}} \) ratio is even less than that of sample AK7446. Even more interesting however, is the extremely low \( \frac{\text{20S/20R-5a,14a,17a}}{\text{20S/20R}} \) ethylcholestane ratio: approximately 0.2. This value is lower than that for any crude oil known to the author. This extremely immature sample, therefore, is almost certainly not the result of alteration of a conventional crude oil, but rather appears to have been derived from "extrusion" of organic matter from a rich, albeit immature source rock. Further, it is clear that the term "pyrobitumen" possesses no genetic connotation whatsoever: while some pyrobitumens such as impsonites probably result from high
thermal regimes, others such as the Utah ingramite (AK7445) discussed here originated with very low thermal input.

4.3 Solid Bitumens -- Source Rock Characteristics

In addition to low thermal maturity, the m/z 217 mass chromatograms in Figure 7 reveal one other characteristic that these two pyrobitumens have in common: the almost total lack of rearranged steranes. The absence of diasteranes in a source rock or oil is often considered to imply a lack of smectite family clays (e.g., montmorillonite) during diagenesis of the sediments, insomuch as such clays are thought to catalyze the backbone rearrangement of biochemically-configured steroidal hydrocarbons. Thus the absence of diasteranes has been noted in oils associated with non-clastic sequences, as such as the oils and rocks of the California mid-Miocene. The absence of these rearranged compounds in the two pyrobitumens shown in Figure 7 can, therefore, tentatively be attributed to a non-clastic source rock. Such a conclusion is consistent with the current stratigraphic location of the Utah ingramite: this solid bitumen is found in the calcareous Green River Formation of the Uinta Basin. Although no definitive solid bitumen-source rock correlation of the Canadian albertite has been attempted (however, see ref. 18), it is very probable that this albertite was also sourced from a calcareous, or at least low-clastics, source rock.
FIGURE 7 M/z 217 mass chromatograms for two pyro-
bitumens; both samples are relatively immature as shown by $^{14}B,^{17}B/^{14}a,^{17}a$ ratios in the Canadian albertite and $20S/20R$ ratios in the Utah ingramite.

Thus, knowledge of the extractable biological marker distribution in solid bitumens can be used to assess source rock type, in an analogous manner to the methods utilized for crude oils.

5. SUMMARY

The petroleum explorationist is commonly faced with the question of the genesis of solid bitumens encountered in the well bore or at outcrop. Because grahamites and pyro-bitumens are related to both crude oils and crude oil source rocks, biological marker technology applicable to oils and rock extracts has a direct application to the study of these solid bitumens. Conventional biomarker efforts in such areas as organic matter origin, correlation and maturation, can be directly applied to the extractable organic matter fraction of grahamites and pyrobitumens. This study has shown that such efforts can be successful in grouping bitumens into co-genetic families, and in assessing the thermal maturity of pyrobitumens. Biological marker studies can assist in assessing the origin of certain solid bitumens. However, it must be remembered that over 99% of certain pyrobitumens are insoluble in common organic solvents. Thus, when we study the extractable fraction we study only 1%
of the sample, and conclusions about the other 99% must be inferred from these results. Future efforts at elucidating the biological marker composition of largely insoluble grahamites and pyrobitumens should therefore be directed toward an understanding of this insoluble fraction, most immediately via pyrolysis-gas chromatography-mass spectrometry. It is only through examining the total biomarker content that we can expect to fully understand the chemical history of grahamites and pyrobitumens.
ACKNOWLEDGEMENTS

I wish to thank the following for their contributions to this study: D. Cameron, D. V. Davis and D. Cardin, for their assistance with the GCMS data; G. H. Smith, for contributing several samples, providing supplementary data, and generously giving me the benefit of his thinking concerning solid bitumens and their origin; M. Jacob and S. A. Bharvani, for laboratory processing of samples, and M. Jicha for typing. I also extend my appreciation to J. M. Moldowan for a thorough review of the manuscript, and to Union Science & Technology Division management for permission to publish these results.

REFERENCES


Biological Markers in Grahamites and Pyrobitumens


Biomarkers as Source Input Indicators in Source Rocks of Several Terrestrial Basins of China


A New Technique for Oil/Source-Rock and Oil/Oil Correlation


9. A. VAN DORSSELAER, These de Doctorat-es-Sciences, Universite Louis Pasteur, Strasbourg, France (1975)


11 A ENSMINGER, These de Doctorat-es-Sciences, Universite Louis Pasteur, Strasbourg, France (1977)


Correlation of Oil-Source Biomarkers in Renqiu Oilfield, North China


Determination of the Mineral-Free Nickel and Vanadium Contents of Green River oil Shale Kerogen


6. J.D. SAXBY, in Oil Shale, edited by T.F. Yen and G.V. Chilingarian (Elsevier, Amsterdam, 1976), Chap. 6, pp. 103-120.


Studies on the Structure of the Terpenoid Sulfide type Biological Markers in Petroleum


Porphyridin Types and Epimers of Triterpanes and Steranes in Coals of Different Ranks in Southeastern Uinta Region


2. E. C. DAPPLES, Econ. Geol., 34, 369-398, (1939); also 35, 109, (1939).


15. T. F. YEN, Genesis and Degradation of Petroleum Hydrocarbons in Harine Environments, Marine Chemistry in


Biomarker Comparisons of Michigan Basin Oils

202 K.W. DUNHAM, P.A. MEYERS AND J. RULLKOTTER

Separation of Vanadium and Nickel Complexes from the Athabasca Oil Sand Asphaltenes


240 DESPINA TOOULAKOU AND ROYSTON H. FILBY


Analysis of Chlorophyll Diagenesis III.
The Effect of Metals on the Phorbide to Porphyrin Transition

7-ethyl-7-despropiomesopyropheophorbide PE(-COz)
7-ethyl-7-despropipoerythrin DOMPP(-COz)
7-ethyl-7-despropiodeoxymesopyropheophorbide DPEP
deoxophyloerythroetioporphyrin DOMPP
deoxomesopyropheophorbide-a methyl ester .. DPE
deoxophyloerythrin methyl ester This page intentionally left blank
Presence of Benzohopanes, Monoaromatic Secohopanes, and Saturated Hexacyclic Hydrocarbons in Petroleums from Carbonate Environments

Incorporation of Petroporphyrins into Geochemical Correlation Problems


Geomimetic synthesis, structure assignment and geochemical correlation applica


Organic Geochemistry


Science 223, 1075-76.


J. W. de Leeuw and G. W. M. Lijmbach) Organic Geochemistry
6,605-617,

Application of Biomarkers for Characterization of Natural Waters: Black Trona Water


7.

8.

9.


434 WANG, Y., WANG, L.-S., YEN, T. F.


31. Trendel, J.-M., Restle, A., Connan, J. and Albrecht,

