



0016-7037(95)00225-1

The ratios of dibenzothiophene to phenanthrene and pristane to phytane as indicators of depositional environment and lithology of petroleum source rocks

WILLIAM B. HUGHES,¹ ALBERT G. HOLBA,² and LEON I. P. DZOU²¹ARCO International Oil and Gas Company, 2300 West Plano Parkway, Plano, TX 75075, USA²ARCO Exploration and Production Technology, 2300 West Plano Parkway, Plano, TX 75075, USA

(Received June 24, 1994; accepted in revised form May 19, 1995)

Abstract—The ratio of dibenzothiophene to phenanthrene and the ratio of pristane to phytane, when coupled together, provide a novel and convenient way to infer crude oil source rock depositional environments and lithologies. Such knowledge can significantly assist in identifying the source formation(s) in a basin thereby providing valuable guidance for further exploration. The ability to infer this information from analysis of a crude oil is especially valuable as frequently the earliest samples in a new area may be shows and/or drill stem test samples from exploratory wells which are characteristically drilled on structural highs stratigraphically remote from the source formation(s).

A cross-plot of dibenzothiophene/phenanthrene versus the pristane/phytane ratios measured on seventy-five crude oils from forty-one known source rocks ranging in age from Ordovician to Miocene consistently classified the oils into the following environment/lithology groups: marine carbonate; marine carbonate/mixed and lacustrine sulfate-rich; lacustrine sulfate-poor; marine and lacustrine shale; and fluvial/deltaic carbonaceous shale and coal. The dibenzothiophene/phenanthrene ratio alone is an excellent indicator of source rock lithology with carbonates having ratios > 1 and shales having ratios < 1 .

The dibenzothiophene to phenanthrene and the pristane to phytane ratios can also be used to classify source rock paleodepositional environments. The classification scheme is based on the premise that these ratios reflect the different Eh-pH regimes resulting from the significant microbiological and chemical processes occurring during deposition and early diagenesis of sediments. The dibenzothiophene/phenanthrene ratio assesses the availability of reduced sulfur for incorporation into organic matter and the pristane/phytane ratio assesses the redox conditions within the depositional environment. Interpretation of these ratios has been aided by quantitative biomarker analysis and by carbon isotope data for pristane and phytane obtained by gas chromatography-isotope ratio mass spectrometry.

1. INTRODUCTION

Various types of crude oil geochemical data have been previously proposed as indicators of the depositional environment and lithology of the parent source rock. These may be divided into three broad categories: biomarkers, carbon isotopes, and elemental composition. Examples of biomarker applications includes the presence or absence of C_{30} desmethyl steranes to discriminate between marine and nonmarine depositional environments (Moldowan et al., 1985; Peters et al., 1986) and the concentrations of various isoprenoid, sterane, and terpane biomarkers to distinguish marine from lacustrine environments and to subdivide marine into evaporitic, deltaic, and carbonate environments (Mello et al., 1988). High diasteranes relative to steranes can serve as indicators of source rocks containing acidic clays (Sieskind et al., 1979) and the distribution of methyl dibenzothiophene isomers to distinguish oils derived from carbonate versus siliciclastic source rocks (Hughes, 1984). Comparison of the carbon isotope ratios of the saturate and aromatic fractions has been proposed (Sofer, 1984) to distinguish between marine-derived and nonmarine derived crude oils (strictly speaking, this method addresses the origin of the organic matter which is frequently characteristic of the environment of deposition). A comparison of saturate and aromatic fraction deuterium isotope concentrations has been mentioned as a way to differentiate carbonate-

derived and shale-derived oils (Schoell, 1984). Examples of the use of elemental composition are the proportionality of vanadium to nickel to infer Eh-pH conditions in the depositional environment (Lewan, 1984) and the association of high sulfur contents with carbonate source rocks (Tissot and Welte, 1984). For additional information on geochemical indicators for depositional environment and lithology, the reader is referred to several recent compilations and reviews (Peters and Moldowan, 1993; Volkman, 1988; Philp and Lewis, 1987; Powell, 1987).

In this study, we propose that two molecular indicators, the ratio of dibenzothiophene to phenanthrene and the ratio of pristane to phytane, when coupled together, provide a novel, convenient, and powerful way to infer crude oil source rock depositional environments and lithologies and to classify source rock paleodepositional environments in terms of their most important microbiological and chemical processes.

The pristane/phytane ratio has had a long history in organic geochemistry. Powell and McKirdy (1973) were apparently the first to suggest that the ratio of pristane (PR) to phytane (PH) was an indicator of the redox conditions in the depositional environment. In a significant study of recent sediments, Didyk et al. (1978) suggested that PR/PH ratios < 1 indicate anoxic environments, PR/PH ratios around 1 indicate alternating oxic, and anoxic conditions and PR/PH ratios > 1 indicate oxic conditions. To explain this correlation, it was

suggested that pristane and phytane originate from the oxidation (and subsequent decarboxylation) or reduction of the phytol side chain of chlorophyll, respectively, and that the pathway which dominates is controlled by the oxic or anoxic conditions during sedimentation. More recently, a number of objections have been raised to this interpretation (ten Haven et al., 1987) which include the possibility of sources other than chlorophyll-derived phytol, i.e., archaeobacterial lipids for phytane (Risatti et al., 1984; Volkman et al., 1986) and tocopherols for pristane (Goossens et al., 1984), and the geological fact that "all fine-grained nearshore, shelf, and hemipelagic sediments are anoxic below a surface oxic layer" (ten Haven et al., 1987).

The dibenzothiophene/phenanthrene ratio is much less familiar and is seldom used. One of the major applications of the ratio is as an indicator of water washing of crude oils (Palmer, 1984; Dahl and Spears, 1986; Williams et al., 1986; Requejo and Halpern, 1990). Decreased ratios are observed in water-washed oils relative to the unaltered oil due to the greater water solubility of dibenzothiophene compared to phenanthrene. This ratio has also been used as part of a detailed study comparing the organic input to a carbonate-anhydrite sequence from Guatemala although no interpretation was given for the ratio (Connan et al., 1986).

This study is divided into two parts. First, we demonstrate the utility of a cross-plot of the dibenzothiophene to phenanthrene ratio versus the pristane to phytane ratio to infer the depositional environment and lithology of crude oil source rocks. The second part of the study describes the use of the dibenzothiophene/phenanthrene and the pristane/phytane ratios for classifying depositional environments. This has led to a new system for classifying depositional environments based on the premise that the values of these two ratios reflect the different Eh-pH regimes resulting from the significant microbiological and chemical processes occurring during deposition and early diagenesis of sediments. Preliminary findings have been previously reported (Hughes et al., 1989).

2. SAMPLES AND ANALYTICAL METHODS

2.1. Samples

Table 1 lists the crude oils in this study along with the name and geologic age of their source and reservoir formations, and information relating to sample origin including country and sedimentary basin. The oils were selected on the basis that strong geochemical documentation for their source formation exists, either in the literature (key references are given in the last column of Table 1) or by a detailed comparison of molecular and isotopic properties of our samples to oils in the literature. Exceptions to this statement are the two offshore Gulf of Mexico oils (1888 and 1104). In these cases, although the source rocks have not been conclusively identified, it is highly probable that the source rocks are marine shales (Thompson et al., 1990). The seventy-five oils in Table 1 represent forty-one different source rocks ranging in age from Ordovician to Miocene.

The oils in Table 1 were classified according to the depositional setting and dominant lithology of their source rocks based on the literature. Environments have been classified as marine, fluvial/deltaic, and lacustrine whereas lithologies are described as carbonate, mixed (marl, argillaceous carbonate and siliceous/phosphatic shale), shale, and coal/carbonaceous shale.

The oils were screened by gas chromatography for possible alteration, such as biodegradation, which could affect the pristane/phytane ratio (Connan, 1984), and/or water-washing, which could affect

the dibenzothiophene/phenanthrene ratio (Palmer, 1984). Any oils showing signs of alteration were excluded from the study.

2.2. Analytical Methods

The analytical methods used for LC, GC, and GC/MS analysis of the oils have been previously reported (Dzou and Hughes, 1993). Selected saturate fractions were analyzed by gas chromatography-isotope ratio mass spectrometry (GC-IRMS) using a VG Isochrom I/II system interfaced to a Hewlett Packard 5890 gas chromatograph equipped with a 50 m \times 0.32 mm i.d. fused silica column coated with SE54 stationary phase. The GC oven was started at 50°C, held isothermally for 2.0 min, and then programmed to 300°C at 5°C/min and held isothermally for 40 min. These analyses were performed in-house and by Geolab Nor, Trondheim, Norway.

2.3. Quantitative Biomarker Analysis

The concentrations of selected components were determined by the surrogate standard method in which standards are added to the pentane soluble fraction of the de-asphalted oil prior to liquid chromatographic separation. 5 β -Cholane was used to quantify components in the saturates and perdeutero-anthracene in the aromatics. The concentrations of pristane and phytane were determined from GC/MS analysis of the saturate fraction using the ion m/z 183. The pristane/phytane ratio obtained in this manner was compared with the ratio obtained from GC analysis of the saturate fraction using peak areas. In all cases, the two ratios agreed very well, indicating that under our GC conditions no coelution of pristane with 2,6,10-trimethyl-7-(3-methylbutyl)-dodecane occurs (Yon et al., 1982). The concentrations of phenanthrene, dibenzothiophene, methylphenanthrenes, and methyl dibenzothiophenes were determined from GC/MS analysis of the aromatic fraction using the ions m/z 178, 184, 192, and 198, respectively.

Response factors for the components of interest relative to the internal standards were determined by the use of synthetic mixtures of the pure compounds and are listed in Appendix A. Concentrations were calculated as $\mu\text{g/g}$ of whole oil. The reproducibility of the quantitative data depends somewhat on the concentration of the component, however, in general the reproducibility of concentrations from multiple GC/MS analyses of the same sample was $\pm 5\%$. Response-corrected concentration data are given in Appendix B.

3. RESULTS AND DISCUSSION

3.1. Empirical Observations

The concentrations of pristane, phytane, dibenzothiophene, the sum of all methyl dibenzothiophenes, phenanthrene, and the sum of all methylphenanthrenes were determined for the seventy-five oils in Table 1 (see Appendix B). The dibenzothiophene/phenanthrene (DBT/PHEN), sum of methyl dibenzothiophenes/sum of methylphenanthrenes (MDBT/MPHEN), and pristane/phytane (PR/PH) ratios calculated from the concentration data; the weight percent sulfur; and the API gravity for the oils are listed in Table 2. The DBT/PHEN ratio is plotted against the PR/PH ratio in Fig. 1 for the oils in Table 1 excepting the lacustrine and Ordovician oils which are considered separately.

Figure 1 reveals that oils generated by source rocks of similar depositional environments and lithologies group together. Thus, all oils from marine, predominantly nonsiliciclastic source rocks have DBT/PHEN ratios > 1 and PR/PH ratios < 1 . This includes oils derived from marine carbonate and marine mixed source rocks. Within this group, oils from marine mixed source rocks, such as the siliceous/phosphatic/calcareous Monterey Shale and the Phosphoria, tend to have

DBT/PHEN ratios < 3 , although some of the oils classified as being from marine carbonate sources, such as the Niagara and the Cretaceous Middle Eastern oils, also have DBT/PHEN ratios < 3 .

In contrast, all oils from marine siliciclastic and fluvial/deltaic source rocks have DBT/PHEN ratios < 0.5 and PR/PH ratios > 1 . Within this group, oils generated from marine shales, such as the Kimmeridge Clay, Woodford, Mowry Shale, Gulf of Mexico source, and Cook Inlet Tuxedni, have PR/PH ratios < 3 , whereas those generated from nonmarine carbonaceous shales and coals have PR/PH ratios > 3 . Thus, the DBT/PHEN ratio alone is a good discriminator of siliciclastic versus nonsiliciclastic source rock lithologies.

Based on the associations between source rock depositional environment and lithology and values of the DBT/PHEN and PR/PH ratios, Fig. 1 can be divided into the zones shown in the figure and described in Table 3. Zone 1 has been subdivided into two zones: Zone 1A contains oils derived from marine carbonate source rocks and Zone 1B contains oils derived from marine carbonate and marine mixed source rocks.

The Smackover-derived oils demonstrate the utility of the DBT/PHEN vs. PR/PH plot for detecting and characterizing different facies of the same source formation. Oils from the Mississippi Interior Salt Basin fall in Zone 1 as expected, whereas oils from the Manila Embayment fall in Zone 3. Thus, while the Smackover in both areas is nominally a marine carbonate, our results show there is a significant difference in source rock depositional environment and/or lithology of oils from the Mississippi Interior Salt Basin compared with oils from the Manila Embayment. The total sulfur contents of the oils are also considerably different ranging from 1.0 to 5.7% (average 2.1%) for five oils from the Mississippi Interior Salt Basin and 0.1 to 0.6% (average 0.3%) for three oils from the Manila Embayment. Fragmentograms for the m/z 217 ion from GC/MS analysis indicate oil 841 from the Manila Embayment has a dramatically increased diasterane content compared with oil 808 from the Mississippi Interior Salt Basin. Traces for the m/z 191 ion of same two oils shows the norhopane/hopane and C_{35}/C_{34} homohopane ratios are < 1 in the Manila Embayment oil but > 1 in the Mississippi Interior Salt Basin oil.

Our results are in agreement with several recent reports of the existence of two types of Smackover oils (Sofer, 1988; Sassen, 1989, 1990; Claypool and Mancini, 1989; Wenger et al., 1990). In particular, Claypool and Mancini (1989) concluded on the basis of sulfur content, pristane/phytane ratio, and isotope data that higher salinity, lower oxygen content and less input of clay minerals and terrigenous organic matter prevailed in the Mississippi Interior Salt basin compared with the Manila embayment in southwestern Alabama. Thus, we have classified the three Manila Embayment Smackover oils as marine shale oils in Table 1 and Fig. 1.

3.2. Lacustrine Oils

Oils derived from lacustrine source rocks (see Table 1) plot in Zones 1B, 2, and principally Zone 3 (Fig. 2a). With the exception of Zone 2, these results indicate that the cross-plot of the DBT/PHEN and PR/PH ratios does not distinguish

oils derived from marine vs. lacustrine source rocks. As will be seen below, this is a consequence of the fact that the DBT/PHEN and PR/PH ratios reflect the Eh and pH, irrespective of whether the depositional environment is marine or lacustrine. Additional information, such as the presence or absence of C_{30} n -propyl steranes (Peters and Moldowan, 1993), must be used to distinguish lacustrine from marine oils.

3.3. Ordovician Oils

With the exception of sample 2474, the eight Ordovician oils in this study (Table 1) have the "typical" Ordovician fingerprint, i.e., a distinct odd-over-even preference in the n - C_{11} to n - C_{19} range, very low amounts of heavier normal alkanes, and extremely low concentrations of isoprenoids (Reed et al., 1986). The oils fall predominantly in Zone 3 in the DBT/PHEN vs. PR/PH plot (Fig. 2b) as a result of their very low DBT/PHEN ratios and PR/PH ratios around 1.

According to Fig. 2b, the Ordovician oils are derived from marine shale source rocks which is inconsistent with the ostensibly carbonate source rocks of some of the oils, i.e., Viola, Trenton, Pacoota, and Knox. The very low DBT/PHEN ratios may be the result of the very high phenanthrene concentrations in these oils (see Appendix B); however, their very low total sulfur contents indicate a general absence of organosulfur components. At this time, we have no explanation for the very low DBT/PHEN ratios of the Ordovician oils but it may be a result of the fact that these oils are derived from a very specific type of organic matter, i.e., the remains of *Gloeocapsomorpha prisca*, which has a very specific composition and low reactivity toward reduced sulfur (Douglas et al., 1991).

3.4. Effect of Maturity on the PR/PH and DBT/PHEN Ratios

Thermal maturity appears to modify only slightly the PR/PH and DBT/PHEN ratios for suites of oils from a common source rock. Previous work has shown that maturity is the major and source a minor control on the composition of the four Kimmeridge Clay Formation-derived oils from the greater Ekofisk area of the North Sea in Table 1 (Hughes et al., 1985). The PR/PH ratios for these oils show little (1.35–1.45), and no systematic, change with maturity which increases in the order Valhall $<$ Eldfisk $<$ Ekofisk $<$ Albuskjell (Samples 2–5 in Table 1) from a vitrinite reflectance equivalent of approximately 0.6 to 1.0%.

The source organic facies for the five Smackover oils within the Mississippi Interior Salt Basin appears to remain essentially constant (Claypool and Mancini, 1989). The observed differences in total sulfur content (5.70–0.97%) and API gravity (17.1–41.0°) are believed to be due to differences in thermal maturity resulting from differences in reservoir temperature (74–90°C). Based on these criteria, the Smackover oils may be divided into two groups: the Toxey oil, which has a sulfur content of 5.70%, and API gravity of 17.1° and the four remaining oils which have sulfur contents of 0.97–1.70% and API gravities of 33.8–41.0°. The Toxey oil appears to be of early oil window maturity ($R_c = 0.62$ based on the empirical correlation between methyl dibenzothiophene

Table 1. Origin of crude oils in study

Sample Number	Source Fm./Age	Reservoir Fm./Age	Location	Basin	Reference
Marine Carbonate					
1	Khatiyah / Cenomanian	Illam / U. Cretaceous	U.A.E. / Dubai	Arabian-Persian Gulf	Hughes, 1984
805	Smackover / Jurassic	Smackover / Jurassic	USA / Alabama	Miss. Inter. Salt	Wenger et al., 1990
808	Smackover / Jurassic	Smackover / Jurassic	USA / Alabama	Miss. Inter. Salt	Wenger et al., 1990
819	Smackover / Jurassic	Smackover / Jurassic	USA / Alabama	Miss. Inter. Salt	Wenger et al., 1990
820	Smackover / Jurassic	Smackover / Jurassic	USA / Alabama	Miss. Inter. Salt	Wenger et al., 1990
823	Smackover / Jurassic	Smackover / Jurassic	USA / Alabama	Miss. Inter. Salt	Wenger et al., 1990
959	Niagara / Silurian	Niagara / Silurian	USA / Michigan	Michigan	Rulikötter et al., 1986
1281	Lodgepole / Miss.	Mission Canyon / Miss.	USA / North Dakota	Williston	Osadetz et al., 1992
1337	Lodgepole / Miss.	Mission Canyon / Miss.	USA / North Dakota	Williston	Osadetz et al., 1992
1587	{Thebes-Brown	Rudeis / E. Miocene	Egypt	Red Sea Rift	{Rohrbach, 1983 &
1588	Limestone /	Rudeis / E. Miocene	Egypt	Red Sea Rift	Chowdhary et al., 1987}
2970	Eocene-Cretaceous}	Nubia C / Devonian	Egypt	Red Sea Rift	
2227	Sunniland / Cretaceous	Rudeis / E. Miocene	Egypt	Red Sea Rift	
2228	Sunniland / Cretaceous	Sunniland / Cretaceous	USA / Florida	S. Florida	Palacas et al., 1984
		Sunniland / Cretaceous	USA / Florida	S. Florida	Palacas et al., 1984
Marine Mixed					
338	Des Moines / M. Penn.	Dakota O / L. Cret.	USA / Colorado	Denver	Clayton, 1989
398	Phosphoria / Permian	Phosphoria / Permian	USA / Wyoming	Big Horn	Orr, 1974
1082	Monterey / Miocene	Monterey / Miocene	USA / California	Santa Maria	Curiale et al., 1985
1119	Monterey / Miocene	Monterey / Miocene	USA / California	Santa Maria	Curiale et al., 1985
1123	Monterey / Miocene	Monterey / Miocene	USA / California	Santa Maria	Curiale et al., 1985
1301	Monterey / Miocene	Monterey / Miocene	USA / California	Santa Maria	Curiale et al., 1985
1507	Monterey / Miocene	Monterey / Miocene	USA / California	Santa Maria	Curiale et al., 1985
2120	Wolfcamp / Permian	Wolfcamp / Permian	USA / Texas	Permian	Unpublished data
2219	Thamama / L. Cretaceous	Burgan / Cretaceous	Kuwait	Arabian-Persian Gulf	Robinson et al., 1991
Marine Shale					
2	Kimmeridge / Jurassic	Tor / Maastrichtian	Norway / North Sea	Central Graben	Hughes et al., 1985
3	Kimmeridge / Jurassic	Tor / Maastrichtian	Norway / North Sea	Central Graben	Hughes et al., 1985
4	Kimmeridge / Jurassic	Tor / Maastrichtian	Norway / North Sea	Central Graben	Hughes et al., 1985
5	Kimmeridge / Jurassic	Tor / Maastrichtian	Norway / North Sea	Central Graben	Hughes et al., 1985
285	Mancos / U. Cret.	Mesaverde / U. Cret.	USA / New Mexico	San Juan	Ross, 1980
391	Mancos / U. Cret.	Mesaverde / U. Cret.	USA / New Mexico	San Juan	Ross, 1980
405	Mowry / L. Cretaceous	Muddy / Dakota / Cret.	USA / Wyoming	Powder River	Monper & Williams, 1979
433	Mowry / L. Cretaceous	Shannon / U. Cret.	USA / Wyoming	Powder River	Monper & Williams, 1979
518	Pierre Shale / Cret.	Pierre Shale / Cret.	USA / Colorado	Denver	Gautier et al., 1984
794	Chainman Shale / Miss.	Guilmette / Devonian	USA / Nevada	Great	Poole & Claypool, 1984
804	Smackover / Jurassic	Smackover / Jurassic	USA / Alabama	Manila Embayment	Claypool & Mancini, 1989
841	Smackover / Jurassic	Smackover / Jurassic	USA / Alabama	Manila Embayment	Claypool & Mancini, 1989
843	Smackover / Jurassic	Smackover / Jurassic	USA / Alabama	Manila Embayment	Claypool & Mancini, 1989
1104	unknown	JP sand / Pliocene	USA / Gulf of Mexico	Gulf Coast	Thompson et al., 1990
1888	unknown	KRA1 / Pliocene	USA / Gulf of Mexico	Gulf Coast	Thompson et al., 1990
1904	Wilcox / L. Eocene	Wilcox / L. Eocene	USA / Louisiana	Gulf Coast	Sassen et al., 1988

Table 1. (Continued)

Sample Number	Source Fm./Age	Reservoir Fm./Age	Location	Basin	Reference
1916	Tuxedni / M. Jurassic	Hemlock / Oligocene	USA / Alaska	Cook Inlet	Magoon & Anders, 1992
2226	Tuxedni / M. Jurassic	Hemlock / Oligocene	USA / Alaska	Cook Inlet	Magoon & Anders, 1992
2274	Beaverhill Lake / U. Dev	Beaverhill Lake / U. Dev.	Canada / Alberta	Western Canada	Hitchon, 1961
2279	Schei Point / Triassic	Heiberg / L. Jurassic	Canada	Sverdrup	Brooks et al., 1992
2280	Schei Point / Triassic	Awinagak / Jurassic	Canada	Sverdrup	Brooks et al., 1992
2281	Schei Point / Triassic	Heiberg / L. Jurassic	Canada	Sverdrup	Brooks et al., 1992
2329	Antelope Shale / U. Mio.	Stevens Sand / U. Mio.	USA / California	San Joaquin	Unpublished data
2330	Antelope Shale / U. Mio.	Stevens Sand / U. Mio.	USA / California	San Joaquin	Unpublished data
2477	Woodford / L. Devonian	Fusselman / Silurian	USA / Texas	Permian	Unpublished data
1977	Woodford / L. Devonian	Fusselman / Silurian	USA / New Mexico	Delaware	Unpublished data
2682	Eagleford / U. Cret.	Woodbine / U. Cret.	USA / Texas	East Texas	Unpublished data
Fluvio/Deltaic					
246	Talang Akar / Olig.	Cibulakan / Olig.-Mio.	Indonesia	Ardjuna	Noble et al., 1991
375	Lewis-Mesaverde / Cret.	Dakota / L. Cretaceous	USA / New Mexico	San Juan	Ross, 1980
2072	Pakawau / L. Cretaceous	Kapuni / Eocene	New Zealand	Taranaki	Read, 1992
2078	Kapuni / Eocene	Kapuni / Eocene	New Zealand	Taranaki	Read, 1992
2222	Latrobe Gp. / Cret.-E. Tert.	Latrobe Gp. / Cret.-E. Tert.	Australia	Gippsland	Philp & Gilbert, 1986
2223	Latrobe Gp. / Cret.-E. Tert.	Latrobe Gp. / Cret.-E. Tert.	Australia	Gippsland	Philp & Gilbert, 1986
2232	Miocene	Kenai / Miocene	USA / Alaska	Cook Inlet	Peters et al., 1986
2292	Richards / Eocene	Reindeer / Tertiary	Canada	Mackenzie Delta	{Snowdon & Powell, 1979
2293	Richards / Eocene	Reindeer / Tertiary	Canada	Mackenzie Delta	& Brooks, 1986}
2381	Mushan / E. Miocene	Mushan / E. Miocene	Taiwan	Northern Taiwan	Dzou, 1990
Lacustrine					
255	Green River / Eocene	Green River / Eocene	USA / Utah	Uinta	Tissot et al., 1978
987	Green River / Eocene	Green River / Eocene	USA / Utah	Uinta	Tissot et al., 1978
502	Salt Lake Gp. / Miocene	Pliocene	USA / Utah	Great	Meissner et al., 1984
2212	Melania / Cretaceous	Gamba / Cretaceous	Gabon	Gabon Coastal	Unpublished data
2234	Melania / Cretaceous	Dentale / Cretaceous	Gabon	Gabon Coastal	Unpublished data
2220	{Pematang Brown Shale / Eocene-Oligocene}	Tertiary	Indonesia	Central Sumatra	Williams et al., 1985
2221	Eocene-Oligocene}	Tertiary	Indonesia	Central Sumatra	Williams et al., 1985
2230	Shahejie / Oligocene	Shahejie / Oligocene	China	Bohai Bay	Shi et al., 1982
Orodivician					
731	Ordovician	Viola / Ordovician	USA / Kansas	Forest City	Reed et al., 1986
866	Ordovician	Trenton / Ord.	USA / Illinois	Illinois	Reed et al., 1986
1145	Ordovician	Pacoata / Ordovician	Australia	Amadeus	Reed et al., 1986
1211	Ordovician	Knox / Ordovician	USA / Virginia	Appalachian	Reed et al., 1986
1401	Winnipeg Shale-Bighorn Gp. / Ord.	Red River / Ordovician	USA / N. Dakota	Williston	Williams, 1974
1529	Utica Shale / Ord.	Dundee / Devonian	USA / Michigan	Michigan	Osadetz et al., 1992
2473	Simpson Gp. / Ord.	Fusselman / Silurian	USA / Texas	Midland	{Reed et al., 1986 & Rullkötter et al., 1986}
2474	Simpson Gp. / Ord.	Fusselman / Silurian	USA / Texas	Midland	Unpublished data

Table 2. Selected geochemical data for crude oils in Table 1

Sample	PR/PH	DBT/PHEN	MDBT/MPHEN	% Sulfur	°API	Zone*
MARINE CARBONATE						
1	0.66	1.79	nd	2.30	26.9	1B
805	0.40	3.99	3.89	5.70	17.1	1A
808	0.52	5.22	4.98	1.70	33.8	1A
819	0.54	7.23	8.17	0.97	41.0	1A
820	0.55	4.54	4.88	1.21	37.8	1A
823	0.53	5.91	7.08	1.01	40.6	1A
959	0.43	1.70	2.34	1.21	59.8	1B
1281	0.59	5.21	3.28	0.93	37.0	1A
1337	0.63	5.03	2.98	0.53	43.2	1A
1587	0.70	1.09	1.04	2.83	26.0	1B
1588	0.66	1.83	1.93	5.32	13.0	1B
2970	0.80	1.87	2.49	5.42	14.0	1B
2227	0.51	1.17	1.99	3.62	23.3	1B
2228	0.53	1.29	1.99	3.26	24.9	1B
MARINE MIXED						
338	0.63	1.51	2.19	3.41	14.4	1B
398	0.53	2.10	2.62	3.06	28.5	1B
1082	0.74	1.42	1.08	2.99	20.8	1B
1119	0.42	2.86	1.87	7.11	nd	1B
1123	0.71	1.42	1.19	2.19	29.3	1B
1301	0.51	1.96	1.33	5.73	6.0	1B
1507	0.67	1.71	1.21	5.19	13.6	1B
2120	0.93	1.86	1.71	0.76	30.3	1B
2219	0.58	1.21	1.98	2.15	31.3	1B
MARINE SHALE						
2	1.39	0.27	nd	0.29	35.5	3
3	1.35	0.20	nd	0.21	33.8	3
4	1.45	0.11	nd	0.17	36.9	3
5	1.45	0.07	nd	0.02	49.5	3
285	1.71	0.06	0.07	0.09	52.3	3
391	1.76	0.05	0.08	0.04	62.3	3
405	1.44	0.06	0.10	0.09	45.5	3
433	1.67	0.09	0.14	0.13	40.0	3
518	1.71	0.22	0.29	nd	29.0	3
794	1.42	0.57	0.40	0.43	31.1	3
804	1.11	0.09	0.19	0.20	37.7	3
841	1.03	0.27	0.34	0.60	31.5	3
843	1.15	0.17	0.27	0.10	40.1	3
1104	1.74	0.19	0.24	0.13	39.4	3
1888	1.77	0.15	0.22	0.12	47.6	3
1904	1.99	0.09	0.10	0.03	45.5	3
1916	2.36	0.05	0.08	0.28	28.6	3
2224	1.37	0.29	0.33	0.07	38.4	3
2226	2.41	0.04	0.05	0.03	37.6	3
2279	1.45	0.04	0.09	0.11	25.7	3
2280	1.18	0.07	0.15	0.15	22.3	3
2281	1.27	0.08	0.11	0.11	25.7	3
2329	1.53	0.14	0.19	0.61	35.9	3
2330	1.51	0.18	0.23	0.65	33.0	3
2477	1.33	0.35	0.39	0.20	40.6	3
1977	1.44	0.52	0.56	0.42	29.3	3
2682	1.60	0.21	0.32	0.28	37.0	3
FLUVIAL/DELTAIC						
246	8.71	0.15	0.18	0.06	35.4	4
375	3.25	0.07	0.09	0.19	59.8	4
2072	6.39	0.09	0.09	0.07	44.0	4
2078	7.88	0.14	0.18	0.08	59.8	4
2222	5.48	0.25	0.18	0.05	44.9	4
2223	5.42	0.27	0.17	0.09	35.8	4
2232	3.96	0.07	0.14	0.11	25.7	4
2292	3.28	0.09	0.10	0.18	31.1	4
2293	4.21	0.13	0.17	0.11	24.0	4
2381	7.01	0.06	0.25	0.08	34.0	4
LACUSTRINE						
255	1.09	0.03	0.06	0.16	nd	3
987	1.35	0.05	0.06	0.09	nd	3
502	0.04	2.04	2.95	7.68	4.9	1B
2212	1.59	0.07	0.14	0.13	29.7	3
2234	2.21	0.09	0.10	0.10	31.1	3
2220	2.21	0.08	0.11	0.06	33.7	3
2221	2.10	0.09	0.13	0.09	33.7	3
2230	0.44	0.18	0.25	0.84	24.9	2
ORDOVICIAN						
731	1.20	0.10	0.12	0.21	33.7	3
866	1.30	0.16	0.25	0.20	40.2	3
1145	0.84	0.11	0.31	0.08	46.8	2
1211	1.31	0.28	0.33	0.09	44.2	3
1401	0.61	0.10	0.19	0.24	42.4	2
1529	1.42	0.11	0.15	0.26	42.9	3
2473	1.72	0.02	0.03	0.16	48.5	3
2474	1.64	0.09	0.17	0.07	44.3	3

* from Figure 3

PR/PH = pristane/phytane

DBT/PHEN = dibenzothiophene/phenanthrene

MDBT/MPHEN = sum of methyl dibenzothiophenes/sum of methyl phenanthrenes

nd = not determined

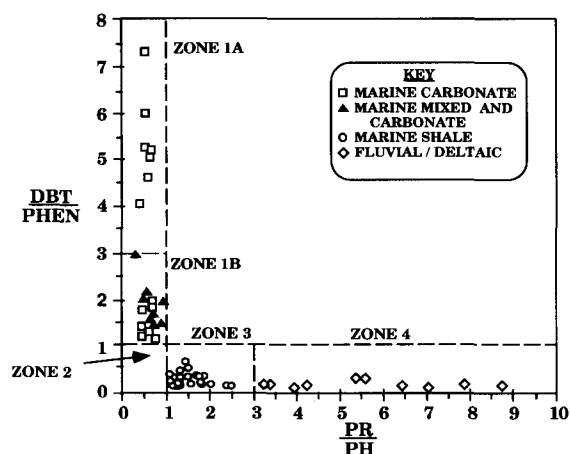


FIG. 1. Oils group according to their source rock depositional environments and lithologies in a cross-plot of the dibenzothiophene/phenanthrene (DBT/PHEN) and pristane/phytane (PR/PH) ratios.

ratio and vitrinite reflectance for Type I and II kerogens published by Radke, 1988) whereas the remaining oils are of similar, peak-generation maturity.

The small change in PR/PH ratio observed (0.40–0.55) in our Smackover oils is consistent with the results of Wenger et al. (1990) who found for a suite of Smackover Type I oils (equivalent to Mississippi Interior Salt Basin oils) that the PR/PH ratio showed little (0.74–0.81), and no systematic, change with maturity as measured by the percent of C_{21} + C_{22} triaromatic steroids to total triaromatic steroids. In contrast to these results, Sofer (1988) found that the PR/PH ratio appeared to change linearly with maturity as measured by changes in the n -alkane distribution. However, we believe that the variation in PR/PH ratio observed by Sofer (1988) can be explained by source facies variations. Close examination of the plot in Sofer (1988) shows the samples tend to fall into two populations; one with PR/PH ratios > 1 and a second with PR/PH ratios < 1. Based on their locations, we believe these two populations correspond to the two Smack-

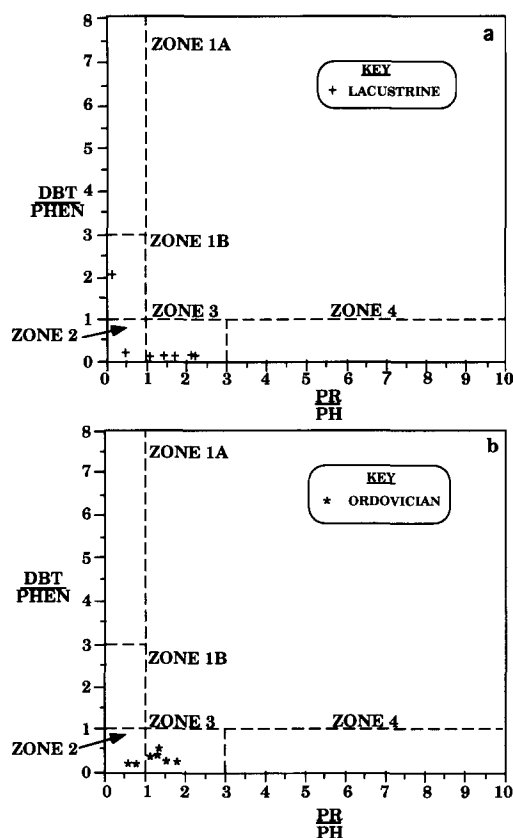


FIG. 2. A cross-plot of the dibenzothiophene/phenanthrene (DBT/PHEN) and pristane/phytane (PR/PH) ratios for (a) lacustrine oils and (b) Ordovician oils.

over facies described by Sassen (1989, 1990), Claypool and Mancini (1989), and Wenger et al. (1990) and revealed by our DBT/PHEN vs. PR/PH plot (Fig. 1).

Similar results were observed by van Graas (1990) for a suite of oils derived the Hanifa Formation, a carbonate containing Type I/II kerogen. The oils appeared to be from the

Table 3. Relationship of crude oil dibenzothiophene/phenanthrene and pristane/phytane ratios to depositional environment and lithology of source rock

ZONE	DBT/PHEN	PR/PH	DEPOSITIONAL ENVIRONMENT	LITHOLOGY
1A	> 3	< 1	Marine	Carbonate
1B	1-3	< 1	Marine and Lacustrine (sulfate-rich)	Carbonate and Mixed*
2	< 1	< 1	Lacustrine (sulfate-poor)	Variable
3	< 1	1-3	Marine and Lacustrine	Shale
4	< 1	> 3	Fluvio/Deltaic	Carbonaceous shale and Coal

* Mixed includes marls, argillaceous carbonates and siliceous/phosphatic rocks

same source rock facies based on source-indicative parameters such as carbon isotopes and sterane carbon number distributions. The maturity of the oils in terms of vitrinite reflectance equivalent (VR/E) ranged from 0.65 to 0.90%, while the PR/PH ratios varied only from 0.80 to 0.95 and showed no systematic trend with VR/E.

Requejo (1994) has reported changes in the PR/PH ratio from 0.8 to 1.9 for a series of extracts of increasing maturity from the calcareous shale Duvernay Formation, western Canada Basin, which contains Type II kerogen. Various types of evidence indicate a uniform organic facies and lithology. However, for samples in the oil window, as evidenced by equilibrium S/R ratios in the homohopanes, there is a variation of only 1.4 to 1.9 in the PR/PH ratio. Thus, while the PR/PH ratio may show a significant change from pre-oil window to oil window maturity little change is observed through the oil window.

The suites of Smackover, Kimmeridge, and Duvernay samples show that oils derived from Type II kerogen show little, if any, maturity effect on the pristane/phytane ratio. This is not true for Type III kerogen. An initial increase followed by a decrease in PR/PH ratio with maturity is well documented for coals (Radke et al., 1980; Boudou, 1981). In a more recent study of coals and vitrinite concentrates using absolute concentrations, Dzou (1990) showed that the change in PR/PH ratio from 5 to 10 was due to the formation and destruction of pristane while the concentration of phytane stays relatively constant. Only at high maturities (>1.1% vitrinite reflectance) is there a sufficient reduction in the PR/PH ratio to move an oil from Zone 4 to Zone 3.

The DBT/PHEN ratio shows a systematic decrease from Valhall (0.27) to Albuskjell (0.07) for the Kimmeridge Clay Formation-derived oils mentioned above (Hughes et al., 1985). In the study of vitrinite concentrates and coals (Dzou, 1990), the DBT/PHEN ratio shows little variation over the vitrinite reflectance range of 0.5–1.8%. The Duvernay extracts show a decrease from around 0.2 to 0.06 for samples in the oil window (Requejo, 1994). For the Smackover-derived marine carbonate oils, the low-maturity Toxey oil has a DBT/PHEN ratio of 3.99 vs. values of 4.54–7.23 for the four more mature oils. The change in the DBT/PHEN ratio is not great over the range of maturity represented by our Smackover oils; however, a suite of common-source oils representing a more systematic change over a greater range of maturities is necessary to better define the effect of maturity on the DBT/PHEN ratio for oils generated from marine carbonates.

In summary, for oil-prone source rocks containing Type I/II and II kerogens, the changes in PR/PH and DBT/PHEN with maturity over the oil window appear to be small for both carbonate and shale source rocks. In no case are the changes sufficient to move an oil from one zone to another with a resulting loss in the ability to infer the lithology and depositional environment of its source.

3.5. Methylthiophenes/Methylphenanthrenes versus Pristane/Phytane

In addition to the DBT/PHEN ratio, we have also calculated the ratio of the sum of 4-, (3 + 2)-, and 1-methyl-

benzothiophene to the sum of 3-, 2-, 9-, and 1-methylphenanthrene (MDBT/MPHEN in Table 2). A plot of this ratio vs. the PR/PH ratio gives essentially the same distribution of oils as Fig. 1. This indicates that the MDBT/MPHEN and DBT/PHEN ratios are highly correlated; indeed, a cross-plot of the two ratios has a linear correlation coefficient of 0.92. Substitution of the MDBT/MPHEN ratio in Fig. 3 might be useful for oils where water-washing is suspected as the methyl homologues will be less affected than the more soluble unsubstituted compounds (Palmer, 1984) provided the pristane/phytane ratios have not been altered by biodegradation which frequently accompanies water-washing.

3.6. Use of PR/PH versus DBT/PHEN Plot

The above results can be generalized into a simple, yet powerful method applicable over a wide maturity range for determining the source rock depositional environment and lithology of crude oils as shown in Fig. 3. The boundaries between the zones in Fig. 3 are drawn as dashed lines in recognition of the fact that these boundaries must be regarded as somewhat "fuzzy" and samples which fall near a zone boundary should be evaluated by additional geochemical data for assessment of depositional environment and lithology. In the practical application of this method, there are several reasons why an oil may plot in Fig. 3 in a position unrelated to the lithology and/or depositional environment of its source rock.

First, an oil can be co-sourced from significantly different types of source rocks. For example, a high DBT/PHEN ratio and a high PR/PH ratio could indicate a mixture of oil from a carbonate and oil from a marine shale source. Oils derived from formations which exhibit extensive vertical and lateral variability will be a weighted average of each subfacies according to its generation potential. If the subfacies are quite different, as in an example recently reported by Miranda and

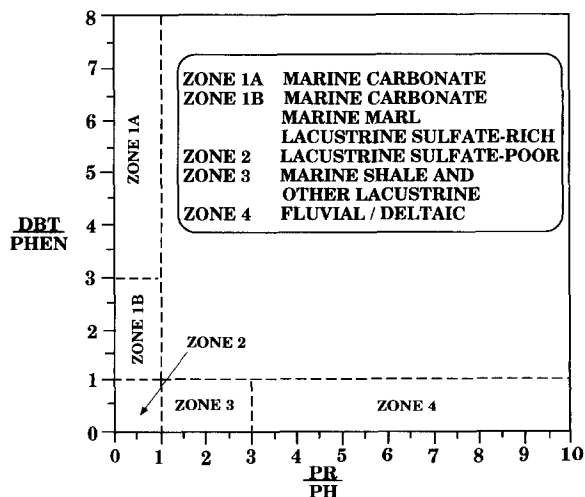


FIG. 3. A cross-plot of the dibenzothiophene/phenanthrene ratio (DBT/PHEN) vs. the pristane/phytane (PR/PH) ratio provides a novel, convenient, and powerful way to infer crude oil source rock depositional environments and lithologies.

Walters (1992), the derived oil may show "conflicting" properties. Indeed, the DBT/PHEN vs. PR/PH cross-plot may be useful for detecting oils from multiple or highly variable source formations.

Second, altered oils may be misclassified. For example, water-washing would lower the DBT/PHEN ratio (Palmer, 1984) moving an oil toward the X-axis. Moderate biodegradation could alter the PR/PH ratio although it is uncertain whether pristane or phytane is preferentially removed. Surface exposure, such as in seep oils, would result in preferential loss of phenanthrenes compared to dibenzothiophenes based on studies of the Exxon Valdez oil spill (Hostettler and Kvenvolden, 1994).

Finally, Fig. 3 should not be applied to nonsource rock extracts. The zones in Fig. 3 are based on the analysis of crude oils and thus reflect those depositional settings which resulted in sediments with a sufficient quantity and quality of organic matter to serve as source rocks. Certainly, sediments may be deposited in environments not represented in Fig. 3. For example, carbonates may be deposited under oxidizing conditions resulting in high pristane/phytane and low DBT/PHEN ratios, but these sediments will be organic poor and not petroleum source rocks.

3.7. Significance of Dibenzothiophene/Phenanthrene Ratio

The insight provided by biomarker ratios is limited by the fact that variations in ratios can arise from multiple causes, i.e., a ratio may increase due to an increase in the numerator, a decrease in the denominator, or a combination of both. This ambiguity can be resolved, in theory, by measuring the absolute concentrations of biomarkers as shown by Requejo (1992). We have used this technique to study the changes in DBT/PHEN ratio. It should be recognized that the concentrations of individual compounds are controlled not only by the extent to which they are formed/destroyed but also by the extent to which all other components are formed/destroyed, i.e., a dilution effect.

Figure 4a and b show the changes in DBT/PHEN ratio as a function of the concentration in $\mu\text{g/g}$ whole oil of phenanthrene and dibenzothiophene, respectively. For oils with DBT/PHEN ratios > 1 , Fig. 4 shows that an increase in the ratio is due to an increase in dibenzothiophene concentration with the phenanthrene concentration staying relatively constant. As expected, the oils with the highest dibenzothiophene concentrations are those from marine carbonate and marine mixed sources. For oils with DBT/PHEN ratios < 1 , the dibenzothiophene concentration is relatively constant and low while the phenanthrene concentration varies over a wide range. Within this latter group of oils, among the highest phenanthrene concentrations are found in oils from Ordovician source rocks, a period when land plants were not abundant. In addition, oils from fluvial/deltaic sources have phenanthrene concentrations comparable to other types of environments. The high abundance of phenanthrene in Ordovician oils and the absence of enhanced abundances in fluvial/deltaic oils bring into question the suggestion that phenanthrene could be gen-

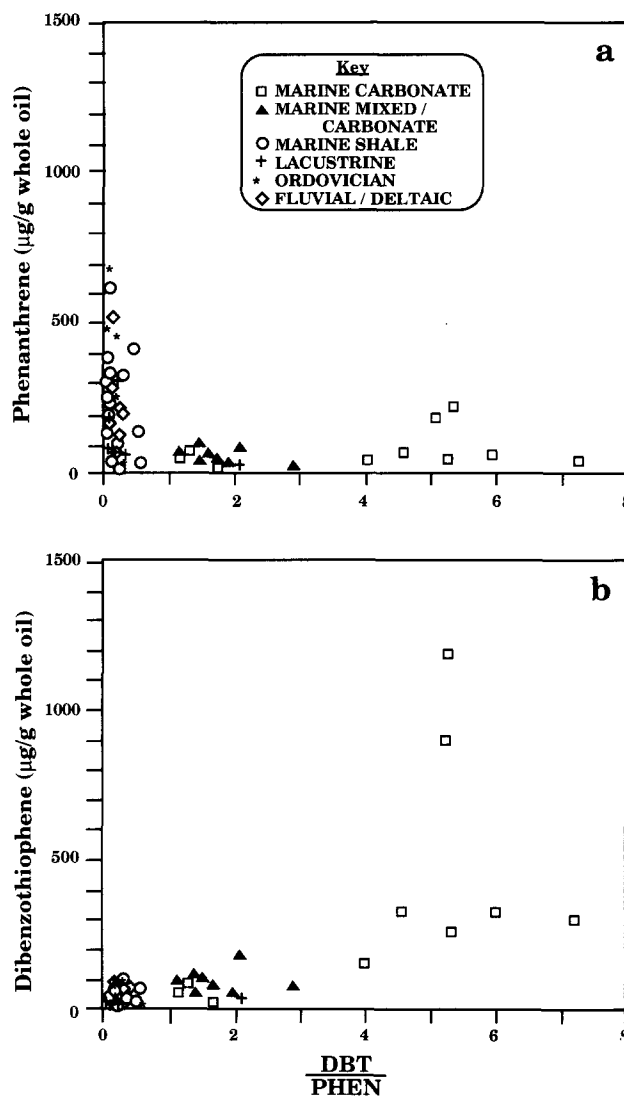


FIG. 4. Relationship between dibenzothiophene/phenanthrene ratio and (a) concentration of phenanthrene and (b) concentration of dibenzothiophene in whole oil showing that high DBT/PHEN ratios are the result of increases in the concentration of dibenzothiophene rather than decreases in the phenanthrene concentration.

erally derived from higher plant terpenoids of the amyrin type (Garrigues et al., 1985).

Both phenanthrene and dibenzothiophene are not inherited from the biomass but are products of diagenesis, catagenesis, and metagenesis. Thus, the DBT/PHEN ratio is predominantly controlled by environmental, and not source, factors. While the detailed synthetic pathway for the formation of dibenzothiophene is not known, its origin must ultimately be attributed to the interaction of hydrogen sulfide or polysulfides with an organic substrate. This fact coupled with the observation that increases in the DBT/PHEN ratio are due to an increase in dibenzothiophene concentration implies that the DBT/PHEN ratio reflects the availability of reduced sulfur for interaction with organic matter in the depositional/diagenetic environment.

3.8. Relationship of DBT/PHEN Ratio to Total Sulfur Content

In agreement with the above discussion, oils in Zones 1A and 1B of Fig. 3 which have higher DBT/PHEN ratios generally have higher total sulfur contents. However, the relationship between sulfur content and the DBT/PHEN ratio is more complex than a simple one-to-one correspondence. Figure 5 shows that oils with the highest DBT/PHEN ratios do not have the highest sulfur contents and, conversely, the oils with the highest sulfur contents do not have the highest DBT/PHEN ratios. Closer examination of Fig. 5 shows there are three groups of oils. Group I has both low sulfur contents (<1%) and low DBT/PHEN ratios (<1) and plot in Zones 3 and 4 of Fig. 1 (marine shale and fluvial/deltaic, respectively). Group II has moderate sulfur contents (0.5–2%) and moderate-high DBT/PHEN ratios (1–7) and plot in Zone 1A (marine carbonate). This group includes all but one of the Mississippi Interior Salt Basin Smackover-derived and the Williston Basin Madison-derived oils. Group III has moderate-high sulfur contents (2–7%) and moderate DBT/PHEN ratios (1–3) and plot in Zone 1B (marine mixed). This group includes oils generated from the Monterey and Phosphoria, the Middle Eastern oils (Egypt, Kuwait and Dubai), and the Salt Lake Group (Rozel Point) oil.

In a study of the chemical speciation of sulfur in high sulfur (>1%) oils Waldo et al. (1991) found two types of oils: sulfide-rich and thiophene-rich (these designations are relative as thiophenic derivatives were the dominant organosulfur components in both types). The sulfide-rich petroleum included Monterey and Salt Lake Group (Rozel Point) oils. The thiophene-rich oils included a Middle Eastern and Adriatic oil, both from marine carbonates. Although we have not determined the sulfur type distribution for the oils in this study, the co-occurrence of certain oils within the groupings of Waldo et al. (1991) and that of Fig. 5 suggests that our Group II oils represent thiophene-rich oils and our Group III oils represent sulfide-rich oils. This would explain the dichotomy that the oils with highest sulfur contents do not have the highest DBT/PHEN ratios since in these cases relatively more sulfur is present as sulfides rather than thiophenes. Within a group the relationship between sulfur content and the DBT/PHEN ratio is more systematic. For example, the Monterey-derived Santa Maria Basin oils show a general decrease in the DBT/PHEN ratio (from 2.86 to 1.42) with decreasing total sulfur content (from 7.11 to 2.19 wt%). With one exception, the marine carbonate oils with DBT/PHEN < 3 (Zone 1B in Fig. 3) are Group III sulfide-rich oils. Whether source or maturity determines if an oil is thiophene-rich or sulfide-rich remains to be determined.

3.9. Significance of Pristane/Phytane Ratio

Quantitative biomarker analysis has also been used to study the variation in the pristane/phytane ratio. Figure 6a and b show the changes in PR/PH ratio as a function of the concentration in $\mu\text{g/g}$ whole oil of phytane and pristane, respectively, for the oils in this study.

Figure 6a clearly shows that the range of phytane concentrations in whole oils is roughly the same over the entire range

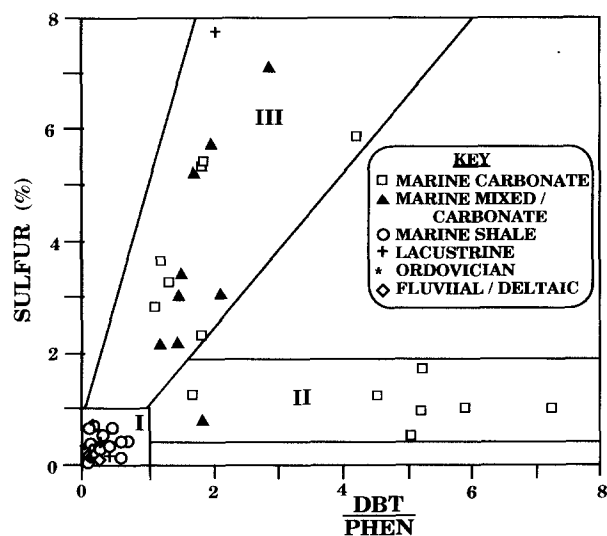


FIG. 5. Relationship between the DBT/PHEN ratio and total sulfur content showing that high sulfur oils appear to fall into two groups.

of PR/PH ratios. Thus, marine carbonate oils, with ratios less than 1, marine shale oils, with ratios of 1–3, and nonmarine oils, with ratios up to 8, have comparable phytane concentration ranges. Maximum phytane concentrations are around 2000 $\mu\text{g/g}$ whole oil. As a group, Ordovician oils have the lowest and lacustrine oils have the highest phytane concentrations. Indeed, high absolute phytane concentrations (>2000 $\mu\text{g/g}$ oil) may serve as an indicator for oils derived from lacustrine source rocks although the converse is not true, i.e., not all lacustrine oils have high phytane concentrations.

The plot in Fig. 6a shows that fluvial/deltaic oils have phytane concentrations over the same range as oils from other types of source rocks. This observation contradicts the suggestion of Mello et al. (1988) that the high PR/PH ratios found in freshwater environments are due to a decrease in phytane which originates from archaeobacteria whose populations are reduced because of the decreased salinity. Our data shows that high (>3) PR/PH ratios result from increased pristane concentrations rather than reduced phytane concentrations (Fig. 6b).

Carbon isotope data for pristane and phytane were obtained from gas chromatography–isotope ratio mass spectrometry (GC–IRMS) of the saturate fraction of a number of oils representing all the zones in Fig. 3 (see Table 4). Despite the twentyfold range (8.71 to 0.40) in pristane/phytane ratio represented by these oils, the differences in δ -values between the two isoprenoids are less than ca. 1‰ when standard deviations are considered. Schoell et al. (1992) report values very similar to ours for pristane ($\delta^{13}\text{C}_{\text{pristane}} = -26.7 \pm 0.3\text{‰}$) and phytane ($\delta^{13}\text{C}_{\text{phytane}} = -26.1 \pm 0.1\text{‰}$) in a Monterey-derived oil from the offshore Santa Maria Basin with a PR/PH ratio of 0.79.

Similar results have been reported by Hayes et al. (1990) for extracts of the marine Cretaceous Greenhorn Formation from the Western Interior Seaway of North America. Pristane $\delta^{13}\text{C}$ values ranged from -32.8 to -29.0‰ and phytane from -32.9 to -28.8‰ for twenty samples ranging in lithology

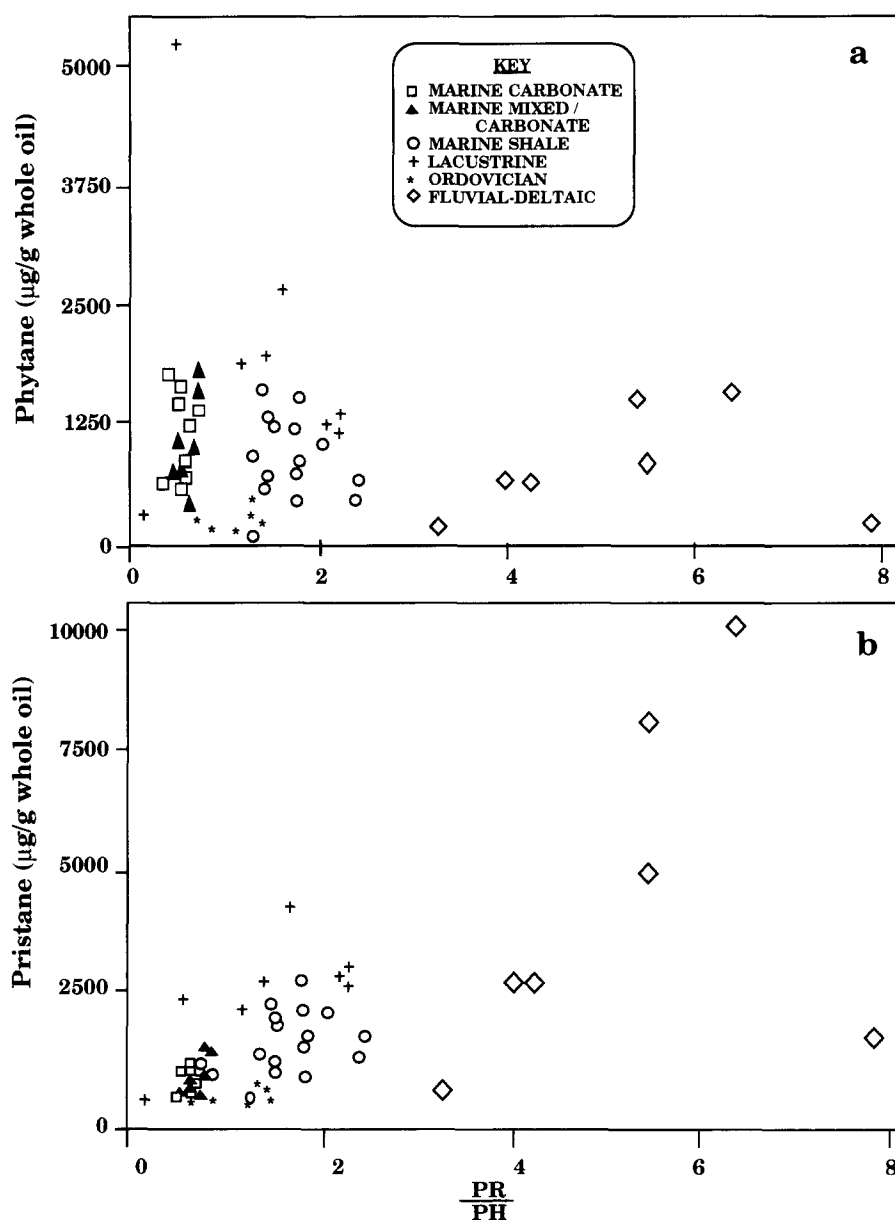


FIG. 6. Relationship between pristane/phytane ratio and (a) concentration of phytane and (b) concentration of pristane in whole oil showing that PR/PH ratios increase largely as the result of increases in the concentration of pristane rather than decreases in the phytane concentration.

from well-laminated calcareous shales to intensely bioturbated limestones representing bottomwater conditions ranging from anoxic to well oxygenated. The difference between $\delta^{13}C_{\text{pristane}}$ and $\delta^{13}C_{\text{phytane}}$ in the same sample ranged from 0 to 1.1‰ with an average difference of 0.4‰. Thus, over a wide range of redox conditions, the carbon isotope values for pristane and phytane are very similar.

A different case is represented by the Messel Shale. GC-IRMS $\delta^{13}C$ values (Freeman et al., 1990) for pristane and phytane are $-25.4\text{‰} \pm 1.0\text{‰}$ and $-31.8\text{‰} \pm 0.8\text{‰}$, respectively. The 6.4‰ difference in the isotope data indicates separate origins for the two isoprenoids. The Messel shale is be-

lieved to be an example of an environment in which methanogenic bacteria were quite active. The δ -value of phytane matched that of coexisting archaeobacterial lipids in the same sediment whereas that of the pristane was consistent with derivation from phytol produced by the same organisms that produced coexisting porphyrins from algal lipids in the same sediment (Hayes et al., 1990). The biomass contributed by the archaeobacteria is an additional source of phytane and accounts, we believe, for the very low pristane/phytane ratio of 0.33 for the Messel sample.

The Salt Lake Group (Rozel Point) oil in this study shows clear evidence for different sources for pristane and

Table 4. Pristane and phytane carbon isotope data for selected oils

SAMPLE NUMBER	SOURCE ROCK (BASIN)	ZONE ^a	PR/PH	$\delta^{13}\text{C}_{\text{PR}}^{\text{b}}$	STD. DEV.	$\delta^{13}\text{C}_{\text{PH}}^{\text{b}}$	STD. DEV.	$\delta^{13}\text{C}_{\text{PH}} - \delta^{13}\text{C}_{\text{PR}}$
502	Salt Lake Group (Great)	1B	0.04	-17.3	0.5	-26.6	0.1	-9.3
805	Smackover (Mississippi Salt)	1A	0.40	-23.8	0.6	-25.6	0.1	-1.8
959	Niagara (Michigan)	1B	0.43	-26.9	0.3	-27.9	0.3	1.0
1507	Monterey (Santa Maria)	1B	0.51	-26.2	0.4	-26.1	0.4	0.1
1281	Lodgepole (Williston)	1A	0.59	-30.1	0.8	-30.5	0.4	0.4
2970	Brown Lst. (Red Sea Rift)	1B	0.68	-32.4	0.3	-32.2	0.1	-0.2
2120	Wolfcamp (Permian)	1B	0.93	-28.3	c	-28.6	c	-0.3
2230	Shahejie (North China)	2	0.44	-29.2	0.2	-30.2	0.2	-1.0
841	Smackover (Manila)	3	1.03	-25.8	0.2	-25.2	0.0	0.6
2281	Schei Point (Sverdrup)	3	1.27	-30.5	0.3	-30.0	1.0	0.5
2477	Woodford (Permian)	3	1.33	-31.0	c	-31.0	c	0.0
405	Mowry (Powder River)	3	1.44	-29.5	0.7	-29.6	0.3	0.1
2329	Antelope Shale (San Joaquin)	3	1.53	-25.2	0.8	-25.0	0.5	-0.2
2682	Eagleford (East Texas)	3	1.60	-29.9	0.6	-29.8	0.6	0.1
2292	Richards (Mackenzie Delta)	4	3.28	-28.7	0.2	-28.4	0.2	0.3
2381	Mushan (Northern Taiwan)	4	7.01	-28.4	0.5	-28.2	0.2	0.2
246	Talang Akar (Ardjuna)	4	8.71	-29.0	0.1	-28.1	0.6	0.9

^a From Figure 1^b Mean of duplicate analyses in o/oo relative to PDB^c One analysis

STD. DEV. = standard deviation

phytane with $\delta^{13}\text{C}_{\text{pristane}} = -17.3 \pm 0.5\text{‰}$, $\delta^{13}\text{C}_{\text{phytane}} = -26.6 \pm 0.1\text{‰}$, and PR/PH = 0.04. The source rock of this oil appears to have been deposited in a hypersaline playa lake environment (ten Haven et al., 1988). The extremely low PR/PH ratio and the 9.3‰ difference in δ -values can be attributed to a large contribution of phytane from halophilic archaeobacteria.

The above data show that pristane and phytane have very similar carbon isotope values in a wide variety of crude oils and sediments exhibiting a very broad range of pristane/phytane ratios, from very low (0.40) to very high (8.71). This is consistent with the two isoprenoids arising by similar biosynthetic pathways from an isotopically similar initial carbon pool. Only in certain restricted environments where archaeobacteria are abundant, such as environments where methanogenesis is extensive or hypersaline environments, is there a contribution of isotopically distinct phytane derived from a different carbon pool.

3.10. Origin of Pristane and Phytane

Based on the literature, there appears to be two major potential sources of pristane and phytane. One source, as suggested by Didyk et al. (1978), is derivation of both isoprenoids from the phytol side-chain of chlorophyll with the relative proportion of the two being determined by whether dysoxic conditions (oxidation and subsequent decarboxylation of phytol leading to pristane) or anoxic conditions (reduction of phytol leading to phytane) prevail during sedimentation/early diagenesis. A second source for pristane only is from the isoprenoidal side-chain of tocopherols via an intramolecular rearrangement resulting in the elimination of pristane (Goossens et al., 1984). Because the basic carbon skeleton of the isoprenoid side chain in both tocopherol and phytol are derived by the same biosynthetic pathway, no differences in carbon isotopic fractionation should be expected. Consequently, the carbon isotope data on pristane and phytane can not be used to differentiate between different precursors for pristane and phytane.

Two major processes which result in preservation of the original biological lipids in sediments are incorporation into macromolecular structures and interaction with reduced sulfur. The two processes can act together, i.e., the cross-linking of lipids into macromolecules by intermolecular incorporation of sulfur. There is abundant evidence that the phytane carbon skeleton is extensively preserved under conditions where H_2S is available (Sinninghe Damsté and de Leeuw, 1990; ten Haven et al., 1990; Kohnen et al., 1991; Rowland et al., 1993). It has been suggested that tocopherol can be easily incorporated into macromolecular structures "probably via the phenolic hydroxyl group or the 5-methyl group which is very reactive under oxidative conditions" (Goossens et al., 1984). We do not know the relative importance of these processes or what other processes might be involved under different environmental conditions and thus what the expected relative amounts of pristane and phytane might be. However, some observations can be made from our data.

The molar ratio of tocopherol/chlorophyll in photosynthetic organisms ranges from 0.01 to 0.12 (Goossens et al., 1984). If pristane comes only from tocopherol and phytane only from phytol (chlorophyll) and if these relative "natural abundances" of precursors are correct, then Zone 4 oils (fluvial/deltaic environments) would represent cases where tocopherol is preserved up to 66 to 660 times more than phytol (PR/PH = 8) and Zone 1 oils would represent cases where tocopherol is preserved up to 6 to 60 times more than phytol (PR/PH = 0.6). Thus, under both anoxic and dysoxic conditions, tocopherol would have to survive at higher to much higher rates than phytol.

The particularly S-rich Salt Lake Group (Rozel Point) oil has the lowest pristane and phytane concentrations of any oil in this study. This is a consequence of the extensive incorporation of biological lipids into the organosulfur fraction of the oil and its low thermal maturity (Sinninghe Damsté et al., 1987). Importantly, since both pristane and phytane concentrations are low, the precursors of both isoprenoids are being affected. The high C_{19} and C_{20} isoprenoid concentrations in

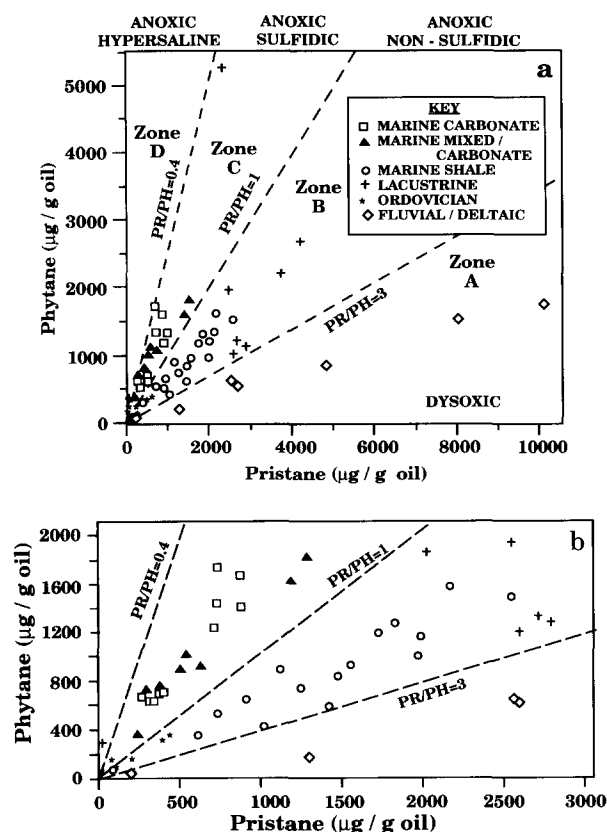


FIG. 7. A cross-plot of the concentration of pristane vs. the concentration of phytane for (a) all samples and (b) samples with $<2000 \mu\text{g/g}$ phytane and $<3000 \mu\text{g/g}$ pristane shows the oils fall along well-defined trends which reflect specific Eh, pH regimes.

most lacustrine oils are due to the fact that these oils are generally sulfur-poor and only small amounts of pristane and phytane are bound as organosulfur derivatives.

3.11. Relationship of PR/PH and DBT/PHEN to Depositional Processes

A cross-plot of the concentrations of pristane and phytane (Fig. 7) indicates that oils tend to fall along three major trends

which define the zones indicated in the figure. Oils within zone A contain considerably more pristane than phytane (average PR/PH ratio of around 6) and are all from fluvial/deltaic source rocks falling in Zone 4 of Fig. 1. Samples within zone B contain a slight to moderate excess of pristane over phytane (average PR/PH ratio of around 1.8) and are all from marine or lacustrine siliciclastic source rocks falling in Zone 3 of Fig. 1. Samples within zone C contain a moderate excess of phytane (average PR/PH ratio of around 0.6) and, excepting two Ordovician oils, are from marine carbonate or mixed source rocks falling in Zones 1A and 1B of Fig. 1. A single sample, the Salt Lake Group (Rozel Point) oil, falls in Zone D (PR/PH ratio of 0.04) and falls in Zone 1B of Fig. 1. We propose that each of the zones in Fig. 7 reflects a discrete Eh-pH (redox) regime which predominated during deposition/early diagenesis of the oils' source rocks.

Based on the above discussions we believe that the PR/PH ratio reflects redox conditions and that the DBT/PHEN ratio reflects the availability of reactive sulfur, primarily hydrogen sulfide (H_2S) and polysulfides (H_2S_n), for interaction with organic matter. Further, for reactive sulfur to be abundant, the sediments must be anoxic since sulfate-reducing bacteria are obligate anaerobes; there must be sufficiently high SO_4^{2-} ion concentrations (such as found in seawater) and there must be sufficiently low concentrations of reactive iron. Based on these principles, the DBT/PHEN and PR/PH ratio provide the basis for classifying depositional environments as shown in Table 5.

In Table 5, [Fe] represents the concentration of iron capable of reacting with reduced sulfur to form iron sulfides, for example, hydrated iron oxides. Similarly, [S] represents the concentration of reduced sulfur capable of reacting with iron to form iron sulfides, for example, sulfide, polysulfides, and elemental sulfur. Under oxidizing conditions, [S] will be small due to the lack of microbial sulfate reduction and in low salinity environments, [S] will be small due to the lack of sulfate.

Oils in Zones 1A and 1B were generated from source rocks deposited under reducing conditions where sulfate reduction occurs and the supply of sulfide is greater than reactive iron (sulfidic conditions) resulting in extensive incorporation of sulfur into organic matter. The Rozel Point oil (502) is an example of a lacustrine oil that falls in Zone 1B. The source

Table 5. Classification of depositional environments according to dominant redox condition

Zone Figure 1	Redox Condition	[Fe]/[S]	PR/PH	DBT/PHEN	Zone Figure 7
1A, 1B	anoxic/sulfidic*	[Fe] < [S]	< 1	> 1	C
2	anoxic/fermentative	[Fe] > [S]	< 1	< 1	D
1A, 1B, 2	anoxic/hypersaline	variable	< 0.4	variable	C, D
3	anoxic/non-sulfidic*	[Fe] > [S]	1-3	< 1	B
4	periodically oxic or dysoxic	[Fe] >> [S]	> 3	< 1	A

* The term sulfidic refers to conditions where free H_2S_n species are present

rock of this oil was deposited in a sulfate-rich, highly reducing environment and yielded, upon subsequent catagenesis, an extremely organosulfur-rich oil (Sinninghe Damsté et al., 1987).

Oils in Zone 3 were generated from source rocks deposited under anoxic conditions where sulfate reduction occurs but the supply of reactive iron is greater than sulfide and pyrite formation is the principal process. Carbonate and mixed lithologies (Zones 1A and 1B) are generally Fe-poor and would result in free sulfide available for reaction with organic matter. For example, the average $\text{Fe}_2\text{O}_3 + \text{FeO}$ content of shales is 6.47 wt% compared with 0.54 wt% for limestones (Pettijohn, 1957). In addition, carbonate environments would have higher pH values. This promotes the formation of the nucleophiles HS^- or HS_n^- over H_2S which would favor the formation of organosulfur compounds by Michael addition to activated double bonds, a process believed to be important in the incorporation of sulfur into organic matter (Orr and Sinninghe Damsté, 1990). The lacustrine oils in Zone 3, such as the those derived from the Green River Formation, represent a combination of low sulfate (and thus sulfide) availability and/or high iron availability.

The oils in Zone 4 are derived from carbonaceous shales or coals deposited in fluvial/deltaic environments where the organic matter was subjected to dysoxic or periodically oxic conditions. Low sulfate concentrations and/or high iron concentrations and higher Eh precluded the formation of high concentrations of reduced sulfur in the porewaters.

The source rocks of oils in Zone 2 were deposited under reducing conditions but low sulfate ion concentrations precluded the formation of significant amounts of reactive sulfur and [S] is low. In this case, fermentation rather than sulfate reduction, may be responsible for the low Eh. Fermentation commonly occurs in sediments; however, since it is preceded by sulfate reduction in the hierarchy of microbiological processes (Deming and Baross, 1993), high DBT/PHEN ratios will result, if sulfate is present and [Fe] is low, and these oils will plot in Zones 1A and 1B. Only when sulfate concentrations are low will the "imprint" due to fermentation, i.e., $\text{PR/PH} < 1$ and $\text{DBT/PHEN} < 1$, be expressed in an oil. In our experience, this condition only occurs in lacustrine settings. Thus, the specific characteristics of both very low PR/PH and DBT/PHEN ratios are limited to oils from lacustrine sources. This situation can arise in fresh to brackish lakes in which sulfate reduction is replaced by fermentation. The converse, however, is not true, that is, not all oils from lacustrine sources will exhibit these characteristics.

The Shengli oil from the Bohai Bay Basin is an example of a Zone 2 oil. The Shahejie Formation source of this oil is reported to have been deposited in a paralic fresh-brackish water lake subject to periodic marine transgressions (Wang et al., 1988). Our GC/MS/MS analysis shows the oil contains abundant C_{30} 24-*n*-propyl cholestanes indicative of significant marine input and gammacerane indicative of enhanced salinity. Apparently, the Shengli oil was derived, at least in part, from a source rock facies deposited during an episode of marine transgression. The resulting enhanced sulfate concentration could account for the somewhat higher DBT/PHEN ratio

and total sulfur content compared to other lacustrine oils (excepting the Salt Lake Group oil).

Oils in Zones 1A, 1B, and 2 with very low PR/PH ratios (< 0.4) represent environments in which phytane is available from archaeobacteria as well as phytol. The association of very low PR/PH ratios with hypersaline environments has been noted by ten Haven et al. (1988). Environments in which methanogenic bacteria are quite active could also be included in this category. In these environments, sulfate reduction can occur; however, hypersaline lacustrine environments may be deficient in sulfate and, because generation of sulfide is limited, incorporation of sulfur into organic matter is minimal. The principal characteristic of these environments is an additional source of phytane leading to very low PR/PH ratios.

In conjunction with Table 5, the cross-plot in Fig. 3 can be used to track changes in contemporaneous depositional environments from one basin to another. For example, several oils from the Miocene Monterey Formation in the Santa Maria Basin (1082, 1119, 1123, 1301, 1507) fall in Zone 1B, whereas oils from the Miocene Antelope Shale in the San Joaquin Basin (2329, 2330) fall in Zone 3. This indicates a transition from reducing sulfidic conditions in the Santa Maria Basin to reducing nonsulfidic in the San Joaquin Basin in agreement with the fact that the more shoreward position of the San Joaquin Basin resulted in deposition of significant amounts of iron-rich siliciclastic sediments (Graham and Williams, 1985).

Similar changes in depositional environment for contemporaneous sediments is illustrated by oils derived from the Jurassic Smackover Formation. Oils generated within the Manila Embayment, which have $\text{PR/PH} > 1$ and $\text{DBT/PHEN} < 1$, reflect an environment where iron availability was such that reducing but nonsulfidic conditions prevailed.

4. CONCLUSIONS

- 1) The ratio of dibenzothiophene to phenanthrene and the ratio of pristane to phytane, when coupled together, provide a novel, convenient, and powerful way to infer crude oil source rock depositional environments and lithologies.
- 2) Phytane in crude oils is derived from phytol and pristane is derived from phytol and possibly tocopherols. In certain restricted environments, e.g. hypersaline, phytane can be derived from archaeobacteria.
- 3) We propose that the ratio of dibenzothiophene to phenanthrene and the ratio of pristane to phytane reflect the different Eh-pH regimes resulting from the significant microbiological and chemical processes occurring during the deposition and early diagenesis of sediments.
- 4) Based on the ratio of dibenzothiophene to phenanthrene and the ratio of pristane to phytane, petroleum source rock depositional environments can be classified as dysoxic, anoxic nonsulfidic, anoxic sulfidic, anoxic fermentative, and anoxic hypersaline (see Table 5).

Acknowledgments—The authors thank the following individuals for samples of crude oils used in this study: P. W. Brooks, R. A. Noble, K. E. Peters, and J. D. Reed. We thank R. Sharp and L. Vo for analytical assistance, and E. Jordan for the in-house GC-IRMS analyses. Reviews by our coworkers R. A. Noble, E. Tegelaar, and A.

Brown and outside reviews by P. Garrigues, A. G. Requejo, and J. Sinninghe Damsté resulted in many constructive suggestions. We thank ARCO for permission to publish this work.

Editorial handling: M. C. Kennicutt II

REFERENCES

- Boudou J.-P. (1981) Chloroform extracts of a series of coals from the Mahakam Delta. *Org. Geochem.* **6**, 431–437.
- Brooks P. W. (1986) Unusual biological marker geochemistry of oils and possible source rocks, offshore Beaufort-Mackenzie delta, Canada. In *Advances in Organic Geochemistry 1985* (ed. D. Leythaeuser and J. Rullkötter); *Org. Geochem.* **10**, 401–406.
- Brooks P. W., Embry A. F., Goodarzi F., and Stewart R. (1992) Organic geochemistry and biological marker geochemistry of Schei Point Group (Triassic) and recovered oils from the Sverdrup Basin (Arctic Islands, Canada). *Bull. Canadian Petrol. Geol.* **40**, 173–187.
- Chowdhury L. R. and Taha S. (1987) Geology and habitat of oil in Ras Budran Field, Gulf of Suez, Egypt. *Bull. AAPG* **71**, 1274–1293.
- Claypool G. E. and Mancini E. A. (1989) Geochemical relationships of petroleum in Mesozoic reservoirs to carbonate source rocks of Jurassic Smackover Formation, southwestern Alabama. *Bull. AAPG* **73**, 904–924.
- Clayton J. L. (1989) Geochemical evidence for Paleozoic oil in Lower Cretaceous O sandstone, northern Denver basin. *Bull. AAPG* **73**, 977–988.
- Connan J. (1984) Biodegradation of crude oils in reservoirs. In *Advances in Petroleum Geochemistry*, Vol. 1 (ed. J. Brooks and D. Welte), pp. 299–335. Academic Press.
- Connan J., Bouroulec D., Dessort D., and Albrecht P. (1986) The microbial input in carbonate-anhydrite facies of a sabkha paleoenvironment from Guatemala: a molecular approach. In *Advances in Organic Geochemistry 1985* (ed. D. Leythaeuser and J. Rullkötter); *Org. Geochem.* **10**, 29–50.
- Curiale J., Cameron A. D., and Davis D. V. (1985) Biological marker distribution and significance in oils and rocks of the Monterey formation, California. *Geochim. Cosmochim. Acta* **49**, 271–288.
- Dahl B. and Spears G. C. (1986) Geochemical significance of a tar mat in the Oseberg field Norwegian sector, North Sea. In *Advances in Organic Geochemistry 1985* (ed. D. Leythaeuser and J. Rullkötter); *Org. Geochem.* **10**, 547–558.
- Deming J. and Baross J. A. (1993) The early diagenesis of organic matter: bacterial activity. In *Organic Geochemistry* (ed. M. H. Engel and S. A. Macko), pp. 119–144. Plenum Press.
- Didyk B. M., Simoneit B. R. T., Brassell S. C., and Eglinton G. (1978) Organic geochemical indicators of paleoenvironmental conditions of sedimentation. *Nature* **272**, 216–221.
- Douglas A. G., Sinninghe Damsté J. S., Fowler M. G., Eglinton T. I., and de Leeuw J. W. (1991) Unique distributions of hydrocarbons and sulfur compounds released by flash pyrolysis from the fossilised alga *Gloeocapsamorpha prisca*, a major constituent in one of four Ordovician kerogens. *Geochim. Cosmochim. Acta* **55**, 275–291.
- Dzou L. I. P. (1990) Quantitative study of biomarkers in coals and vitrinite concentrates of different maturity and a geochemical study of oils and condensates from K Field, offshore Taiwan. Ph.D. dissertation, Univ. Texas, Dallas.
- Dzou L. I. P. and Hughes W. B. (1993) Geochemistry of oils and condensates, K Field, offshore Taiwan: a case study in migration fractionation. *Org. Geochem.* **20**, 427–462.
- Freeman K. H., Hayes J. M., Trendel J.-M., and Albrecht P. (1990) Evidence from GC-MS carbon-isotopic measurements for multiple origins of sedimentary hydrocarbons. *Nature* **353**, 254–256.
- Garrigues P., Saptorahardjo A., Gonzalez C., Sehrung P. W., Albrecht P., Saliot A., and Ewald A. (1985) Biogeochemical aromatic markers in the sediments from Mahakam Delta (Indonesia). In *Advances in Organic Geochemistry 1985* (ed. D. Leythaeuser and J. Rullkötter); *Org. Geochem.* **10**, 959–964.
- Gautier D. J., Clayton J. L., Leventhal J. S., and Reddin N. J. (1984) Origin and source-rock potential of the Sharon Springs Member of the Pierre Shale, Colorado and Kansas. In *Hydrocarbon Source Rocks of the Greater Rocky Mountain Region* (ed. J. Woodward, et al.), pp. 369–385. Rocky Mountain Assoc. Geol.
- Goossens H., de Leeuw J. W., Schenck P. A., and Brassell S. C. (1984) Tocopherols as likely precursors of pristane in ancient sediments and crude oils. *Nature* **312**, 440–442.
- Graham S. A. and Williams L. A. (1985) Tectonic, depositional and diagenetic history of Monterey Formation (Miocene), central San Joaquin basin, California. *Bull. AAPG* **69**, 385–411.
- Hayes J. M., Freeman K. H., Popp B. N., and Hoham C. H. (1990) Compound-specific isotopic analyses: A novel tool for reconstruction of ancient biogeochemical processes. In *Advances in Organic Geochemistry 1989* (ed. B. Durand and F. Behar); *Org. Geochem.* **16**, 1115–1128.
- Hitchon B. (1961) Formation fluids. In *Geologic History of Western Canada* (ed. R. G. McCrosian and R. P. Glaister), pp. 200–217. Alberta Society of Petroleum Geologists.
- Hostettler F. D. and Kvenvolden K. A. (1994) Geochemical changes in crude oil spilled from the Exxon Valdez supertanker into Prince William Sound, Alaska. *Org. Geochem.* **21**, 927–936.
- Hughes W. B. (1984) The use of thiophenic organosulfur compounds in characterizing crude oils derived from carbonate versus siliciclastic source rocks. In *Petroleum Geochemistry and Source Rock Potential of Carbonate Rocks* (ed. J. G. Palacas); *AAPG Studies in Geology* **18**, 181–196.
- Hughes W. B., Holba A. G., Miiller D. E., and Richardson J. S. (1985) Geochemistry of greater Ekofisk crude oils. In *Petroleum Geochemistry in Exploration of the Norwegian Shelf* (ed. B. M. Thompson et al.), pp. 75–92. Graham and Trotman Ltd.
- Hughes W. B., Holba A. G., and Dzou L. (1989) A method for determining the depositional environment and lithology of crude oil source rocks. 1989 International Am. Chem. Soc. Meeting, Honolulu, Hawaii, December 17–22, 1989.
- Kohnen M. E. L., Sinninghe Damsté J. S., and de Leeuw J. W. (1991) Biases from natural sulphurization in paleoenvironmental reconstruction based on hydrocarbon biomarker distributions. *Nature* **349**, 775–778.
- Lewan M. D. (1984) Factors controlling the proportionality of vanadium to nickel in crude oils. *Geochim. Cosmochim. Acta* **48**, 2231–2238.
- Magoon L. B. and Anders D. E. (1992) Oil-to-source rock correlation using carbon-isotopic data and biological marker compounds, Cook Inlet-Alaska Peninsula, Alaska. In *Biological Markers in Sediments and Petroleum* (ed. J. M. Moldowan et al.), pp. 241–274. Prentice Hall.
- Meissner F. F., Woodward J., and Clayton J. L. (1984) Stratigraphic relationships and distribution of source rocks in the Greater Rocky Mountain region. In *Hydrocarbon Source Rocks of the Greater Rocky Mountain Region* (ed. J. Woodward et al.), pp. 1–34. Rocky Mountain Assoc. Geol.
- Mello M. R., Gaglianone P. C., Brassell S. C., and Maxwell J. R. (1988) Geochemical and biological marker assessment of depositional environments using Brazilian offshore oils. *Mar. Petrol. Geol.* **5**, 205–223.
- Miranda R. M. and Walters C. C. (1992) Geochemical variations in sedimentary organic matter within a ‘homogeneous’ shale core (Tuscaloosa Formation, Upper Cretaceous, Mississippi, U.S.A.). *Org. Geochem.* **18**, 899–911.
- Moldowan J., Seifert W. K., and Gallegos E. J. (1985) Relationship between petroleum composition and depositional environment of petroleum source rocks. *Bull. AAPG* **69**, 1255–1268.
- Momper J. A. and J. A. Williams (1979) Geochemical exploration in the Powder River basin. *Oil Gas J.* **77**, 129–134.
- Noble R. A., Wu C. H., and Atkinson C. D. (1991) Petroleum generation and migration from Talang Akar coals and shales offshore N. W. Java, Indonesia. *Org. Geochem.* **17**, 363–374.

- Orr W. L. (1974) Changes in sulfur content and isotope ratios of sulfur during petroleum maturation—study of Big Horn Basin Paleozoic oils. *Bull. AAPG* **58**, 2295–2318.
- Orr W. L. and Sinninghe Damsté J. S. (1990) Geochemistry of sulfur in petroleum systems. In *Geochemistry of sulfur in Fossil Fuels* (ed. W. L. Orr and C. M. White); *ACS Symposium Series* **429**, 2–29.
- Osadetz K. G., Snowdon L. R., and Brooks P. W. (1992) Oil families and their sources in Canadian Williston Basin, (southeastern Saskatchewan and southwestern Manitoba). *Bull. Canadian Petrol. Geol.* **40**, 254–273.
- Palmer S. E. (1984) Effect of water washing on C_{15+} hydrocarbon fraction of crude oils from northwest Palawan, Philippines. *Bull. AAPG* **68**, 137–149.
- Palacas J. G., Anders D. E., and King J. D. (1984) South Florida basin—a prime example of carbonate source rocks of petroleum. In *Petroleum Geochemistry and Source Rock Potential of Carbonate Rocks* (ed. J. G. Palacas); *AAPG Studies in Geology* **18**, 71–96.
- Peters K. E. and Moldowan J. M. (1993) *The Biomarker Guide*. Prentice Hall.
- Peters K. E., Moldowan J. M., Schoell M., and Hemphins W. B. (1986) Petroleum isotopic and biomarker composition related to source rock organic matter and depositional environment. In *Advances in Organic Geochemistry 1985* (ed. D. Leythaeuser and J. Rullkötter); *Org. Geochem.* **10**, 17–27.
- Pettijohn F. J. (1957) *Sedimentary Rocks*. Harper & Row.
- Philp R. P. and Gilbert T. D. (1986) biomarker distributions in Australian oils predominantly derived from terrigenous source material. In *Advances in Organic Geochemistry 1985* (ed. D. Leythaeuser and J. Rullkötter); *Org. Geochem.* **10**, 73–84.
- Philp R. P. and Lewis C. A. (1987) Organic geochemistry of biomarkers. *Annu. Rev. Earth Planet. Sci.* **15**, 363–395.
- Poole F. G. and Claypool G. E. (1984) Petroleum source-rock potential and crude-oil correlation in the Great Basin. In *Hydrocarbon Source Rocks of the Greater Rocky Mountain Region* (ed. J. Woodward et al.), pp. 179–229. Rocky Mountain Assoc. Geol.
- Powell T. G. (1987) Depositional controls on source rock character and crude oil composition. In *Twelfth World Petroleum Congress, Houston, Texas. Preprints Earth Science Modeling, Vol. 2, Exploration*, 31–42.
- Powell T. G. and McKirdy D. M. (1973) Relationship between ratio of pristane to phytane, crude oil composition and geological environment in Australia. *Nature* **243**, 37–39.
- Radke M. (1988) Applications of aromatic compounds as maturity indicators in source rocks and crude oils. *Mar. Petrol. Geol.* **43**, 1675–1679.
- Radke M., Schaefer R. G., Leythaeuser D., and Teichmüller M. (1980) Composition of soluble organic matter in coals: relation to rank and liptinite fluorescence. In *Advances in Organic Geochemistry 1983* (ed. P. A. Schenck et al.), pp. 423–430. Pergamon.
- Reed J. R. (1992) Exploration geochemistry of the Taranaki basin with emphasis on Kora. *Proc. 1991 Oil Explor. Conf.*, 364–372. Ministry of Commerce, New Zealand.
- Reed J. R., Illich H. A., and Horsfield B. (1986) Biochemical evolutionary significance of Ordovician oils and their sources. In *Advances in Organic Geochemistry 1985* (ed. D. Leythaeuser and J. Rullkötter); *Org. Geochem.* **10**, 347–358.
- Requejo A. G. (1992) Quantitative analysis of triterpane and sterane biomarkers: methodology and applications in molecular maturity studies. In *Biological Markers in Sediments and Petroleum* (ed. J. M. Moldowan et al.), pp. 222–240. Prentice Hall.
- Requejo A. G. (1994) Maturation of petroleum source rocks-II. Quantitative changes in extractable hydrocarbon content and composition associated with hydrocarbon generation. *Org. Geochem.* **21**, 91–105.
- Requejo A. G. and Halpern H. IA. (1990) A geochemical study of oils from the South Pass 61 Field, Offshore Louisiana. In *Gulf Coast Oils and Gases, Proceedings of 9th Annual Res. Conf.* (ed. D. Schumacher and B. F. Perkins), pp. 37–57. Gulf Coast Section SEPM.
- Risatti J. B., Rowland S. J., Yan D. A., and Maxwell J. R. (1984) Stereochemical studies of acyclic isoprenoids-XII. Lipids of methanogenic bacteria and possible contributors to sediments. *Org. Geochem.* **6**, 93–104.
- Robinson B. W., Hirner A. V., and Lyon G. L. (1991) Stable carbon and sulfur isotope distributions of crude oil and source rock constituents from Burgan and Raudhatain oil fields (Kuwait). *Chem. Geol. (Isotope Geosci. Sect.)* **86**, 295–306.
- Rohrbach B. G. (1983) Crude oil geochemistry of the Gulf of Suez. In *Advances in Organic Geochemistry 1981* (ed. M. Bjorøy et al.), pp. 39–48. Wiley.
- Rowland S., Rockey C., Al-Lihaibi S. S., and Wolff G. A. (1993) Incorporation of sulphur into phytol derivatives during simulated early diagenesis. *Org. Geochem.* **20**, 1–5.
- Ross L. M. (1980) Geochemical correlation of San Juan basin oils—a study. *Oil Gas J.* (Nov. 3), 102–110.
- Rullkötter J., Meyers P. A., Schaefer R. G., and Dunham K. W. (1986) Oil generation in the Michigan Basin: a biological marker and carbon isotope approach. In *Advances in Organic Geochemistry 1985* (ed. D. Leythaeuser and J. Rullkötter); *Org. Geochem.* **10**, 359–375.
- Sassen R. (1989) Migration of crude oil from the Smackover source rock to Jurassic and Cretaceous reservoirs of the northern Gulf rim. *Org. Geochem.* **14**, 51–60.
- Sassen R. (1990) Geochemistry of carbonate source rocks and crude oils in Jurassic Salt Basins of the Gulf Coast. In *Gulf Coast Oils and Gases, Proceedings of 9th Annual Res. Conf.* (ed. D. Schumacher and B. F. Perkins), pp. 37–57. Gulf Coast Section SEPM.
- Sassen R., Tye R. S., Chinn E. W., and Lemoine R. C. (1988) Origin of crude oil in the Wilcox trend of Louisiana and Mississippi: Evidence of long-range migration. *Transactions-Gulf Coast Association of Geological Societies* **38**, 27–34.
- Schoell M. (1984) Recent advances in petroleum isotope geochemistry. *Org. Geochem.* **6**, 645–663.
- Schoell M., McCaffrey M. A., Fago F. J., and Moldowan J. M. (1992) Carbon isotopic composition of 28,30-bisnorhopanes and other biological markers in a Monterey crude oil. *Geochim. Cosmochim. Acta* **56**, 1391–1399.
- Shi J. Y., Mackenzie A. S., Alexander R., Eglinton G., Gowar A. P., Wolff G. A., and Maxwell J. R. (1982) A biological marker investigation of petroleum and shales from Shengli oilfield, The People's Republic of China. *Chem. Geol.* **35**, 1–31.
- Sieskind O., Joly G., and Albrecht P. (1979) Simulation of the geochemical transformations of sterols: superacid effect of clay minerals. *Geochim. Cosmochim. Acta* **43**, 1675–1679.
- Sinninghe Damsté J. S. and de Leeuw J. W. (1990) Analysis, structure and geochemical significance of organically-bound sulfur in the geosphere: state of the art and future research. In *Advances in Organic Geochemistry 1989* (ed. B. Durand and F. Behar); *Org. Geochem.* **16**, 1077–1101.
- Sinninghe Damsté J. S., de Leeuw J. W., Kock-van Dalen A. C., de Zeeuw M. A., de Lange F., Rijpsma I. C., and Schenck P. A. (1987) The occurrence and identification of series of organic sulphur compounds in oils and sediment extracts. I. a study of Rozel Point oil, U.S.A. *Geochim. Cosmochim. Acta* **51**, 2369–2391.
- Snowdon L. R. and Powell T. G. (1979) Families of crude oils and condensates in the Beaufort-Mackenzie Basin. *Bull. Canadian Petrol. Geol.* **27**, 139–162.
- Sofer Z. (1984) Stable isotope compositions of crude oils: application to source depositional environments and petroleum alteration. *Bull. AAPG* **68**, 31–49.
- Sofer Z. (1988) Biomarkers and carbon isotopes of oils in the Jurassic Smackover trend of the Gulf Coast, U.S.A. *Org. Geochem.* **12**, 421–432.
- ten Haven H. L., de Leeuw J. W., Rullkötter J., and Sinninghe Damsté J. S. (1987) Restricted utility of the pristane/phytane ratio as a palaeoenvironmental indicator. *Nature* **330**, 641–643.
- ten Haven H. L., de Leeuw J. W., Sinninghe Damsté J. S., Schenck P. A., Palmer S. E., and Zumberge J. E. (1988) Application of biological markers in the recognition of palaeo hypersaline environments. In *Lacustrine Petroleum Source Rocks* (ed. A. J. Fleet et al.); *Geol. Soc. Special Pub. No. 40*, 309–325.
- ten Haven H. L., Rullkötter J., Sinninghe Damsté J. S., and de Leeuw J. W. (1990) Distribution of organic sulfur compounds in

- Mesozoic and Cenozoic sediments from the Atlantic and Pacific Oceans and the Gulf of California. In *Geochemistry of Sulfur in Fossil Fuels* (ed. W. L. Orr and C. M. White); *ACS Symposium Series* 429, 613–632.
- Thompson K. F. M., Kennicutt II M. C., and Brooks J. M. (1990) Classification of offshore Gulf of Mexico oils and gas condensates. *Bull. AAPG* 74, 187–198.
- Tissot B. P. and Welte D. H. (1984) *Petroleum Formation and Occurrence—A New Approach to Oil and Gas Exploration*. Springer-Verlag.
- Tissot B., Deroo G., and Hood, A. (1978) Geochemical study of the Uinta Basin: Formation of petroleum from the Green River formation. *Geochim. Cosmochim. Acta* 42, 1469–1485.
- van Graas G. W. (1990) Biomarker maturity parameters for high maturities: calibration of the working range up to the oil/condensate threshold. In *Advances in Organic Geochemistry 1989* (ed. B. Durand and F. Behar); *Org. Geochem.* 16, 1025–1032.
- Volkman J. K. (1988) Biological marker compounds as indicators of the depositional environments of petroleum source rocks. In *Lacustrine Petroleum Source Rocks* (ed. A. J. Fleet, et al.); *Geol. Soc. Special Pub. No. 40*, 103–122.
- Volkman J. K. and Maxwell J. R. (1986) Acyclic isoprenoids as biological markers. In *Biological Markers in the Sedimentary Record* (ed. R. B. Johns), pp. 1–42. Elsevier.
- Waldo G. S., Carlson R. M., Moldowan J. M., Peters K. E., and Penner-Hahn J. E. (1991) Sulfur speciation in heavy petroleum: information from X-ray absorption near-edge structure. *Geochim. Cosmochim. Acta* 55, 801–814.
- Wang T., Pu F., and Swain F. M. (1988) Geochemical characteristics of crude oils and source beds in different continental facies of four oil-bearing basins, China. In *Lacustrine Petroleum Source Rocks* (ed. A. J. Fleet et al.); *Geol. Soc. Special Pub. No. 40*, 309–325.
- Wenger L. M., Sassen R., and Schumacher D. (1990) Molecular characteristics of Smackover, Tuscaloosa and Wilcox-reservoired oils in the eastern Gulf Coast. In *Gulf Coast Oils and Gases, Proceedings of 9th Annual Res. Conf.* (ed. D. Schumacher and B. F. Perkins), pp. 37–57. Gulf Coast Section SEPM.
- Williams H. H., Kelly P. A., Janks J. S., and Christensen R. M. (1985) The Paleogene rift basin source rocks of Central Sumatra. *Proceedings of the Fourteenth Annual Convention of the Indonesian Petroleum Association* 1, 57–90.
- Williams J. A. (1974) Characterization of oil types in Williston Basin. *AAPG Bull.* 58, 1243–1252.
- Williams J. A., Bjoroy M., Dolcater D. L., and Winters J. C. (1986) Biodegradation in South Texas Eocene oils—effects on aromatics and biomarkers. *Org. Geochem.* 10, 451–461.
- Yon D. A., Maxwell J. R., and Rybach G. (1982) 2, 6, 10-trimethyl-7-(3-methylbutyl)-dodecane, a novel sedimentary biological marker compound. *Tetrahedron Lett.* 23, 2143–2146.

APPENDIX A

RESPONSE FACTORS FOR SELECTED MOLECULAR MARKERS

Saturates (relative to 5 β -cholane)

Compound	Reference ion (m/z)	Response factor ¹
Pristane	183	6.0
Phytane	183	10.0

Aromatics (relative to anthracene-d₁₀)

Compound	Reference ion(m/z)	Response factor ¹
Phenanthrene	178	0.85
Methylphenanthrene	192	0.80
Dibenzothiophene	184	0.70
Methyldibenzothiophene	198	0.90

¹Response Factor = (A)wt * (IS)area/(IS)wt * (A)area, where A = compound of interest and IS = internal standard. Areas of 5 β -cholane and anthracene-d₁₀ measured from m/z 217 and m/z 188 mass fragmentograms, respectively.

APPENDIX B
CONCENTRATION DATA FOR SELECTED MOLECULAR MARKERS

SAMPLE	PR WH OIL	PR TOP OIL	PH WH OIL	PH TOP OIL	DBT WH OIL	DBT TOP OIL	PHEN WH OIL	PHEN TOP OIL	MDBT WH OIL	MDBT TOP OIL	MPHEN WH OIL	MPHEN TOP OIL
Marine Carbonate												
0001	-	-	-	-	-	-	-	-	-	-	-	-
0805	274.0	323.0	688.5	811.7	163.4	192.6	40.9	48.2	606.5	715.0	138.7	163.5
0808	381.8	543.8	740.0	1053.9	280.8	399.9	53.8	76.7	1149.4	1637.0	205.3	292.4
0819	376.7	644.4	692.6	1184.6	323.8	553.8	44.8	76.6	1614.7	2762.0	175.6	300.3
0820	384.6	591.9	705.6	1086.1	324.6	499.6	71.5	110.1	1410.0	2170.2	257.0	395.5
0823	338.0	628.4	632.9	1176.8	338.1	628.6	57.2	106.4	1594.8	2965.1	200.3	372.4
0959	741.1	1248.5	1735.6	2923.8	35.9	60.4	21.1	35.6	276.6	465.9	104.9	176.7
1281	718.2	998.8	1227.6	1707.3	1212.3	1686.1	232.7	323.7	1879.5	2614.0	509.3	708.4
1337	885.6	1269.9	1399.1	2006.2	927.9	1330.5	184.4	264.5	1563.8	2242.4	466.6	669.1
1587	-	-	-	-	-	-	-	-	-	-	-	-
1588	-	-	-	-	-	-	-	-	-	-	-	-
2970	2266.1	4025.0	2832.6	5031.3	62.6	111.1	33.3	59.3	212.3	377.1	85.1	151.1
2227	732.2	859.8	1438.6	1689.2	75.3	88.4	64.4	75.7	308.5	362.2	137.5	161.5
2228	882.7	1123.8	1652.9	2104.4	91.9	117.0	71.1	90.6	359.9	458.2	160.7	204.6
Marine Mixed												
0338	243.6	271.4	384.3	428.1	117.4	130.8	77.7	86.5	544.6	606.7	221.5	246.7
0398	543.4	622.4	1025.3	1174.3	182.5	209.0	86.9	99.5	826.9	947.1	280.0	320.7
1082	1187.6	1504.8	1613.6	2044.6	58.0	73.4	40.8	51.7	131.2	166.3	108.3	137.2
1119	302.1	318.1	719.3	757.4	71.8	75.6	25.1	26.4	101.9	107.3	48.4	51.0
1123	1285.9	1551.2	1803.5	2175.5	121.2	146.2	85.2	102.8	318.1	383.8	238.3	287.5
1301	380.8	400.9	749.5	789.3	59.6	62.7	30.4	32.0	100.0	105.3	66.3	69.8
1507	624.6	636.8	932.2	950.5	91.3	93.1	53.3	54.3	168.7	172.0	124.4	126.8
2120	-	-	-	-	-	-	-	-	-	-	-	-
2219	504.4	685.8	874.2	1188.6	99.9	135.8	82.4	112.1	494.0	671.6	221.8	301.6

APPENDIX B (Continued)

SAMPLE	PR WH OIL	PR TOP OIL	PH WH OIL	PH TOP OIL	DBT WH OIL	DBT TOP OIL	PHEN WH OIL	PHEN TOP OIL	MDBT WH OIL	MDBT TOP OIL	MPHEN WH OIL	MPHEN TOP OIL
Marine Shale												
0002	-	-	-	-	-	-	-	-	-	-	-	-
0003	-	-	-	-	-	-	-	-	-	-	-	-
0004	-	-	-	-	-	-	-	-	-	-	-	-
0005	-	-	-	-	-	-	-	-	-	-	-	-
0285	1260.1	2330.4	739.1	1366.8	19.9	36.9	346.5	640.7	50.4	93.2	636.2	1176.6
0391	621.3	2172.4	352.8	1233.6	6.5	22.7	126.3	441.6	25.2	88.2	271.5	949.3
0405	1831.9	2769.1	1275.7	1928.4	16.6	25.1	272.3	411.5	61.8	93.4	536.9	811.5
0433	1558.1	2074.6	934.1	1243.8	20.0	26.7	219.0	291.6	68.3	90.9	421.9	561.8
0518	1986.6	2003.1	1163.8	1173.5	7.8	7.8	34.8	35.1	31.2	31.4	95.8	96.6
0794	741.8	793.4	520.9	557.2	21.4	22.9	37.3	39.9	16.7	17.8	37.0	39.6
0804	-	-	-	-	-	-	-	-	-	-	-	-
0841	4839.6	6888.6	4698.7	6687.9	138.7	197.5	562.2	800.2	592.2	842.9	1413.6	2012.0
0843	-	-	-	-	-	-	-	-	-	-	-	-
1104	2558.9	3208.1	1472.3	1845.9	7.8	9.8	42.1	52.7	26.6	33.4	99.1	124.2
1888	1483.9	2924.6	837.9	1651.4	16.0	31.6	108.5	213.9	62.5	123.2	248.5	489.8
1904	-	-	-	-	-	-	-	-	-	-	-	-
1916	1009.6	1752.3	428.7	744.1	10.0	17.3	213.5	370.5	35.1	61.0	409.2	710.2
2226	1440.4	2180.9	597.7	905.0	11.0	16.7	251.5	380.8	31.7	48.0	524.2	793.7
2224	2172.2	3146.4	1584.4	2294.9	94.9	137.4	325.7	471.8	284.5	412.0	776.1	1124.2
2279	1729.0	2098.9	1194.9	1450.5	12.6	15.3	313.1	380.1	64.6	78.4	659.3	800.4
2280	100.3	125.9	85.0	106.7	23.3	29.3	336.5	422.6	65.3	82.0	443.0	556.3
2281	1120.9	1170.7	884.0	923.3	47.8	49.9	617.7	645.2	103.4	107.9	810.3	846.3
2329	-	-	-	-	-	-	-	-	-	-	-	-
2330	-	-	-	-	-	-	-	-	-	-	-	-
2477	-	-	-	-	-	-	-	-	-	-	-	-
1977	922.6	1192.5	643.0	831.0	72.4	93.6	139.1	179.8	227.4	293.9	358.8	463.7
2682	6974.3	8010.9	4246.4	5006.8	84.3	99.4	581.6	685.8	324.7	382.8	1433.7	1690.4
Fluvial/Deltaic												
0246	22040.5	29295.7	2530.5	3363.4	46.0	61.1	316.2	420.3	106.3	141.3	518.9	689.7
0375	193.6	4718.3	59.5	1451.3	8.0	194.9	110.9	2703.3	13.7	334.3	129.6	3158.6
2072	10210.3	11155.7	1598.6	1746.6	24.1	26.3	277.8	303.6	48.5	53.0	471.8	515.5
2078	1304.4	13056.0	165.5	1656.6	15.3	152.7	111.1	1111.8	28.7	287.8	142.3	1424.5
2222	4773.4	7237.1	871.9	1321.8	50.0	75.8	202.2	306.6	96.4	146.1	477.8	724.4
2223	8241.9	9574.9	1522.0	1768.2	63.9	74.2	232.5	270.1	112.2	130.4	575.2	668.2
2232	2573.7	3891.0	649.4	981.8	11.6	17.6	166.5	251.8	13.9	21.0	90.3	136.6
2292	-	-	-	-	-	-	-	-	-	-	-	-
2293	2600.2	3999.1	617.6	949.9	67.4	103.7	528.2	812.4	201.2	309.4	1043.8	1605.3
2381	8818.7	9715.2	1258.0	1385.9	64.7	71.3	1075.0	1184.3	126.6	139.5	1366.4	1505.3
Lacustrine												
0255	2018.3	2343.8	1858.5	2158.2	5.0	5.8	178.4	207.1	26.7	31.0	386.3	448.6
0987	2555.6	2801.5	1898.7	2081.3	8.2	9.0	167.2	183.3	25.6	28.0	370.4	406.1
0502	9.8	10.2	264.9	276.6	23.6	24.7	11.6	12.1	63.4	66.1	19.1	19.9
2212	4244.8	4786.9	2674.7	3016.3	7.7	8.7	102.9	116.1	28.9	32.5	189.5	213.7
2234	2608.4	3457.1	1180.3	1564.3	8.2	10.8	92.9	123.1	24.9	33.0	220.3	292.0
2220	2784.7	3447.7	1262.9	1563.6	21.5	26.7	262.9	325.5	65.2	80.7	531.3	657.7
2221	2719.6	3301.9	1295.6	1573.1	22.0	26.7	243.7	295.9	73.1	88.7	486.5	590.6
2230	2304.4	2501.9	5261.2	5712.1	14.2	15.4	79.8	86.6	48.1	52.3	168.5	183.0
Ordovician												
0731	112.2	123.7	93.5	103.1	25.4	28.0	260.7	287.4	72.8	80.3	537.6	592.6
0866	462.4	473.8	355.7	364.5	69.5	71.3	444.9	455.9	242.4	248.4	870.4	891.9
1145	56.7	81.4	67.7	97.2	50.7	72.8	471.1	676.0	459.1	658.8	1335.1	1915.7
1211	414.9	608.5	316.2	463.8	15.3	22.5	55.1	80.8	93.2	136.7	250.6	367.6
1401	99.3	126.2	162.7	207.0	65.2	82.9	686.0	872.4	252.3	320.9	1165.8	1482.6
1529	224.2	311.3	157.4	218.6	42.1	58.5	366.9	509.5	158.3	219.9	915.2	1270.9
2473	-	-	-	-	-	-	-	-	-	-	-	-
2474	1862.6	3423.1	1135.7	2087.2	25.6	47.1	360.8	663.0	144.6	265.8	749.5	1377.4

* all concentrations in µg/g of whole oil (WH OIL) or topped oil (TOP OIL)

PR = pristane

PH = phytane

DBT = dibenzothiophene

PHEN = phenanthrene

MDBT = sum of methyl dibenzothiophenes

MPHEN = sum of methyl phenanthrenes