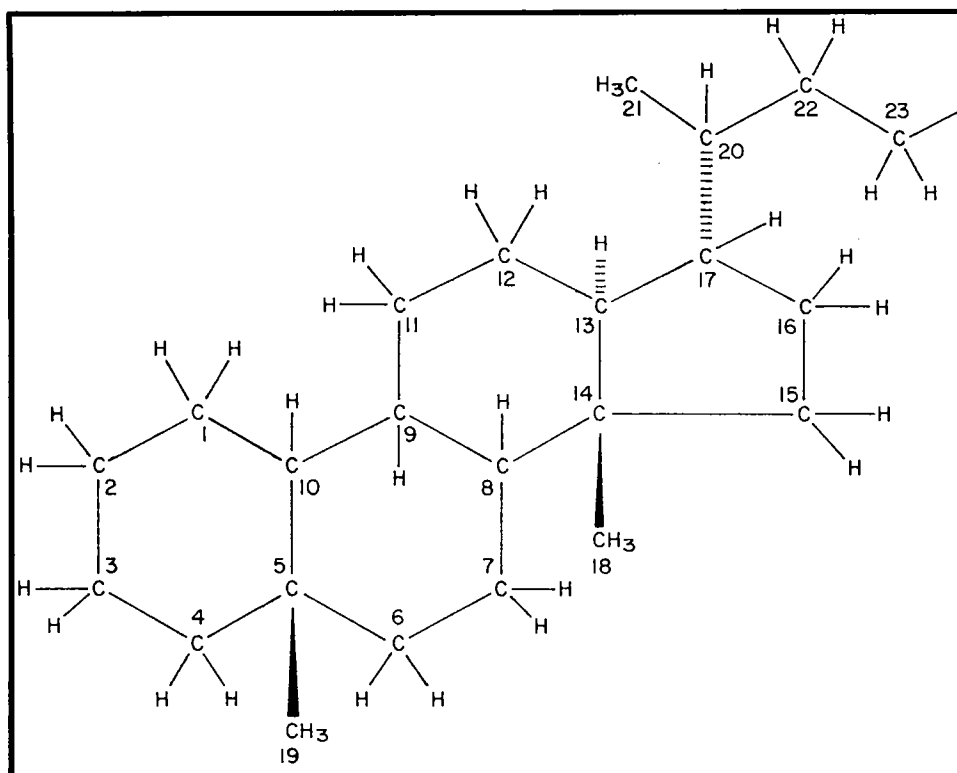


Oil-Oil and Oil-Rock Correlations: A Chemist's Perspective

Jane L. Weber



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OIL-OIL AND OIL-ROCK CORRELATIONS:
A CHEMIST'S PERSPECTIVE

by

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ABSTRACT

Organic geochemical concepts that can be related to the generation and maturation of petroleum offer a base for a growing number of parameters used in oil-oil and oil-rock correlations. Application of these parameters makes it possible to assess the influence on an oil of source material, the extent of degradation, and possibly migration history. Capillary-column gas chromatography/mass spectrometry, the most powerful analytical approach to correlation studies, can be applied at the molecular level to virtually every aspect of petroleum correlation. However, even with the wide array of diagnostic tools available, correlations are not routine. Each oil or rock extract, composed of thousands of compounds, is unique, and each therefore presents a separate problem.

INTRODUCTION

Techniques for making oil-oil or oil-rock correlations have evolved considerably since the days when crude oils were classified according to their physical properties and an oil was related to a source rock on the basis of geologic considerations alone. With the advent of organic geochemistry and the higher levels of information derived from it, application of geochemical parameters to oil-oil and oil-rock correlation

studies has become widespread. Development of new and powerful analytical techniques (gas chromatography/mass spectrometry, in particular) has provided a means for extending geochemical interpretations to the molecular level. The ability to (1) distinguish subtle chemical differences in oils or rock extracts, (2) make estimates of distance of migration and of maturity level, and (3) assess extent of degradation now permits far more detailed reconstructions of basin history than were possible heretofore. This review, using the currently popular organic-geochemistry theory of petroleum generation as a base, focuses on recent developments in correlation studies by categorizing work published since 1980. The references cited are not an exhaustive list; rather they are intended to provide a starting point from which the interested reader can further pursue the subject.

BACKGROUND

Although the flow of literature in this field is ever increasing, according to Waples (1981) surprisingly few conclusive correlations have been published. Also, authors do not always arrive at the same interpretation. Organic geochemistry, especially petroleum geochemistry, is still a relatively young discipline and suffers the problems and uncertainties associated with immaturity. Serious gaps in understanding still persist.

While most geologists fully subscribe to the organic geochemical model of petroleum generation via thermal breakdown of kerogen, i.e., organic matter finely disseminated in source beds, the theory is still being developed, and sometimes even its main tenets are questioned. Less widely accepted theories being advanced center on (1) a hot

($\geq 200^{\circ}\text{C}$), deep ($\sim 7,000$ m) origin (Price, 1980a,b,1981,1982,1983); (2) a cool ($50-80^{\circ}\text{C}$), shallow ($\leq 2,800$ m) origin following anaerobic transformation of organic matter (Yi-Gang, 1981); or (3) outgassing of primordial hydrocarbons from the Earth's mantle (Gold and Soter, 1980; Giardini and Melton, 1981; Giardini and others, 1982; Melton and Giardini, 1984). Special cases of oil generation may exist. For example, Snowden and Powell (1982) theorize that hydrocarbons in many Canadian basins resulted from low-temperature thermal reactions involving resin-rich material. After studying the regional stratigraphy, pattern of oil occurrence, and "plumbing system" of Saudi Arabia, Wilson (1982) suggested that Saudi fields are an example of early-generated oil.

Some geologists rule out carbonate facies as sources of commercially important deposits, because carbonates are lithified, contain little organic matter, and lack water or other means of effective hydrocarbon expulsion. This idea has been ably refuted (Yi-Gang, 1981; Ibe and others, 1983; Palacas, 1984). However, it should be noted that the usual chemical criteria for evaluating source rocks evolved from shale studies and have been found misleading and inadequate when applied to limestones.

Even for those researchers who agree on the basic principles of petroleum genesis, there is still no single measurement or group of measurements which can unequivocally explain the distribution of individual components in a source-rock extract or in a crude oil that has accumulated in a reservoir. These components are estimated by Winters (1983) to number in the tens of thousands. It is difficult to distinguish between the complex factors which influence (1) the composition of the original organic matter, (2) the geologic history of the source rock,

(3) migration phenomena, and (4) alteration processes active in the source rock and reservoir. The following quotes emphasize the uniqueness and difficulty of each correlation and the necessity for a wide array of diagnostic tools from which to choose.

Hunt (1979): "Crude oil correlation is not routine, in that each problem may require a different approach . . . source rocks do not yield oils of the same composition throughout their generation history."

Ross (1980): "It has been our experience that a technique which may clearly define oil types in one area might not necessarily be successful in another."

Mackenzie and others (1983): "Crude oil accumulations are often aggregates of different oils, derived from source beds of different levels of maturity."

Alexander and others (1983): "The final composition of a crude oil therefore could be vastly different from that of the hydrocarbon in its source rocks."

Waples (1981): "Because bitumen and petroleum differ so dramatically in composition, it is very difficult to make definitive source rock-oil correlations."

Saxby (1982): "It may be concluded that accurate identification of source rocks from extract data alone is at best difficult and at worst impossible."

Correlation studies are based on recognition of compositional similarities between reservoired oil(s) and oil left in the source rock. These similarities may indicate a genetic relationship, although superficially the oils may look very different. Conventional theory presupposes not only that the composition of a generated oil remains

essentially unchanged, but also that certain parameters are representative of a particular source rock over its entire drainage area. An oil, however, may be a mixture of oils from different sources, and a specific sample of a potential source rock represents only one component of a dynamic system. Furthermore, the rock may have petroleum-producing facies of limited extent. Consequently, it is frequently easier to determine that oils are not related than the reverse. On the other hand, the inability to get complete agreement between all parameters may be due to a researcher's limited objectives, or to the manner in which a "single oil type" is defined, or to a failure to consider processes affecting various parameters and the amount of change expected from such processes.

In a study involving eight source rocks analyzed by 19 laboratories, Dembicki (1984) found that differences in sample preparation, analytical procedures, and definition of measurement units made it difficult if not impossible to compare data among the laboratories. In the absence of standardized procedures and standard reference samples, which a more mature discipline could offer, the multi-analysis approach is necessary and also serves as an internal calibration system. The choice of correlation parameters is dictated by the availability of specialized equipment in the laboratory and the expertise of the investigator. However, since conclusions based on specific hydrocarbons or groups of hydrocarbons may not reflect the history of an oil as a whole, the array of tests selected should span both a wide range of molecular weights and a wide range of compounds. Correlations based on a single parameter are hardly convincing.

Geochemical parameters being used in oil-oil and oil-rock

correlations are increasing in number and sophistication. Bulk parameters such as API gravity, sulfur content, optical activity, or percent saturates or aromatics have lost much of their former significance and, with the exception of stable-isotope ratios and nickel-vanadium proportionality, will not be considered here. Such parameters are still included in correlation investigations, but their role seems to have been downgraded to that of supporting evidence.

CORRELATION PARAMETERS BASED ON SPECIFIC-COMPOUND MEASUREMENTS

Alkanes (Saturates or Paraffins)

The straight-chain, branched, and cyclic alkanes are usually examined initially by gas chromatography (GC). Application of the carbon-number distribution pattern of alkanes (especially the normal, or straight-chain, species; Fig. 1) is probably the most widely used biomarker technique (Philp and Gilbert, 1980), because of the amount and variety of information that can be so easily obtained.

Profile maxima of n-alkanes can indicate whether a specific source interval is derived primarily from marine or from terrestrial organic matter (Hunt, 1979; Vogler and others, 1981; Philp and others, 1982; Kinghorn, 1983) and whether the oil or bitumen is mature or immature (Burns and Bein, 1980; Waples, 1981; Kinghorn, 1983). A prominent naphthenic (cycloalkane) "hump" in the high-molecular-weight region of a gas chromatogram or a bimodal naphthenic envelope can signal immaturity (Clayton and Swetland, 1980; McKirdy and Kantsler, 1980; Welte and others, 1982; Alexander and others, 1983; Kinghorn, 1983), but a hump of unresolved complex mixtures can also result from biodegradation or

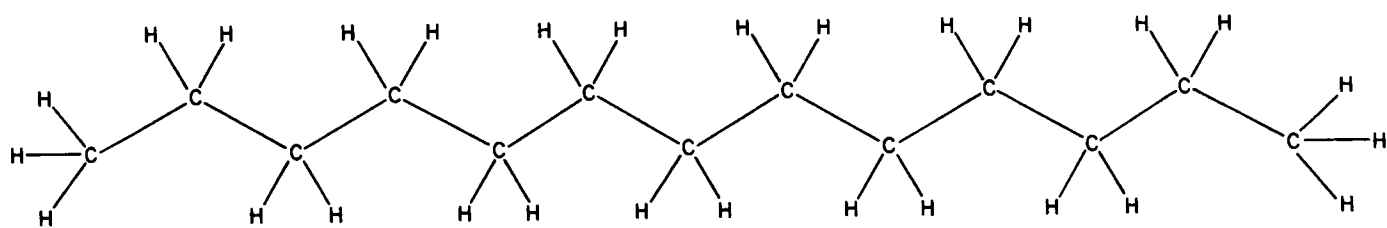


Figure 1. C_{13} , an example of a straight-chain (normal) alkane.

water-washing (Burns and Bein, 1980; Bockmeulen and others, 1983; Volkman and others, 1983a). Absence or depletion of n-alkanes often indicates that degradation or water-washing has occurred.

Bissada (1983) used n-alkane patterns to confirm correlations in his study of the Moray Firth Basin; he concluded from similarities in the C_{15}^+ n-alkane distributions of six crudes that they are from the same or similar source beds. The averaged C_{17}^+ n-alkane distribution of these six oils is virtually identical to the averaged C_{17}^+ n-alkane distribution of 17 Kimmeridgian shale samples. From this evidence Bissada inferred a genetic relationship between the shales and the associated oils.

Ala and others (1980) considered the GC profile of C_{12} - C_{28} n-alkanes to be their "most impressive evidence" in correlating Iranian oils with rock extracts from the Zagros petroleum province. They studied nine oils from two reservoirs and 141 surface and core samples from five potential source rocks. All available evidence pointed to the Albian as the major source for the two reservoirs.

Contrasting these two studies, in characterizing otherwise apparently related crudes from the Bolivar Coastal Fields, Bockmeulen and others (1983) found that n-alkane distributions exhibited "the most obvious differences among the oils."

Alexander and others (1981) thought that C_{15}^+ n-alkanes reflected both genetic and maturation effects, primarily the former. Using experimental data from laboratory pyrolysis of source rocks to first determine maturation influences, these workers established a correlation-parameter reliability scale based on eight parameters commonly used to diagnose genetic relationships. They weighted individual parameters from 5 to 30 points, allocating a total of 100 points. They

also set for each parameter the degree of agreement necessary between samples to qualify as a correlation. On this scale, C_{15}^{+} n-alkane distribution patterns rated a moderate 15 points.

Kinghorn (1983) believed that the shape of an oil's alkane spectrum could relate wholly or in part to thermal maturation, genetic material, or post-generation processes (e.g., biodegradation). Perhaps Waples's (1981) conclusion that "n-alkanes are only rough indicators of the total effects" which determine the characteristics of an oil best explains their significance as correlation parameters. Although alkane data are useful in conjunction with other information, alkanes are not sufficiently specific to provide reliable data that can stand alone. Furthermore, n-alkane patterns are of limited use where biodegradation or water-washing is involved.

Biodegradation.--With an estimated 10% of the world's known petroleum reserves destroyed, and another 10% altered by bacteria (Hunt, 1979), the necessity of being able to match a degraded oil with a nondegraded oil or extract is obvious. In correlation work, this capability must be expanded to the point where degree of degradation can be determined. Assuming that bacterial degradation sequentially removes n-alkanes, branched alkanes, and some naphthenes and aromatics, and, in extreme cases, alters steroid and triterpenoid alkanes (see, for example, Alexander and others, 1983; Philp, 1983; Spiro and others, 1983; Volkman and others, 1983b; Palmer, 1984), ratios of various alkanes, such as methylbutane/n-pentane or n-heptane/total C_7 alkanes, are frequently used to indicate extent of microbial alteration (Welte and others, 1982). Effects of water-washing, which is requisite to biodegradation (Alexander and others, 1983), can be measured by

ratios of branched or cyclic alkanes to the more water-soluble light aromatics (e.g., benzene or toluene). (See, for example, Welte and others, 1982; Spiro and others, 1983.)

Basing his explanation on the foregoing scheme of stepwise destruction, Philp (1983) suggested that the coexistence of n-alkanes and demethylated hopanes (the latter frequently associated with severe degradation) in oils from the San Jorge Basin in Argentina resulted from biodegradation followed by an influx of new oil.

Carbon-Number Preference

Data on n-alkanes are also used in correlation studies to measure predominance of odd-numbered carbon atoms per chain as quantified by the odd-even preference (OEP) or the carbon preference index (CPI). OEP is more flexible in that it can be applied to any molecular weight range, but CPI is more commonly used. High molecular weight (i.e., C₂₅+) odd-carbon-numbered molecules predominate over even-numbered ones by as much as a factor of 5 (Waples, 1981) in most young sediments, especially those deposited under terrestrial conditions (Hunt, 1979; Philp and Gilbert, 1980; Kinghorn, 1983; Spiro and others, 1983). Predominance of even-numbered n-alkanes has been associated with reducing conditions (Vogler and others, 1981; Ji-Yang and others, 1982; Seifert and others, 1983) and carbonate rocks, which are believed always to have an original even-numbered dominance (Ross, 1980; Kinghorn, 1983; Spiro and others, 1983). In a study of oils from three closely located Nevada fields (French, 1983), one oil showed a slight even-carbon preference in the n-C₁₈ to n-C₂₆ range and unusually high pristane and phytane peaks. French attributed these factors to late-stage generation from a carbonate-evaporative sequence.

As catagenesis proceeds, odd dominance is gradually lost until the peak of oil generation has been reached, at which point little or no odd preference remains (Hunt, 1979; Waples, 1981; Kinghorn, 1983). Bacteria do not seriously alter the odd-carbon preference of hydrocarbons (Hunt, 1979), but the different mobilities of different source materials may cause a migrated oil to have a lower OEP than its counterpart remaining in the source rock (Yi-Gang, 1981).

Alexander and others (1981) believed that a correlation based on CPI likely is fortuitous; they therefore rated this parameter only 5 on their reliability scale. Other factors also restrict the usefulness of CPI: It cannot be used with lower Paleozoic sediments, because land plants were absent during the early Paleozoic (Hunt, 1979). CPI values less than unity, including the lack of odd dominance in carbonates, are subject to various interpretations (Hunt, 1979; Ji-Yang and others, 1982; Kinghorn, 1983). Immature algal matter yields anomalously low values (Kinghorn, 1983). CPI is meaningless in samples with low amounts of n-alkanes.

Light Hydrocarbons

Illich and others (1981) reported that there are 60 to 125 gasoline-range hydrocarbons (C_5 to C_{10}) typically available in oils for correlation purposes. In a case study of high-API-gravity oils and condensates from the Santa Cruz Basin in Bolivia, they identified 6 n-alkanes, 20 isoalkanes, 22 cycloalkanes, and 12 aromatics. Data obtained from these compounds were used to determine similarity statistics, perform cluster analysis, and make dendrograms which suggested that Santa Cruz Basin oils and condensates have a common Devonian source. Thompson (1983) classified oils as normal, mature,

supermature, or biodegraded, based on his assessment of their thermal history as determined by content of gasoline-range hydrocarbons.

A technique employed by Clayton and Swetland (1980) in their study of 77 oils and 68 shale samples from the Denver Basin involved looking at C_7 compounds in order to minimize effects due to migration and sampling. Theorizing that light-hydrocarbon content depends strongly on the chemical composition of the parent organic matter, they further characterized their samples on the familiar ternary plot of straight-chain, branched, and cyclic alkanes. Cluster analysis of 18 C_6 - C_7 compound ratios revealed subtle differences not evident in the ternary plot. From these and other geochemical analyses, the authors concluded (1) that the Cretaceous oils were not derived from local sources but migrated laterally into the area, and (2) that the Permian Lyons oil was genetically unrelated to the Cretaceous oils.

Bockmeulen and others (1983) used distribution of components in the C_4 - C_7 range and minor peak similarities in the C_9 - C_{11} region to show similarities among 30 heavy, presumably degraded Venezuelan crudes. Based on these similarities, they concluded that all the oils appeared to belong to the same family, although two of them had unusual n-alkane patterns that could not be explained by bacterial degradation.

In an attempt to determine if a field contained "new oil" or merely more of previously discovered "old oil" (for purposes of crude-oil pricing in Australia), Thornton and others (1980) made detailed chemical comparisons of oils from the field in question and from two other fields in the Gippsland Basin. They used various ratios of significant C_4 - C_7 compounds, as well as mass spectroscopic measurements of C_{15}^+ carbon isotopes, selected heavy aromatics, and C_{27} - C_{30} steranes. On simultaneous data plots for all three oils, they were able to observe

distinct groupings or bands of data, from which they concluded that the field in question was a discrete hydrocarbon accumulation. It was their opinion that gasoline-range hydrocarbons, although useful in correlation work, are "not always as reliable as the C₁₅⁺ analyses."

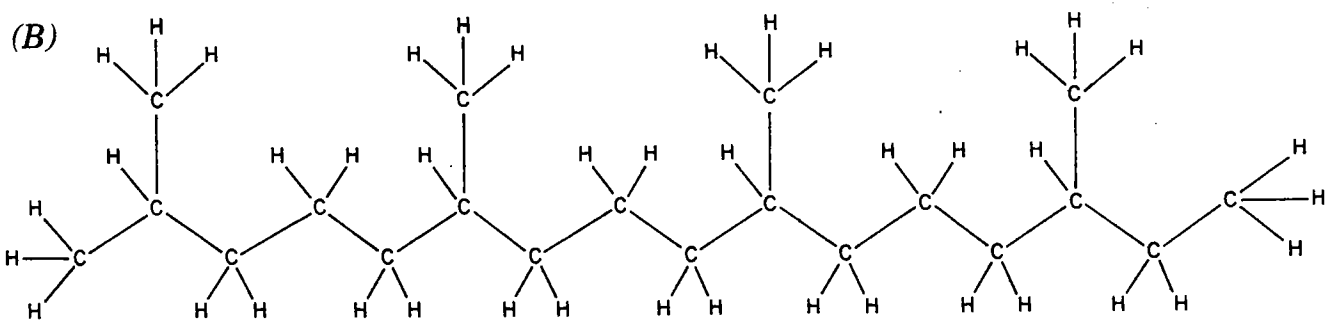
Acyclic Isoprenoids

Isoprenoids, the most useful group of branched hydrocarbons in correlation studies, are routinely identified by GC analysis of the saturate fraction. The most abundant isoprenoids (up to 55% of the total) are normally pristane and phytane (Fig. 2), both generally believed to be remnants of the side chain of chlorophyll (Hunt, 1979; Waples, 1981; Kinghorn, 1983), although Illich (1983) argued that some pristane may also result from diagenesis of higher-molecular-weight non-phytane compounds (e.g., terpanes). Concentrations as high as 5,000 ppm pristane and 3,000 ppm phytane have been reported for oil (Ekweozor and Strausz, 1983).

Isoprenoid ratios and distributions have been used in oil-oil and oil-source correlation studies as follows:

1) To indicate redox conditions of the depositional environment. Pristane/phytane ratios <1 are associated with reducing environments (Van den Bark and Thomas, 1981; Katz and Elrod, 1983; Spiro and others, 1983), whereas pristane/phytane ratios >1 imply an oxic system (Vogler and others, 1981; Welte and others, 1982; Kinghorn, 1983).

2) To indicate the nature of the original organic material. A dominant pristane peak on a chromatogram or pristane/phytane ratios >3 suggest a terrestrial source, perhaps even a peat swamp. Marine source material usually has a low pristane/n-C₁₇ value. McKirdy and Kantsler



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(1980) equated an extended C_{15} - C_{25} regular isoprenoid homologous series in sediments with hypersaline depositional conditions.

3) To indicate thermal history. During diagenesis and early catagenesis, pristane/phytane ratios generally increase to a maximum and then decrease (Hunt, 1979). For oils of terrestrial origin, higher pristane/ n - C_{17} ratios suggest a geologically young oil (Kinghorn, 1983); pristane/ n - C_{17} values between 1 and 0.5 indicate an older oil. For values <0.5 , this parameter becomes less sensitive to maturation effects (Snowden and Powell, 1982).

4) To indicate alteration. High concentrations of acyclic isoprenoids relative to the n -alkanes as measured by pristane/ n - C_{17} , for example, can mean microbial activity in the reservoir, or, if such concentrations are present in extracts, during diagenesis (Volkman and others, 1983b).

Usually, specific compound ratios (e.g., pristane/phytane, pristane/ n - C_{17} , phytane/ n - C_{18}) or isoprenoid profiles are presented as just one of several parameters used for correlation (see, for example, Clayton and Swetland, 1980; Ross, 1980; Magoon and Claypool, 1981a; Seifert and Moldowan, 1981; Vogler and others, 1981; Spiro and others, 1983). In a Russian study, however, after an initial screening via n -alkane distributions, pristane/phytane and (pristane + phytane)/(n - C_{17} + n - C_{18}) were the sole basis for correlating 25 oils and 250 rock extracts (Yakubson and others, 1981). Volkman and others (1983b) considered isoprenoids less specific than polycyclic alkanes, but used them as secondary correlation parameters.

Pyrolysis experiments conducted by Alexander and others (1981) indicated that isoprenoid/ n -alkane ratios are largely determined by the stage of generation at the time of oil expulsion, implying that one source can yield many ratios. To reduce this stage-of-generation effect, they

proposed a new ratio, $(\text{pristane} + \text{n-C}_{17})/(\text{phytane} + \text{n-C}_{18})$, with a rating of 15 on their correlation-parameter reliability scale. [This combined ratio had been used previously by Atlantic Richfield laboratory personnel when the chromatographic column they normally used did not resolve pristane and phytane from nearby n-alkanes (Roe and Polito, 1979).] In addition, they "corrected" the pristane/phytane ratio for maturation effects (see below, under Aromatic Hydrocarbons) and thus were able to allocate it 20 points. Isoprenoid/n-alkane ratios were worth only 5 points.

Depth and age of producing formation caused variations in pristane/phytane, pristane/n-C₁₇, and phytane/n-C₁₈ ratios in a geochemical correlation study by Zein El-din and Shaltout (1982). Nevertheless, they found the combined $(\text{pristane} + \text{n-C}_{17})/(\text{phytane} + \text{n-C}_{18})$ ratio and $\delta^{13}\text{C}$ data of C₁₅+ fractions "most useful" for relating Egyptian oils to a common or similar marine origin. Ji-Yang and others (1982) noted that it was "difficult" to use pristane/phytane ratios in their study of 11 oils and six shales from the Shengli Field in China because the values varied too much with subtle depositional differences and maturation level.

As the examples in the preceding paragraphs illustrate, acyclic-isoprenoid data are another set of correlation parameters that have widespread acceptance but generate a diversity of opinion as to their significance.

Steroid and Terpenoid Hydrocarbons

The combination of gas chromatography and mass spectrometry (GC-MS), especially as applied to the characterization of steranes (Fig. 3) and triterpanes (Fig. 4), the saturated counterparts of

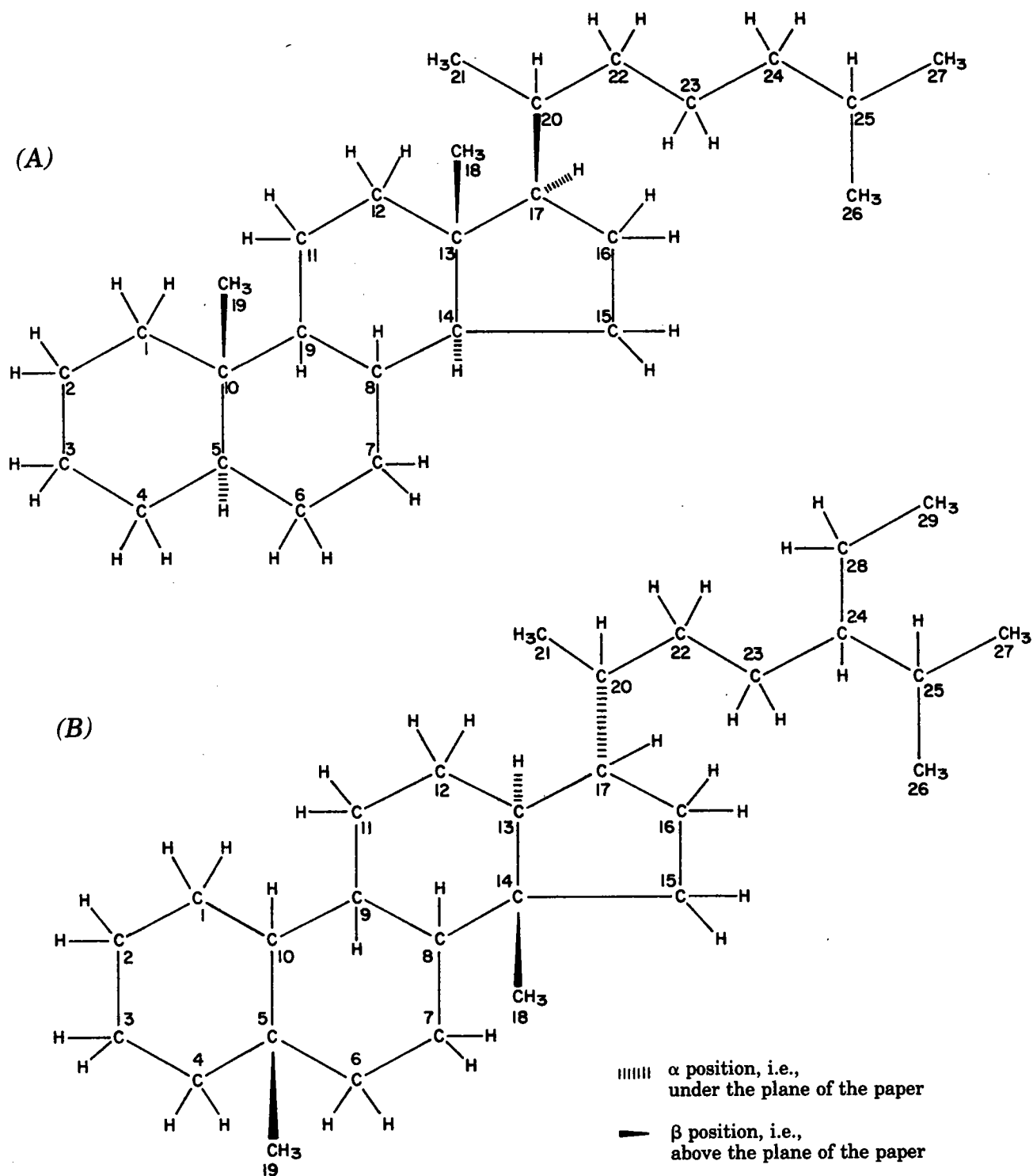


Figure 3. Structure and numbering system of representative steranes, showing the stereochemistry at selected carbon atoms. **A**, a C_{27} sterane with $5\alpha(H), 14\alpha(H), 17\alpha(H)-20R$ configuration. **B**, a C_{29} rearranged sterane (diasterane) with $13\alpha(H), 17\beta(H)-20S$ configuration.

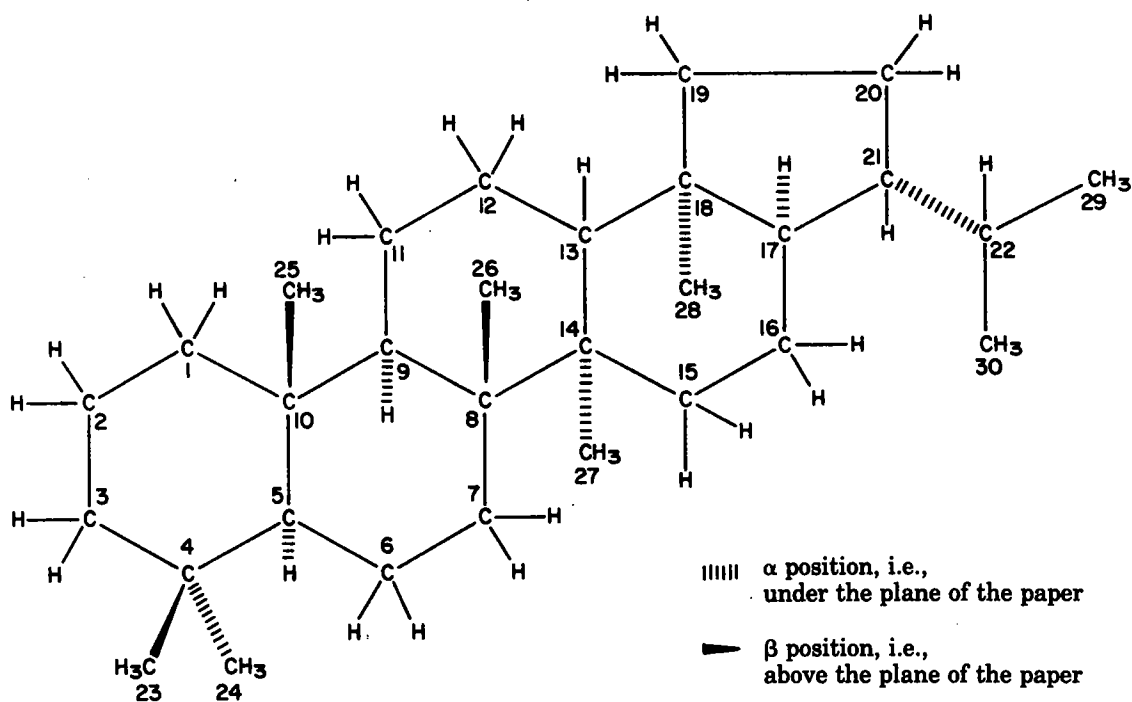


Figure 4. Structure and numbering system of a representative hopane (a C_{30} hopane with $17\alpha(H), 21\beta(H)-22S$ configuration, which is a pentacyclic triterpane), showing the stereochemistry at selected carbon atoms.

functionalized biological precursors, has been used extensively in correlation studies. The resolution of capillary-column gas chromatography and the sensitive detection and computer-aided identification capability of a mass spectrometer have been joined to produce the most powerful analytical instrumentation currently available in this field. Because GC-MS can discriminate between stereoisomers and other subtle structural changes in steroids and triterpenoids, identical distribution patterns on mass fragmentograms signify that oils are from the same source, or from similar sources. Using this approach and calculating various ratio parameters, one can investigate almost every aspect of petroleum correlation.

For example, Volkman and others (1983b) studied a suite of Australian source rocks and oils from reservoirs which apparently were charged at different times and at different burial depths and which had experienced various levels of biodegradation. In this study, certain triterpenoids and C_{27}/C_{29} steranes and diasteranes were interpreted to reflect type of organic input. Various polycyclic-alkane ratios--such as

- (1) $C_{29}^{5\alpha,14\alpha,17\alpha(20S)}/C_{29}^{5\alpha,14\alpha,17\alpha(20R)}$ steranes,
- (2) $C_{29}^{5\alpha,14\beta,17\beta(20R)}/C_{29}^{5\alpha,14\alpha,17\alpha(20R)}$ steranes,
- (3) $C_{27}^{13\beta,17\alpha(20S)}/C_{27}^{13\beta,17\alpha(20R)}$ diasteranes,
- (4) C_{30} moretane/ C_{30} hopane,
- (5) T_m/T_s (defined below), and
- (6) 22S/22R homohopanes--

were used to assess maturity conditions. Migration effects were evaluated by sterane ratios (e.g., $C_{29}^{5\alpha,14\beta,17\beta(20R)}/C_{29}^{5\alpha,14\alpha,17\alpha(20R)}$ and C_{29} diasteranes/ C_{29} steranes), and demethylated hopanes were used to assess severe levels of degradation. Mild degradation was measured by gas chromatography of whole oils and

saturate fractions, noting the relative abundance of light hydrocarbons, n-alkanes, isoprenoids, and bicyclic alkanes, as well as the prominence of the unresolved complex-mixture hump. Volkman and co-workers concluded: "The only reliable way of determining whether these oils are related . . . is by a comparison of their distributions of polycyclic alkanes."

Philp and Gilbert (1980), writing that "the most powerful programme currently available for correlation studies is that used for mass fragmentography," noted that it has the potential to provide information on type of organic matter, thermal history, and microbial history. However, several authors urged caution in applying this technique (to the exclusion of others) as it relates to steranes and triterpanes (see, for example, Mackenzie and others, 1983; Volkman and others, 1983b; Hoffman and others, 1984). Mackenzie's (1984) thought-provoking discussion of this topic deserves special emphasis. He pointed out among other considerations that the distribution of biological markers such as steranes and triterpanes (1) may constitute <1% of an oil or extract mixture, (2) may not always represent the other organic compounds present, (3) may vary as the parent kerogen passes through different stages of maturation, and (4) conceivably could be affected by migration. Furthermore, biomarkers solvent-extracted from a sediment may bear little relationship to those expelled naturally as crude petroleum.

Because correlation parameters derived from GC-MS techniques are based only on empirical evidence obtained from field samples and laboratory studies, observed variations in compound distributions cannot be definitively interpreted at present. Whereas some ratios are almost unanimously interpreted to reflect a particular aspect of petroleum

formation, other ratios are variously interpreted, resulting in some conflict and ambiguity. To further complicate the reader's ability to understand and follow an interpretation, the range over which a correlation measurement is thought to be effective is not always clearly stated. The utility and applicability of some of these molecular measurements in correlation studies have been summarized by Mackenzie and others (1982). The extent to which a biologic compound has been transformed into a geologic fossil (i.e., the amount of thermal stress or maturation the sample has endured) is translated into mathematical terms by devising a ratio of concentrations of product(s) and precursor. For GC-MS-derived parameters, configurational isomerization at C-17, C-21, and C-22 in the hopanes (i.e., certain pentacyclic triterpanes) and at C-14, C-17, and C-20 in the non-rearranged steranes is commonly involved. Correct identification of compounds and their various isomers is necessary if such a correlation parameter is to be valid. Noting that a C_{30} hydrocarbon molecule can exist in hundreds of forms, Ourisson and others (1984) pointed out that several compounds with similar structures may be superposed on one GC peak. Instances in which co-elution of critical compounds was recognized (e.g., Seifert and Moldowan, 1981; Ji-Yang and others, 1982; Rohrback, 1983; Volkman and others, 1983b; Hoffman and others, 1984) may represent only a fraction of the cases where this problem exists.

The degree of isomerization in hopanes is a popular GC-MS-determined maturation parameter (Mackenzie and others, 1980; Philp and Gilbert, 1980; Volkman and others, 1983a,b; Sandstrom and Philp, 1984). Biologically synthesized hopanes, consisting primarily of the $17\beta,21\beta$ configuration, convert to fossil hopanes having either the $17\alpha,21\beta$ or $17\beta,21\alpha$ (moretane) configuration. With increasing maturation,

the moretanes further isomerize to the thermally more stable $17\alpha,21\beta$ hopanes. Thus, both $17\alpha,21\beta/17\beta,21\beta$ and moretane/hopane ratios can be employed as maturity parameters (see, for example, Ji-Yang and others, 1982; Schoell and others, 1983).

The chiral (i.e., optically active) center at the C-22 position in hopanes can exhibit a natural R or geologically isomerized S configuration. Many workers (Mackenzie and others, 1980,1982; Philp and Gilbert, 1980; Ji-Yang and others, 1982; Rohrback, 1983; Volkman and others, 1983b) believe that the 22S/22R epimerization ratio of hopanes varies directly with maturity, reaching a maximum conversion of 60% in mature sources and crudes. However, using C_{32} hopanes from Mahakam Delta sediment extracts, Schoell and others (1983) found that the ratio rose sharply to values above unity and remained there while samples were still at submature levels.

An example of an ambiguous parameter obtained by GC-MS is the ratio of two C_{27} triterpanes, $17\alpha-22,29,30$ trisnorhopane/ $18\alpha-22,29,30$ trisnorhopane (T_m/T_s), which has been used as a source parameter (Shen, 1984), a maturation parameter (Volkman and others, 1983b), or both (McKirdy and others, 1983; Sandstrom and Philp, 1984). Because T_m means triterpane affected by maturity, and T_s means triterpane affected by source (Philp, personal communication), the ratio should be applied as a maturation parameter only to oils suspected of having a common source. Rohrback (1983) found the inverse (T_s/T_m) more sensitive for mature oils and less sensitive at low to moderate levels of thermal stress. Shen (1984) found T_m/T_s valuable as a tool for oil-matching while looking for a way to identify quickly the source of oil spills. With values ranging from 0 to 3.9, no match was indicated if the ratio difference exceeded 20%. Although Shen reported that T_m/T_s was

not affected by weathering or mild biodegradation, Palmer (1984) found that water-washing decreased T_s relative to T_m . Volkman and others (1983b) observed anomalous T_m/T_s ratios when a C_{30} tetracyclic triterpane co-eluted with T_m on certain GC columns. Also, McKirdy and others (1983) pointed out that in carbonates this ratio may be less responsive to thermal stress than in shales and therefore is questionable as a maturity parameter.

Other correlation parameters open to more than one interpretation are the distributions of mono- and tri-aromatized steroids. These distributions have been used (1) to assess source material (Seifert and others, 1983), (2) to assess maturity (Mackenzie and others, 1981, 1983; Ji-Yang and others, 1982; Philp and others, 1982), and (3) to describe migration effects (Ji-Yang and others, 1982; Hoffman and others, 1984). Seifert and others (1983) applied these distributions to extending and quantifying their previous conclusions regarding co-sourcing of the major oil accumulations in Prudhoe Bay, Alaska. Three different shale sources being available (post-Neocomian, Shublik, and Kingak), they were able to conclude that Kuparuk River oil comes mainly from the post-Neocomian, Sag River oil comes mainly from the Shublik shale, Sadlerochit oil originates from all three shales, and Kingak oil has its source only in the Kingak shale. However, Mackenzie and others (1982), in their general discussion on the geologic fate of steroids, wrote that it has yet to be proved that measurements derived from these chemical fossils can be used to assess extent of migration independent of both maturity and depositional environment.

In a manner similar to that described above for hopanes, natural $5\alpha, 14\alpha, 17\alpha(20R)$ steranes are thought to isomerize with increasing geologic thermal stress to $5\alpha, 14\beta, 17\beta(20R)$ fossil steranes, sometimes via

the $5\alpha,14\alpha,17\alpha(20S)$ intermediate (Seifert and Moldowan, 1981). At maturity, the mix of R and S epimers is thought to be 1:1 (Ji-Yang and others, 1982; Mackenzie and others, 1982; Schoell and others, 1983); but Alexander and others (1983) noted that the ratio would approach unity at maturity only in nondegraded samples, as they found the 20R epimer more susceptible to attack by bacteria. Other researchers (McKirdy and others, 1983; Volkman and others, 1983a; Sandstrom and Philp, 1984) also observed an effect of bacterial action on the ratio. The overall conversion of a $5\alpha,14\alpha,17\alpha$ sterane to its corresponding $5\alpha,14\beta,17\beta$ form is useful as a maturation parameter (McKirdy and others, 1983; Sandstrom and Philp, 1984), although Hoffman and others (1984) did not observe the expected ratio increase, which is thought to reach 75% at maturity (Ji-Yang and others, 1982; Mackenzie and others, 1982). Suggesting that certain isomers migrate faster than others, several investigators (McKirdy and others, 1983; Seifert and Moldowan, 1981; Philp and others, 1982; Volkman and others, 1983b) have tried to use various isomeric sterane ratios to explain migration effects.

The relative proportions of $5\alpha,14\alpha,17\alpha$ steranes of different carbon numbers (e.g., C_{27}/C_{29} or C_{28}/C_{29}) as a rough indicator of source or depositional environment have wide acceptance in correlation work (Hunt, 1979; Ji-Yang and others, 1982; Mackenzie and others, 1982,1983a; Seifert and others, 1983). C_{29} steranes are believed to reflect a terrigenous contribution (from higher plants), whereas C_{27} steranes are thought to imply a marine source (Volkman and others, 1983b; Palmer, 1984).

Skeletal alterations of (non-rearranged) steranes to (rearranged) diasteranes provide still another useful correlation tool measurable on GC-MS fragmentograms. This parameter has been discussed in terms of

burial depth (Mackenzie and others, 1980), migration (Volkman and others, 1983b), and sensitivity to inorganic clay or carbonate matrix of the source rock (Ji-Yang and others, 1982; McKirdy and others, 1983).

Several workers have questioned the appropriateness of using the steranes and triterpanes as correlation parameters because of compositional changes brought about by bacterial attack (Welte and others, 1982; Bjorøy and others, 1983; Spiro and others, 1983; Volkman and others, 1983a; Sandstrom and Philp, 1984). Laboratory simulation experiments were conducted in an attempt to study this problem (Goodwin and others, 1983). While much remains to be explained about the supposed role of microorganisms in the selective destruction of R-configured steranes and the demethylation of hopanes (Philp and others, 1982; Sandstrom and Philp, 1984), there seems to be a growing consensus that these changes probably occur only under severe conditions, at a very late stage of petroleum biodegradation (Philp and Gilbert, 1980; Mackenzie and others, 1982; Rullkötter and Wendisch, 1982; Alexander and others, 1983; Durand, 1983; Philp, 1983; Volkman and others, 1983a,b; Palmer, 1984; Shen, 1984). This could explain why not all researchers have found evidence for microbial alteration of steranes and triterpanes. In some cases it is possible that GC resolution is not sufficient to separate certain compounds, such as a demethylated C_{29} hopane from a regular C_{29} hopane (Philp, 1983), or T_m from C_{30} n-alkane (Spiro and others, 1983); it is also possible that the sudden "appearance" of a component may result solely from the removal of a more labile compound through microbial attack (Philp, 1983; Volkman and others, 1983a).

In addition to the individual-compound applications mentioned above, overall sterane/triterpane distribution patterns are a common correlation

parameter (McKirdy and Kantsler, 1980; Thornton and others, 1980; Seifert and Moldowan, 1981; Van den Bark and Thomas, 1981; Welte and others, 1982; Zhencai and others, 1982; Rohrback, 1983). Mackenzie and others (1982) discuss the utility of these distribution patterns in correlating weathered oil spills with their presumed sources; this utility stems from the relative involatility of steranes and hopanes and their relative resistance to microbial attack.

Other studies involving GC-MS "fingerprinting" as an aid in correlation concern tricyclic terpanes, including the 20-carbon diterpanes. Tricyclic diterpanes proved useful to Zumberge (1983) in confirming correlations by previous investigators of Paleozoic oils from the Williston Basin; Zumberge also had found these compounds useful in matching biodegraded with non-biodegraded Colombian crudes. Having found diterpanes in Ordovician Red River oil, Zumberge suggested that they originated from marine plants or from thermally degraded heavier compounds. Other researchers (for example, Snowden and Powell, 1982; Philp and others, 1983) have associated diterpenoids with a resin contribution. In his study of crude oils from the Gulf of Suez, Rohrback (1983) observed that some diterpanes (1) increase in quantity with increasing maturity (suggesting that they are thermally stable or else represent breakdown products of heavier compounds), (2) decrease in quantity with increasing thermal stress, or (3) show no appreciable change. The ability of tricyclic terpanes to survive biodegradation has been documented in Goodwin and others (1983), Aquino Neto and others (1983), and Sandstrom and Philp (1984). Moldowan and others (1983) reported on a technique for separating and observing tricyclic terpanes apart from their ubiquitous cousins, the pentacyclic triterpanes. By increasing knowledge of biomarkers such as these and relating them to

their biogenic precursors, researchers eventually will be able to discriminate oils from adjacent parts of the stratigraphic column in a single basin.

Technological advances in mass spectrometry have contributed to its increasing popularity in oil-oil and oil-source correlation studies. Monitoring in multiple-ion or single-ion detection modes provides much greater sensitivity than scanning the entire mass spectrum. Another advance is high-resolution MS, which holds promise for the analysis of untreated, unfractionated whole oil and rock extracts (Bjorøy and others, 1983; Mackenzie and others, 1983). Still another advance is field ionization mass spectroscopy, in which an applied electric field selectively removes one electron without further fragmenting the molecule; Ljimbach and others (1983) employed this method to determine the distribution of 1- to 5-ring naphthenes for genotyping unaltered and biotransformed oils and rock extracts, as well as to assess the degree of organic metamorphism of nonbiodegraded oils.

Aromatic Hydrocarbons

Detailed analysis of the aromatic fraction is not now in general use in correlation studies because even capillary gas chromatography is incapable of separating this extremely complex mixture. However, relative amounts of heavy aromatic components as determined by mass spectrometry have been found helpful in comparing crude oils (Thornton and others, 1980; Welte and others, 1982; Spiro and others, 1983; Shen, 1984). Alexander and others (1981) used proton magnetic resonance to determine "percentage of aromatic protons," a bulk property which they used to "correct" pristane/phytane ratios for degree of source maturation. More recently (1984), they found that

1,8-dimethylnaphthalene appears to function as a maturity indicator, even in the more mature gas-forming zone. Source-maturity assessment schemes based on phenanthrene and its methyl or dimethyl derivatives (Radke and others, 1982; Mackenzie and others, 1983) or the alkylation of perylene (Louda and Baker, 1984) have also been suggested.

During the investigation of a well in the Anadarko Basin, Price and others (1981) found that GC profiles of fractions from rock extracts and area crudes bore no resemblance to each other, although they did find similarities among the aromatic fractions of the oils in the basin. From this they suggested that "gas chromatography of the aromatic fractions of crude oils and rock extracts may be a useful tool in defining both oil-source and oil-family relationships." The capacity for connecting a capillary-column gas chromatograph to a Fourier transform infrared spectrophotometer (GC-FTIR) now exists. In the next few years we may expect to see the power of this instrument combination contributing greatly to the study of aromatic compounds, complementing the capabilities of GC-MS in identifying trace constituents in petroleum.

Porphyrins (Including Vanadium-Nickel Proportionality--A Bulk Parameter)

Porphyrins, a class of heterocompounds consisting of tetrapyrrole complexes, were first identified in sedimentary bitumen and petroleum by Treibs in 1934. Although these compounds have been known for fifty years, in-depth studies of them have been fettered by their complexity and a lack of effective analytical procedures. Petroporphyrins, (Fig. 5) thought to be derived from chlorophyll (Barwise, 1982; Mackenzie and others, 1982; Baker and Louda, 1983), occur mainly as nickelous (Ni^{+2}) or vanadyl (VO^{+2}) complexes of two major skeletal types, namely, the deoxyphyloerythroetioporphyrins (DPEP) and the etioporphyrins (etio)

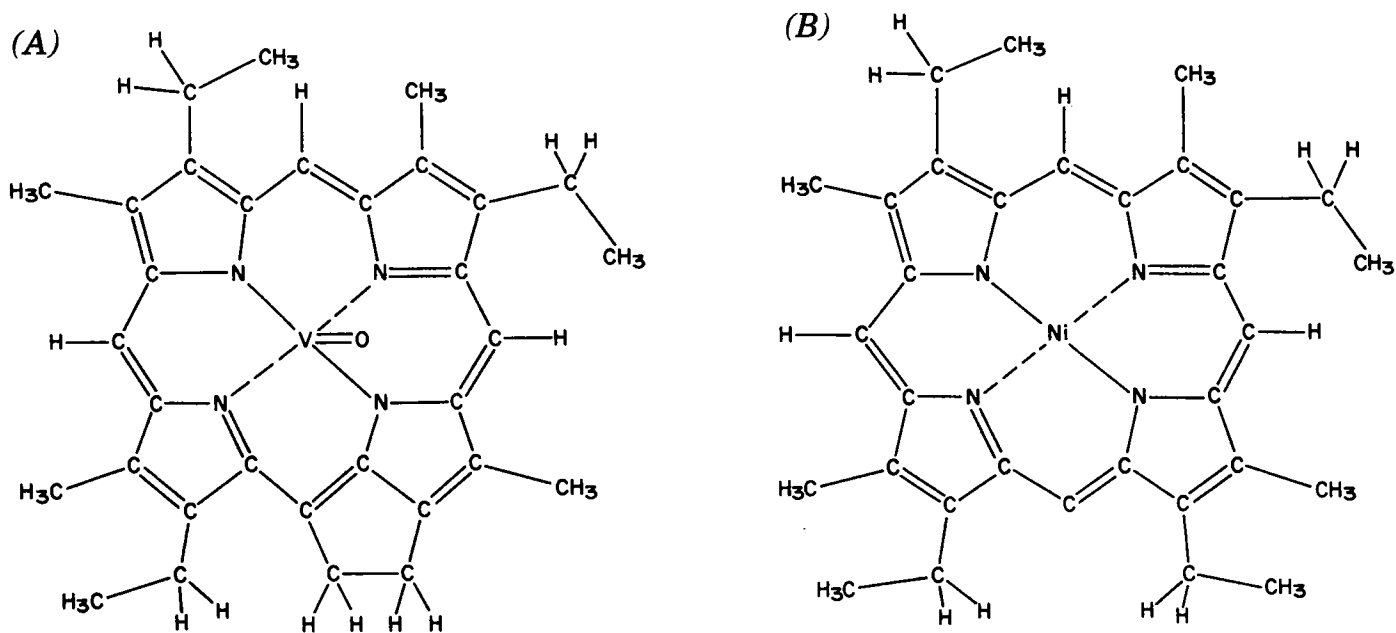


Figure 5. Petroporphyrins. A, vanadyl deoxyphytyloerythroetioporphyrin (DPEP). B, nickel etioporphyrin (etio).

(Hajlbrahim and others, 1981; Quirke and others, 1982; Baker and Louda, 1983; Barwise and Park, 1983). Analytical methods (e.g., neutron-activation analysis and flameless atomic-absorption spectroscopy) aimed at the metallic moiety of the complex are used to obtain a proportionality factor between nickel and vanadium, represented as Ni/V, V/Ni, or $V/(Ni + V)$, the last being Lewan's (1980) choice because its finite limits make plotting easier. Absolute amounts of these metals can range from none detectable (Spiro and others, 1983) to hundreds of parts per million in crudes (Hunt, 1979; Lewan, 1980) and thousands of parts per million in rock bitumens (Lewan and Maynard, 1982). However, Fish and others (1984) recently reported that the preponderance (~50-80%) of both nickel and vanadium compounds in heavy crude petroleums is thought to be non-porphyrin in nature.

It is generally agreed that expulsion mechanisms, migration phenomena, reservoir entrapment, and weathering processes do not appreciably alter the Ni/V ratio (Hunt, 1979; Lewan, 1980, 1984; Vogler and others, 1981; Waples, 1981), but the influences of time and temperature are in dispute. Hunt (1979) considered vanadyl complexes to be thermally less stable than nickel complexes (see also Curiale and Harrison, 1981); but Kinghorn (1983) noted that nickel porphyrins start to disappear at shallow depths and are completely gone at depths where similar changes occur in the vanadyl porphyrins (see also Mackenzie and others, 1982; Barwise and Park, 1983). Baker and Louda (1983) cited in vitro studies with geologic counterparts to support both ideas, namely, that (1) nickel porphyrins resist thermal destruction better than the vanadyl species, and (2) vanadyl porphyrins survive longer than their corresponding nickel chelates. They suggested that the relative destruction of nickel and vanadium porphyrins may rest in an interplay

of thermal and catalytic stabilities. Fish and others (1984) offered the possibility that, in the reducing environment of a petroleum reservoir, pyrrole rings may become sufficiently hydrogenated to make the metalloporphyrins susceptible to demetallation and decomposition.

Lewan (1980) noted variable results in the metals ratio but at that time attributed them to stratigraphic and regional differences. He maintained that the parameter was a good one, especially for correlation of oil with source rock, and that proper implementation merely required understanding and accounting for such geologically related differences. In a later paper, Lewan (1984) defined three depositional regimes by their Eh, pH, and sulfide activity, and then determined for each the value of the vanadium-nickel fraction (<0.10 , $0.10-0.90$, >0.50) to be expected in source rocks and/or oil expelled from that regime. Other authors found the ratio too inconsistent to be useful as a correlation parameter (e.g., Vogler and others, 1981; Barwise and Park, 1983); the latter authors analyzed extracts of a Permian marl slate from England for Ni- and V-containing porphyrins. In five adjacent core sections sampled only centimeters apart, these workers found Ni-bearing porphyrins in the range 3.3-6.4mg/100g sediment. The range for V-containing porphyrins was 1.2-4.6 mg/100g sediment. Barwise and Park suggested different contributing sources as a possible reason for such diverse figures.

This last example points out a problem that many geochemical researchers fail to recognize--or at least fail to address--in their reported conclusions and interpretations. This problem is how well a particular sample represents an entire formation or stratigraphic unit. Ala and others (1980) wrote that organic matter is frequently "concentrated in bands rather than being disseminated uniformly in the

rocks," and that "it was often impossible to take a single specimen as representative of an individual 20 ft core." Sampling, as a general topic, is not treated in this paper, but its importance for arriving at valid correlations cannot be overstated.

The current trend in petroporphyrin research seems to be shifting toward the ligand segment of the molecule. This is in keeping with the generalized movement away from measurement of gross properties to measurement of more-specific ones. Hampered before by the involatility of porphyrins, investigators can now simultaneously fractionate and fingerprint these complex mixtures with high-pressure liquid chromatography (HPLC), although resolution at present is less than desirable. In trying to match eight oils from the Gulf of Suez area with 15 Eocene cores, Hajlbrahim and Okla (1983) found three different petroporphyrin profiles for the shales and two for the oils, but could not conclude that Eocene strata served as a source of the oil. While various methods to enhance resolution--including demetallation, prior separation of Ni from V constituents, derivatization to increase polarity range, and nonaqueous reverse-phase chromatography--are being investigated, some workers have combined the separating power of HPLC with the detection capability of MS (Barwise, 1981; Hajlbrahim and others, 1981; Quirke and others, 1982). Quirke and others caution, however, that averaged mass spectra are necessary to prevent compounds of low concentration from going undetected on a single pass through the spectrometer.

DPEP porphyrins are thought to transform gradually into the etio species. The ratio of this relationship, DPEP/etio or DPEP/(etio + DPEP), has been applied as a correlation parameter in oil-oil (Barwise and Park, 1983) and oil-rock studies (Barwise, 1982; Ji-Yang and

others, 1982; Hajlbrahim and Okla, 1983), but its efficacy as a maturity indicator apparently is limited. Barwise (1982) and Barwise and Park (1983) consider the ratio effective only in the major zone of oil generation. Mackenzie and others (1982) suggested that whereas this is the effective range for V-containing porphyrins, the DPEP/etio ratio for Ni-containing porphyrins is usable only at lower maturity levels. Geologic porphyrins as sensitive indicators of depositional conditions (Baker and Louda, 1983), thermal history of sediments (Barwise and Park, 1983), and migration effects (Hohn and others, 1982) have now been introduced into the arsenal of correlation tools. As porphyrin characterization and identification progress, Hohn and others (1982) envisioned them as supplementing established hydrocarbon-derived parameters in correlation work.

CORRELATION PARAMETERS BASED ON BULK MEASUREMENTS

Stable Isotopes

Of all the correlation parameters in current use, probably none entails more controversy than the $^{13}\text{C}/^{12}\text{C}$ ratio. That it is a sensitive index of genetic input is rarely disputed (Alexander and others, 1981; Waples, 1981; Yeh and Epstein, 1981; Kinghorn, 1983; Sofer, 1984), but its reliability is diminished by disagreement surrounding the roles played by thermal processes (Alexander and others, 1981; Chung and others, 1981; Yeh and Epstein, 1981; Snowden and Powell, 1982; Lewan, 1983; Rohrback, 1983; Sofer, 1984), and microbial attack (Sofer, 1981, 1984; Waples, 1981; Mankiewicz, 1982); whether terrigenous oils are more isotopically negative than marine oils is also a problem (Vogler and others, 1981; Yeh and Epstein, 1981; Kinghorn, 1983; Sofer, 1984).

Because worldwide variations in $^{13}\text{C}/^{12}\text{C}$ are quite small, what constitutes experimental error and what is considered natural variation within a particular sample assume great importance (Alexander and others, 1981; Chung and others, 1981; Waples, 1981). Sofer (1984) argued that true variability in isotopic composition in higher plants and marine life, together with mixing of such organic matter, should result in a relatively wide range of isotopic values for any oil.

Complicating interpretations, compound classes within a crude oil or extract are thought to show a 2-3‰ systematic enrichment of ^{13}C with increasing polarizability, i.e., in the order alkanes to aromatics to heterocompounds (see, for example, Hirner and others, 1981; Sofer, 1984). Also, an oil is normally lighter than the related sediment bitumen which, in turn, is lighter than the related kerogen (Alexander and others, 1981; Magoon and Claypool, 1981b; Waples, 1981). If one superimposes on these variations a possible change (up to 2‰) due to bacterial alteration, water-washing, and/or migration (Hunt, 1979; Burns and Bein, 1980; Waples, 1981; Mankiewicz, 1982; Palmer, 1984; Sofer, 1984), it is relatively easy to understand why application of this parameter can be ambiguous. Variability caused by these external effects tends to mask any genetic relationship, especially if measurements have been made on whole oil. For this reason, comparisons should be attempted only between heavy fractions of the same compound class (e.g., C_{15}^+ saturate to saturate or C_{15}^+ aromatic to aromatic). Some researchers (e.g., Stahl, 1980; Kinghorn, 1983; Lewan, 1983) believed that the aromatic fraction yields the most-consistent $\delta^{13}\text{C}$ results, because of its resistivity to natural alteration and insensitivity to handling, but Chung and others (1981) found the range of variation to be unacceptable. To increase the utility of isotope measurements, cross

plots or other means of studying the difference between saturate and aromatic values are used (Burns and Bein, 1980; Thornton and others, 1980; Alexander and others, 1981; Magoon and Claypool, 1981a; Sofer, 1981, 1984; Zein El-din and Shaltout, 1982). Alternatively, isotope type curves (introduced by Stahl) are employed (see, for example, McKirdy and others, 1983; Sandstrom and Philp, 1984); interpretation of these curves has been questioned by Chung and others (1981), and Hirner and others (1981), Lewan (1983), and Stahl himself (1980) pointed out some limitations of this approach.

In spite of its uncertain meaning, the ratio of stable carbon isotopes is currently considered an important parameter in making oil-oil correlations (Rosenfeld and others, 1980; Magoon and Claypool, 1981a; Seifert and Moldowan, 1981; Zein El-din and Shaltout, 1982; Bissada, 1983). Curiale and Harrison (1981) used carbon-isotope ratios for oil-asphaltite correlations, whereas Burns and Bein (1980), McKirdy and Kantsler (1980), Ross (1980), and Magoon and Claypool (1981b) applied the method to matching oils with potential source rocks. Kinghorn (1983) viewed isotope techniques as one of the most successful methods for making oil-oil correlations, because "none of the alteration factors is able to change the stable isotope ratio." Alexander and others (1981) termed carbon-isotope ratios their "most reliable correlation parameter" and gave them the highest rating of 30 points on their weighted diagnostic scale because they "reflect the isotopic composition of carbon in the living petroleum precursors and are relatively unaffected by petroleum formation processes." In spite of the popularity of carbon-isotope studies, unsuccessful attempts to use such measurements have also been documented (Van den Bark and Thomas, 1981; Vogler and others, 1981; Reitsema, 1982).

Literature references to other stable-isotope combinations employed in correlation studies during the last few years involve sulfur (Clayton and Swetland, 1980; Curiale and Harrison, 1981; Hartman and Hammond, 1981; Magoon and Claypool, 1981a; Spiro and others, 1983); hydrogen (Yeh and Epstein, 1981; Mankiewicz, 1982; Kinghorn, 1983); and nitrogen (Magoon and Claypool, 1981a; Kinghorn, 1983). Gaffney and others (1980) found sulfur-isotope ratios to be strongly dependent on initial biological input, independent of thermal maturation except in the presence of reservoir sulfate, and partly responsive to microbial activity (see also Thode, 1981; Rohrbach, 1983).

LITERATURE CASE STUDIES

Characterization of crude oils and identification of their sources are necessary endeavors in fields ranging from petroleum exploration to oil-spill identification to assessment of economic potential for a geographic area. Accordingly, correlation case studies are wide-ranging in extent and purpose and exhibit a diversity best illustrated by a series of examples. Only superficial reference will be made here to any geologic arguments offered in the original investigations.

1. In the first phase of a study involving 32 oils from the San Juan Basin, Ross (1980) was able to group the oils into four genetic types based on C_{13} - C_{20} isoprenoid profiles, pristane/phytane ratios, and a plot of $\delta^{13}C$ vs. optical rotation of the saturate fraction. Whole-range GC profiles, C_4 - C_7 light-hydrocarbon distributions and infrared aromatic fingerprints provided no clear-cut differentiation of the oils. Ross then applied the same techniques in an attempt to link the oils to 28 outcrop samples, cuttings, and core samples. From carbon-isotope data and

pristane/phytane ratios, he was able to correlate one Jurassic and two Cretaceous oils (one marine and one nonmarine) with local bituminous rocks, but he was unable to establish a firm correlation between a Pennsylvanian-type oil and bitumen extracted from Pennsylvanian rocks.

2. The only two formations with sufficient potential volume to be considered sources in the giant Ekofisk field are the Paleocene Lista and Upper Jurassic Kimmeridgian Clay. Van den Bark and Thomas (1981) used vitrinite reflectance, total organic carbon, soluble organic matter, pristane/phytane, OEP, rearranged/natural steranes, 30-carbon triterpanes, cholestane/ergostane, C_{25} - branched and cyclic hydrocarbons, and benzothiophene derivatives to conclude that the Kimmeridgian was the source. Carbon-isotope and n-alkane data were inconclusive in this study.

3. Using an average of 10 parameters obtained from high-resolution gas chromatography of C_6 - C_7 hydrocarbons, Philippi (1981) devised a similarity coefficient and tested it on 10 presumed oil-source-rock pairs. The maximum being 1.00, a coefficient ≥ 0.80 implied good correlation, whereas a value < 0.73 meant poor correlation. Erroneous values resulted from biodegraded oil, immature source rocks, or oils derived from more than one source.

4. In a geochemical correlation study of four oils, four asphaltites, and two bituminous rocks from the Dead Sea area, Spiro and others (1983) relied on the distribution patterns of various classes of hydrocarbons (i.e., C_{15}^+ n-alkanes, isoprenoids, steranes, triterpanes, and homologous aromatics), CPI, pristane/phytane, pristane/n- C_{17} , and phytane/n- C_{18} . Supporting evidence was provided by sulfur content, sulfur-isotope data, and vanadyl porphyrins. Other parameters used were bulk composition (including the saturates/aromatics ratio),

specific-compound ratios in the C_2 - C_8 range, and, for the asphalts, optical reflectance and fluorescence. Geochemical characteristics indicated (1) that maturity levels vary in the order oils > asphalts > rocks, and (2) that oils, asphalts, and the Nebi Musa rocks belong to one geochemical province, the oils and asphalts having been derived from a common type of source rock.

5. Curiale and Harrison (1981) were able to match three oils and six asphaltites from the Ouachita Mountains in Oklahoma on the basis of data from n-alkanes, isoprenoids, Ni and V, carbon and sulfur isotopes, density measurements, elemental analysis, bulk composition, and gas chromatograms of asphaltic extracts and whole oil.

6. Alexander and others (1980,1981,1983) published several articles concerning the nature and source of Windalia oil in Western Australia, modifying their earliest conclusions as additional information was obtained. Although the Windalia was deficient in n-alkanes, other geochemical properties were inconsistent with a typical bacterially altered crude. Based on nuclear-magnetic-resonance measurements of aromaticity, which they proposed as an index of thermal maturity of the oil, Alexander and co-workers (1980) originally suggested that the Windalia migrated from source rocks at an early stage of diagenesis. Further study (1981), which included the use of carbon isotopes, pristane/phytane, pristane/ n - C_{17} , phytane/ n - C_{18} , (pristane + n - C_{17})/ (phytane + n - C_{18}), naphthene/ n -alkane, CPI, and n -alkane distributions in the oil and 37 rock extracts, not only supported their contention that the Windalia was not biodegraded, but also indicated it had its source in the Winning Group sediments. Noting in 1983 that "partially biodegraded mature oils often resemble immature oils in composition," they used GC-MS to assess the severity of biodegradation of several Australian

crudes. Their finding that the Windalia contains n-alkanes above C_{10} (minor degradation), high relative amounts of bicyclanes (moderate biodegradation), and demethylated hopanes (extreme biodegradation) finally led them to conclude that the Windalia resulted from a series of episodes of accumulation and bacterial degradation. (See also Volkman and others, 1983a.)

7. Using sulfur content and carbon- and sulfur-isotope data in attempting to identify the source(s) of beach tars along southern California, Hartman and Hammond (1981) were able to distinguish oils (1) escaping from seeps, (2) from nearby fields, and (3) from tankers. They confined their analysis to asphaltenes, because of the insensitivity of this fraction to weathering. The majority (81%) of collected tars were traceable to two areas of natural seepage; the remaining 19% were classified as having unknown origin. Transport pathways and tar-deposition patterns attributed to seasonal changes in Santa Monica Bay surface currents were consistent with the inferred sources.

8. Welte and others (1982) were able to group more than 60 high-maturity oils from the Vienna Basin into a single oil and a single-source family of oils with two sub-families. Degree of water-washing and biodegradation were assessed with specific branched/n-alkane and alkane/aromatic ratios in the C_2 - C_8 region. Although the oils exhibited different stages of biodegradation, these workers were able to show family relationships with similar sterane-triterpane distributions and GC-MS grouping of aromatics above molecular weight 150. C_{15}^+ saturates, CPI, and pristane/phytane ratios provided information on type of source material and maturity level. Investigation of Neogene sediments from the same basin indicated that these strata do not have the potential for generation of liquid

hydrocarbons. Welte and co-workers therefore concluded that the source of the Vienna Basin oils must be rocks underlying the Neogene Basin.

9. Using API gravity, sulfur and nitrogen content, C_{15}^+ saturates, pristane/phytane, CPI, $\delta^{13}C$ of whole oils and fractions, and $\delta^{34}S$ measurements, Magoon and Claypool (1981a) were able to separate 40 North Slope crude oils into two genetic types. Nitrogen isotopes had little value for distinguishing these oils.

TRENDS IN CORRELATION WORK

The most noticeable trend in recent correlation work is identification of individual trace constituents of oils and bitumens, often to the point of distinguishing one isomer from another. Although the main emphasis has traditionally been on hydrocarbons, nitrogen and sulfur compounds are starting to receive more attention. Whereas geochemical concepts of petroleum generation and maturation are already helpful in correlation, migrational effects will gain utility only as the mechanics of hydrocarbon migration become more fully understood. Visual comparison of detailed data such as fragmentograms or chromatograms is being progressively replaced by objective and systematic methods involving statistical analysis, computer enhancement, and other computer-assisted manipulations. Technological advances are making it possible to bypass certain tedious and time-consuming procedures, such as fractionation of oils and extracts. The shift from qualitative to quantitative interpretations of reactions responsible for petroleum formation and transformation permits a new dimension in correlation work. Laboratory simulation experiments, notably artificial maturation of kerogen by pyrolysis, are contributing to knowledge in this area.

Two problems mentioned by a number of researchers, but addressed specifically by Winters (1983) and Durand (1983), are more academic than technical, but pertinent nevertheless to the direction in which correlation studies seem to be headed. One problem is the apparent lack of cooperation between geologists, chemists, and biologists in striving for a unified, interdisciplinary understanding of organic matter in the subsurface geosphere. The second problem, not unique, but especially relevant to correlation investigations, involves the race to develop ever more sophisticated technology, and to generate ever more detailed information without the time, effort, or ability necessary to effectively assimilate and interpret such data. Increased analytical capabilities and computer acquisition and appraisal of generated data constitute very powerful tools for future oil-oil and oil-rock correlation studies. These studies will be of maximum use, however, only when integrated with other components of basin analysis.

SUMMARY

Important developments of the last five years have led to more-definitive interpretations in oil-oil and oil-source-rock correlations. Geochemical theories on the formation and alteration of petroleum have been refined. Advances in analytical technology have permitted detailed probing of petroleum constituents at the molecular level. Parameters proposed to characterize oils and rock extracts have increased in both number and degree of specificity. However, during this same period, no real progress has been made in arriving at a standardized approach to correlation studies. Until that happens, each attempted correlation will, of necessity, be an unique problem.

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