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Review

Early developments in petroleum geochemistry

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Abstract

Petroleum geochemistry is the outgrowth of the application of the principles and methods of organic chemistry to petroleum refining and petroleum geology. This paper reviews 120 years of petroleum geochemistry, from about 1860 to 1980, and includes a discussion of the formal recognition of petroleum geochemistry as an earth-science discipline starting in 1959 when a general petroleum geochemistry symposium was first organized at Fordham University, New York. A chronology of significant events, including concepts, techniques, and textbook publications, is presented. Because petroleum geochemistry has been a tool for petroleum exploration from the beginning, the early developments of surface prospecting, source-rock identification, and oil/oil and oil/source correlation are discussed, along with the application of geochemistry to petroleum migration, accumulation, and alteration. In addition the paper deals with the biomarker revolution, which began in earnest about 1964, and with early models of geothermal history. Concepts in petroleum geochemistry have continually evolved, enhanced by the development of new analytical techniques, leading to new discoveries concerning the origin and occurrence of petroleum.

1. Introduction

The roots of petroleum geochemistry go back to the last part of the nineteenth century, when petroleum was recognized to be an important natural resource, and to the first part of the twentieth century, when developments in organic chemistry provided a means to determine the complex composition of petroleum. Concurrent with the latter was the application of chemical principles to the geology of petroleum, including its origin, migration, accumulation, and alteration; the goal was to enhance petroleum exploration and production. This practical combination of petroleum chemistry and petroleum geology became known as petroleum geochemistry. Petroleum is understood here to mean crude oil, crude-oil products, natural gas, and related bitumens. This paper reviews (1) the early history of the field of petroleum geochemistry, (2) some of the major advances prior to about 1980, and (3) how the early history and major advances laid the foundation for present practices in the field.

2. Chronology of significant events to 1980

Although the roots of petroleum geochemistry go back to the nineteenth century, mankind knew of the occurrence and use of some forms of petroleum as early as 3800 BC (Rossini, 1960). Since then, natural seeps of both oil and gas have been found in various places on earth, including China, Burma, Azerbaijan, Romania, Iran, India, Trinidad, Cuba, and North America. In many places, surface wells and shafts were drilled or dug to increase the flow rate of petroleum to the surface for collection purposes (Hunt, 1979). By the end of the eighteenth century an oil field with over 500 wells had been developed in Burma, and the last half of the next century saw the early development of a petroleum

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industry in what became the USSR. The first discovery and production of oil in North America was at Oilsprings, Ontario, Canada, in 1858. Early uses of petroleum included sealants, illuminants, lubricants, and products for medicinal purposes.

The United States petroleum industry started in 1859 with the drilling of the Drake well at an oil seep near Titusville, Pennsylvania. This well produced about 25 bbl/day from a depth of 69.5 feet (21.2 m) (Rossini, 1960). Production from this new U.S. industry has increased at an astonishing rate, reaching a maximum of 9.6 million bbl/day in 1970.

The chemical technique of distillation was first used, and is still used, to fractionate petroleum into its various cuts, or fractions, the most valuable of which was kerosine for illumination, replacing the previous illuminant of choice, whale oil. The primary role of kerosine as an illuminant was short-lived, however, because of the invention of the light bulb and the internal combustion engine, which required gasoline and later diesel fuel. Thus the gasoline distillation cut for automobiles became more important than the kerosine cut for lamps. Fig. 1 illustrates a flow chart showing the major separation steps of a modern refinery (Hunt, 1979). All fractions now are used for a variety of purposes including fueling automobiles, trucks, airplanes, and ships; commercial and industrial heating; paving of road surfaces; and as feedstock for the manufacture of plastics and lubricants.

The important petroleum chemical and geochemical milestones that followed the first production of petroleum in the United States (1859) are listed below:

~1860: Distillation of petroleum to obtain kerosine and later gasoline on a large scale. Other chemical processes such as thermal cracking and polymerization were adopted later to increase the yield of gasoline to meet growing industrial demand (Hunt, 1979). About this same time geologists recognized that the source of petroleum is likely to be organic matter deposited with sediment in a basin. T.S. Hunt (1863) observed that in Paleozoic rocks of North America, the organic matter which yielded the bitumen must be derived either from marine vegetation or from the remains of marine animals. He wrote that the transformation of organic matter into bitumen does not differ greatly from that which produces bituminous coals.

1915: Introduction of the carbon-ratio-theory which relates metamorphism of coal to the occurrence of petroleum (White, 1915). Oil fields in the eastern United States do not occur where the fixed carbon content exceeds 60%; gas fields are not found beyond fixed carbon values of 65–70%. This theory proposed that petroleum occurrence is limited by thermal history.

1926: Establishment of the American Petroleum Institute's (API) Project 4 to investigate the origin and environment of petroleum source sediments (Trask, 1932). Two important conclusions resulted from this project. First, the distribution of organic matter in various modern sediments indicates that liquid petroleum does not occur in sediments at the time of deposition and, therefore, soluble organic matter in modern sediments is not an important factor in petroleum origin (Trask and Wu, 1930). Second, much (if not most) petroleum comes from the non-extractable organic matter (kerogen) in sediments.

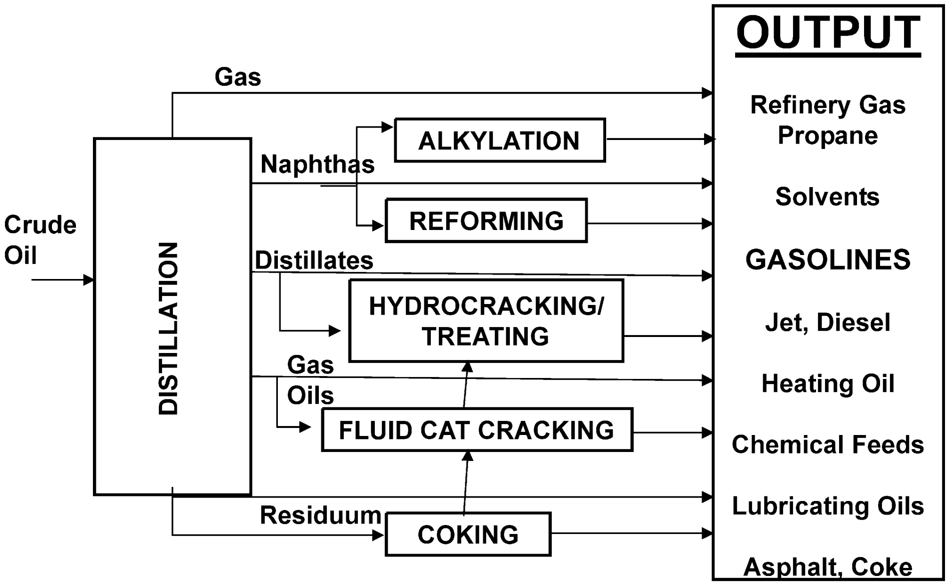


Fig. 1. Crude oils are the source of a wide variety of refined products and feedstocks for the petrochemical industry. This flow chart shows a simplified refinery crude oil distillation process and the associated refined products.

1927: Organization of API Project 6 to study the hydrocarbon constituents of a representative petroleum (from the Brett No. 6 well, Ponca City, Oklahoma Field). This ambitious project required exhaustive fractionation, including five forms of distillation, two forms of extraction, four forms of adsorption, two forms of crystallization, and two forms of separation using molecular sieves. By June 1960, 175 hydrocarbon compounds, representing about 60% of the crude oil, had been isolated and identified (Rossini, 1960). By the time the project ended in the mid-1960s, more than 295 compounds had been identified.

1929: Beginning of surface prospecting by geochemical means to explore for subsurface petroleum deposits. The first possibility of a direct surface prospecting method appeared in a patent filed in Germany and the United States entitled "Detecting the Presence of Profitable Deposits in the Earth" (Laubmeyer, 1933) in which soil gas was assayed for hydrocarbons as an indicator of petroleum in the subsurface. Prospecting methods were also used in the USSR (Sokolov, 1933). Later in the United States, Horvitz (1939) and Rosaire (1940) established a commercial company to provide surface prospecting services to the petroleum industry.

1931: The American Chemical Society's Petroleum Research Fund (PRF), the outgrowth of two funds established in 1926 by the API and the Universal Oil Products Company (UOP), began to support fundamental research and education in the petroleum field.

1933: Discovery of porphyrin pigments in shale, and later in oil and coal, marks the first result of modern studies on the geochemistry of organic molecules (Treibs, 1936). Free-base as well as metal-complex porphyrins were found and demonstrated to be degradation products from chlorophyll. This observation showed there is a link between biochemicals in living matter and the compounds found in petroleum. In the following year Vernadskii (1934), in his *Outlines of Geochemistry*, reiterated the importance of sedimentary organic matter in the origin of petroleum.

1942: API Project 43 was initiated to study the transformation of organic matter into petroleum by radioactive and thermal sources of energy and by bacteriological and biochemical processes. The results of these studies greatly influenced ideas at the time on the origin of petroleum. The work showed that hydrocarbons derived from the organic matter of living organisms are adequate in quantity to yield hydrocarbons found in petroleum (summarized in Whitehead and Breger, 1963).

1952: Sustained interest in molecular organic geochemistry was initiated by the finding of liquid hydrocarbons in recent sediments by Smith (1952). This observation changed the course of petroleum geochemistry, momentarily, because it challenged the conventional wisdom expounded by Trask and Wu (1930) that liquid hydrocarbons are not present in recent sediments. Also in 1952, Oakwood et al. (1952) observed optical activity in petroleum fractions thought to contain steroids and terpenoids, an observation confirmed much later by Whitehead (1971).

1954: The first successful source rock–crude oil correlation was carried out in the Uinta Basin of Utah. Four major source rock types were identified and correlated with the liquid hydrocarbons in the basin using a variety of techniques such as fractionation, column chromatography, infrared analysis and elemental analysis (Hunt et al, 1954). This led to the identification of a variety of shales and carbonate rocks that were acting as source rocks for oils in nearby reservoirs (Hunt and Jamieson, 1956).

1955: Development of mass spectrometric analyses of high molecular weight hydrocarbons in which the mass spectral data were corrected to a monoisotopic basis for carbon and hydrogen, leading to the discovery of *n*-paraffin distributions (Fig. 2) in crude oils and sediment extracts (Stevens et al., 1956; Bray and Evans, 1961).

1958: In contrast to the idea that petroleum could be accounted for by a selection and concentration of hydrocarbons in recent sediments (Smith, 1952, 1954; Meinschein, 1959), Forsman and Hunt (1958) and Bray and Evans (1961) suggested, correctly, that hydrocarbon mixtures in recent sediments cannot serve directly as precursors for petroleum hydrocarbons. Rather, sediment organic matter including hydrocarbons must be altered and transformed to produce petroleum. The structure and properties of kerogen were investigated (Forsman and Hunt, 1958), and the important role of kerogen in petroleum generation was finally accepted (Abelson, 1963) and has been reviewed in detail by Durand (1980).

1958: Carbon isotopic studies were applied to petroleum and other sedimentary organic materials (Silverman and Epstein, 1958). This practical application of isotope geochemistry was a natural extension of the work of Craig (1953), who firmly established carbon isotopes as an important part of the chemistry of organic molecules.

~1960: Gas chromatography (later coupled with mass spectrometry) became commercially available, leading to the separation, identification, and determination of distributions of many kinds of organic compounds found in sediments and crude oils. The *n*-alkanes and *n*-fatty acids (Cooper, 1962; Cooper and Bray, 1963) and isoprenoid hydrocarbons (Bendoriatis et al., 1962) were among the first compounds investigated.

1963: Publication of *Organic Geochemistry*, edited by I.A. Breger (1963), which contains 15 papers, many of relevance to petroleum geochemistry. This book is the first compilation, in English, of papers covering organic and petroleum geochemistry.

1964: Development of the biomarker concept where biomarkers, also called biological markers (Eglinton et

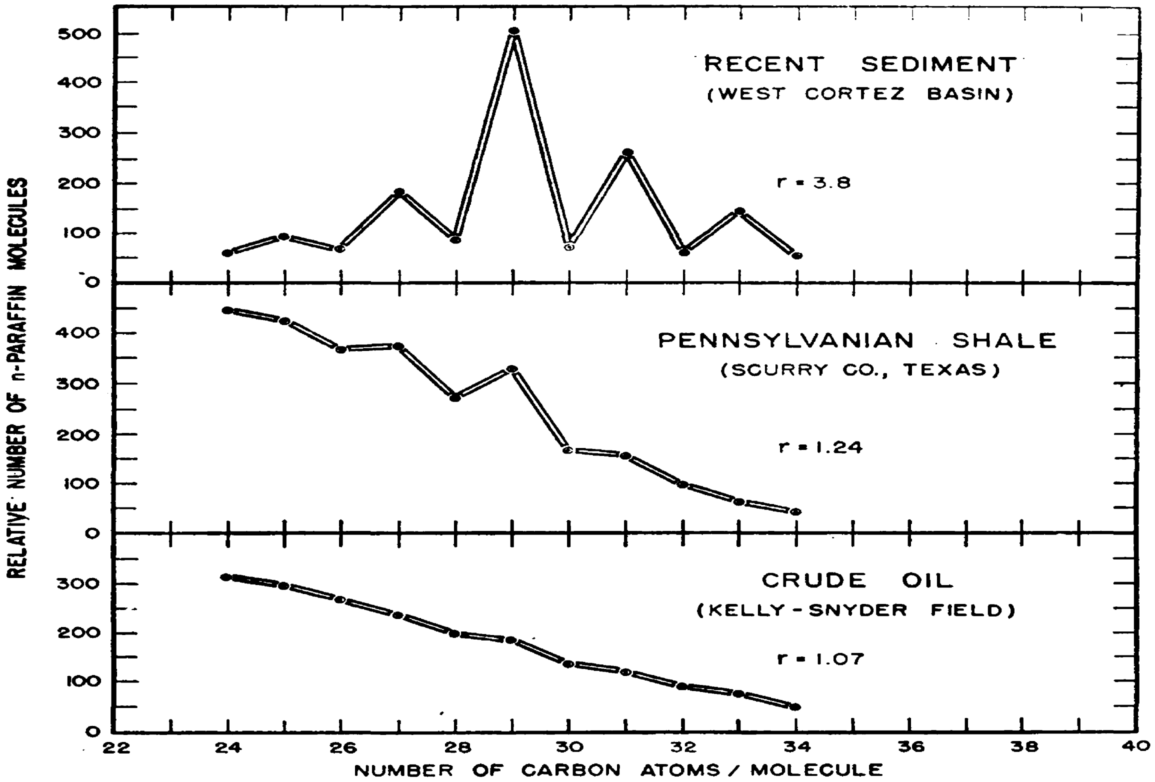


Fig. 2. Distributions of *n*-alkanes in recent sediments, crude oils and shales have been investigated extensively since the 1950s. Variations in the odd/even distributions of the *n*-alkanes was recognized as a potential maturity indicator by Stevens et al. (1956). One of the earliest illustrations of the odd/even predominance of *n*-alkanes in immature sediments and plankton plus the smooth distribution of these components in crude oils is shown in this figure (reproduced with permission from Bray and Evans, 1961).

al., 1964), molecular markers, chemical fossils (Eglinton and Calvin, 1967) and geochemical fossils (Tissot and Welte, 1978), led to comparison of structurally similar organic compounds in sediments and crude oils with their probable precursors in living organisms. Biomarkers were also used to make oil–rock correlations and oil–oil correlations, and to understand petroleum occurrence and origin.

1969: Publication of *Organic Geochemistry—Methods and Results*, edited by G. Eglinton and M.T.J. Murphy (1969), provided a comprehensive collection of 31 papers, many of direct interest to petroleum geochemists. It is essentially the first textbook in the field.

1977: Development and use of Rock-Eval, a standardized pyrolysis method of source-rock characterization and evaluation (Espitalié et al., 1977). Rock-Eval became a principal analytical tool in petroleum geochemistry. The type of kerogen is characterized by its Rock-Eval-determined hydrogen index and oxygen index, which show good correlations with H/C and O/C ratios, respectively, of kerogen. The indices can be plotted as a modified van Krevelen diagram (Fig. 3 a,b), from which kerogen in rocks has been classified as types I, II, III, and IV. Types I and II are considered oil-prone, whereas types III and IV are gas-prone.

1978: Publication of *Petroleum Formation and Occurrence* by Tissot and Welte (1978), the first textbook on petroleum geochemistry. The journal *Organic Geochemistry*, which serves as an outlet for many research papers on petroleum geochemistry, was first published in 1977 under the editorship of I.A. Breger. In 1983 the journal became affiliated with the European Association of Organic Geochemists (EAOG), and in 1985 the publication was designated the Official Journal of the EAOG.

1979: One of the most significant developments in petroleum geochemistry was the introduction of the laboratory technique of hydrous pyrolysis by the Amoco geochemists Lewan and Winters (Lewan et al., 1979). Whereas fingerprinting methods provide a snapshot at a specific point in time, hydrous pyrolysis is a method to simulate the maturation of an immature kerogen or source rock, and yields information on the nature of the products that a specific kerogen generates with increasing maturity. This technique is discussed in more detail below.

1979: Publication of *Petroleum Geochemistry and Geology* by Hunt (1979), the second textbook directed

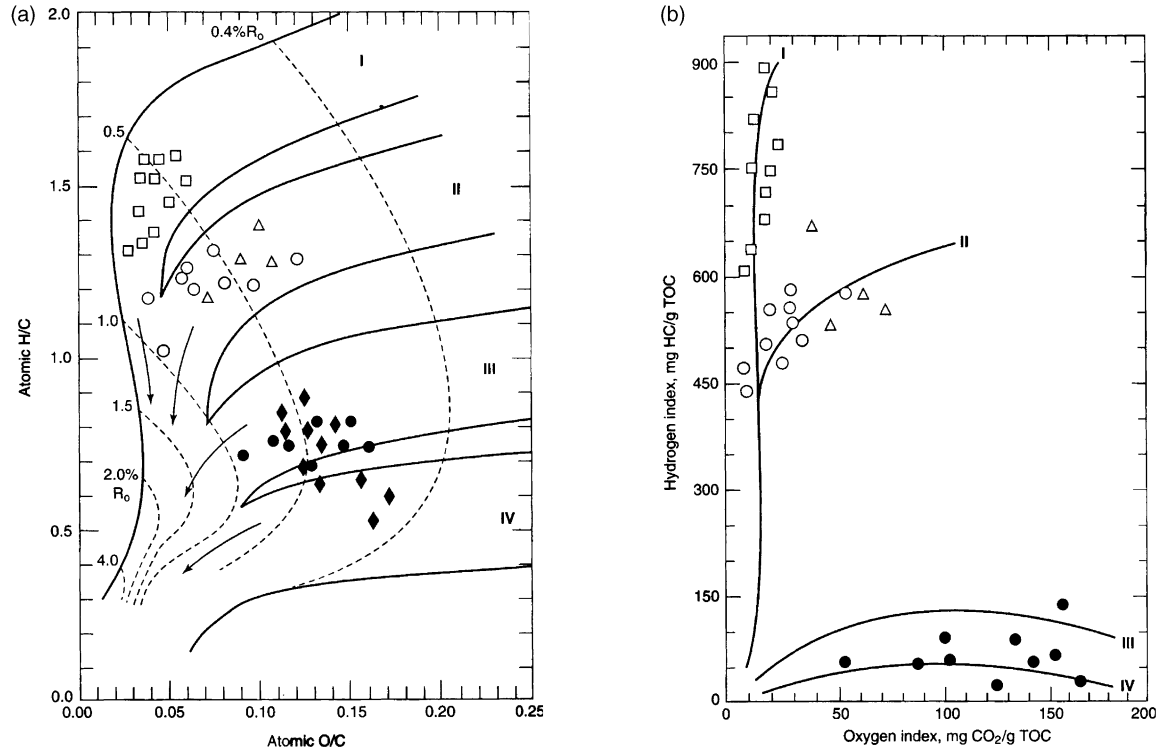


Fig. 3. (a) van Krevelen diagram showing four different types of kerogen at different maturity levels. The open square symbols are type I, Eocene Green River Shale, USA; open triangles are type II, Jurassic of Saudi Arabia, and open circles are type II from the Toarcian Shale of France; shaded circles are type III, Tertiary of Greenland; and shaded diamonds are type IV, Upper Tertiary, Gulf of Alaska. The dashed lines are isorank lines based on vitrinite reflectance,%R_o. (b) Classification of kerogen types on the basis of the HI and OI from Rock Eval data. The symbols are the same as for Fig. 3a although the Alaskan samples are not included in this diagram (reproduced with permission from Hunt, 1996).

specifically to petroleum geochemistry and its application to petroleum geology.

3. Formal recognition of petroleum geochemistry

Petroleum geochemistry was first recognized as a scientific discipline in 1959 when a meeting entitled "General Petroleum Geochemistry Symposium" was held in conjunction with the 5th World Petroleum Congress. This symposium was organized by B. Nagy, E.G. Baker, and P. Witherspoon, moderated by G. Hobson, and took place at Fordham University in New York. During the same year, B. Nagy also organized the Organic Geochemistry Division (OGD) of The Geochemical Society, and the OGD met for the first time in 1960 with the Geological Society of America in Denver, Colorado.

Three years later in September 1962, the 1st International Meeting on Organic Geochemistry (IMOG) was held in Milan, Italy, co-chaired by U. Colombo and G. Hobson. About one-third of the 39 papers presented were about petroleum geochemistry. International meetings have been held approximately every other year since then. Six petroleum geochemists from the United States, P. Witherspoon, H. Smith, S. Silverman, N. Stevens, P.A. Dickey and J. Hunt, attended the 1st IMOG, while on their way to Budapest, Hungary, for the 3rd International Scientific Conference on Geochemistry, Microbiology and Petroleum Chemistry in October 1962. This meeting demonstrated that petroleum geochemistry had been an active discipline in Cold War countries (Russia, Hungary, Czechoslovakia, Romania, and East Germany).

During 1963, a Gordon Research Conference entitled "Origin of Petroleum" was held at Tilton School, New Hampshire, co-chaired by H. Smith and F. Rossini. Keynote addresses on petroleum geology and petroleum geochemistry were given by H. Edberg and J. Hunt, respectively. For the next 6 years, Gordon Research Conferences dealt with broad issues in geochemistry, including petroleum geochemistry. In 1968 the Conference was titled "Organic Geochemistry," and since then a Gordon Research Conference on Organic Geochemistry has been held biennially at Holderness School, New Hampshire, and petroleum geochemistry has always been an important topic of discussion.

4. Surface prospecting

One of the earliest applications of petroleum geochemistry was to surface prospecting for subsurface hydrocarbon accumulations. DeGolyer (1940) claimed that visible evidence of oil at the surface had been responsible for the discovery of more oil than any other prospecting technique up to that time. Oil seeps have always been relatively easy to observe, and with the multitude of satellite imagery techniques available today, they are far more easily observed than in past years. Surface prospecting has had varying degrees of success over the years, and has also been received with varying levels of skepticism. Many of the early publications only reported successes, gave no indication of the rates of success, and certainly no indication of the spectacular failures. Others implied that a successful discovery of a surface anomaly would indicate a drilling target at the center of the anomaly, completely ignoring the fact that volatile components do not necessarily migrate vertically but instead take pathways of least resistance to the surface via faults and fissures (summarized in Philp and Crisp, 1982).

Used as a regional tool in conjunction with other data such as geophysics, regional geology and stratigraphy, surface prospecting can provide an extremely powerful indicator for the presence of hydrocarbons, particularly in frontier basins, but not the exact location of the trap. The use of the technique as a regional tool rather than a specific anomaly indicator has led to wider acceptance. Philp and Crisp (1982) reviewed surface prospecting as conducted prior to about 1980.

A petroleum seep is defined as visible evidence at the earth's surface of the present or past leakage of oil, gas or bitumen from the subsurface. Seeps have been utilized at least since ancient tribes of the Near East recovered blocks of asphalt from the Dead Sea, and many studies have demonstrated the worldwide correlation between seeps and earthquakes, with most visible seeps being near past or present areas of tectonic activity. The presence of seeps in a basin can considerably reduce the exploration risk because these seeps indicate that petroleum-forming processes have been active in the subsurface. In a situation where the major pathway for seeps is along a fault, the intensity and shape of the seep will be significantly different from those situations where vertical leakage has occurred, and this difference permits their distinction. For example, Fig. 4 illustrates a case where high pressure gases move up a fault in a

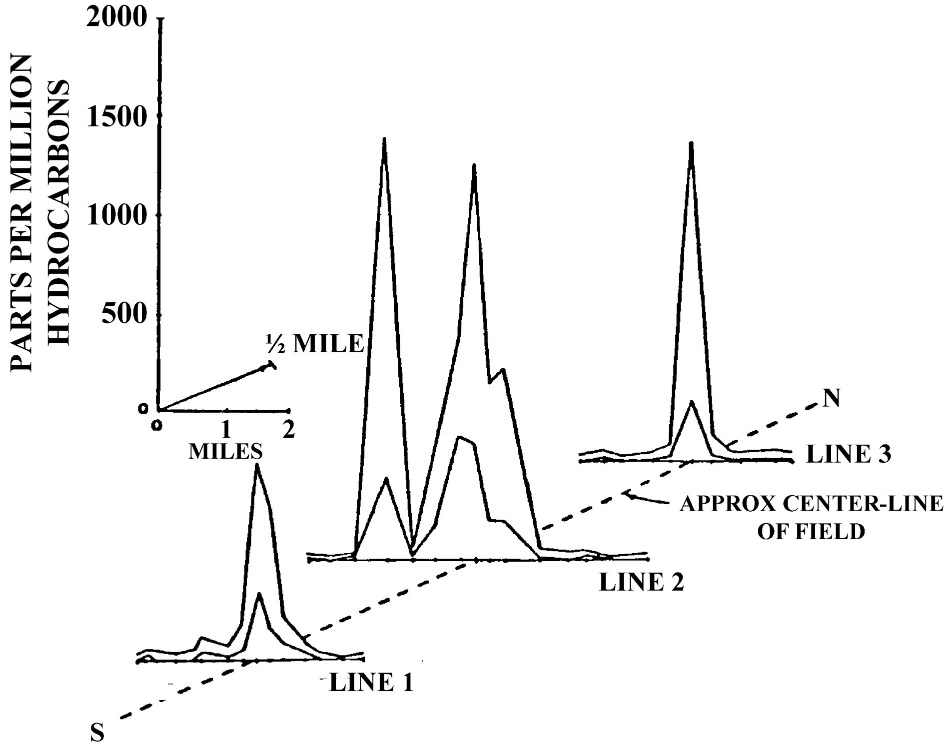


Fig. 4. Surface prospecting for subsurface accumulations of hydrocarbons was one of the earliest forms of petroleum geochemistry. Much of the early work was directed towards the determination of gaseous anomalies at the surface particularly in areas where faults were associated with petroleum producing regions. In this example, surface geochemical profiles across a major fault in an oil producing area of Michigan are shown. The top curve for each profile is total gas, and the bottom curve is C_{2+} fraction (reproduced with permission from McIver, 1985).

petroleum producing area. Gas concentrations along the fault were more than 50 times background concentration levels.

Early investigators assumed that hydrocarbons would migrate vertically, and any resulting surface anomaly would be directly over the location of the trap. This concept has changed considerably over the years, and it is now known that a number of factors may affect the location of any surface anomaly relative to the underlying hydrocarbon accumulation. Overlying geology, groundwater, depth of accumulation, degree of fracturing, and many other factors will ultimately determine the relative position of any surface feature or anomaly. Weathering effects such as evaporation of volatiles, leaching of water soluble constituents, microbial degradation, polymerization, and auto-oxidation may also affect the appearance of the seep and ultimately lead to the oil being converted to solid bitumen.

Systematic development of geochemical methods for oil and gas prospecting was first initiated by Laubmeyer (1933) in Germany, Sokolov et al. (1963) in Russia, and Horvitz (1939, 1972) and Rosaire (1940) in the United States. Reviews of the early Russian work can be found in Kartsev et al. (1954), Sokolov (1959), Sokolov and Mironov (1962) and Sokolov et al. (1963). Rosaire (1940) discussed early prospecting techniques in the United States, particularly those applied to gases in soil and groundwater. Pirson (1940) described various onshore methods, and Chillingar and Karim (1962) described the application of surveys to surface sediments, drilling fluids, and cores. Both DeGolyer (1940) and Link (1952) emphasized the importance of the relationship between oil and gas seeps and underlying accumulations of hydrocarbon reserves. Reviews of surface prospecting by Davis (1967) included discussions of microbial prospecting methods, infra-red analyses of soil extracts (Bray, 1956a) and the utilization of carbon isotopes as a means of characterizing soil lipids (Bray, 1956b).

Early studies were typically restricted to the analysis of methane and total non-methane hydrocarbons in soil gases using condensation, combustion, and a manometer. Traditional methods for surface prospecting were based on determining soil–gas content, which may be present as free, adsorbed, or dissolved gas. Surface soil samples were taken over a grid pattern, returned to the laboratory, and headspace analyses were undertaken by gas chromatography (GC) after treatment of the samples to release the trapped gases. Prior to the routine use of GC, gas contents were typically determined volumetrically. The resulting gas concentrations were plotted and contoured on a grid pattern, and any surface anomalies with gas concentrations above background levels were readily detected. Sokolov (1933) and Laubmeyer (1933) both found higher concentrations of gas in soil air over productive zones. Nechayeva (1968) noted that in western Siberia it was possible to distinguish between gas fields, gas condensate fields, and oilfields on the basis of hydrogen content at the surface. Characterization of adsorbed gases required treatment of the soils with acid to release the adsorbed gases, and for many years the method of Horvitz (1939) was used for this purpose, along with the combustion and manometer methods of Kartsev et al. (1954). Debnam (1965) and Horvitz (1972) later developed methods involving gently heating the soil sample under vacuum, followed by acid treatment, to release the adsorbed gases. A number of authors noted correlations between gas content, lithological characteristics and type of organic matter in the sample (McCrossan et al., 1972; Poll, 1975). Finally it should be noted that a number of workers developed methods to measure concentrations of dissolved hydrocarbons in formation waters. Results from the Russian work were described by Sokolov (1959), Kartsev et al. (1954), and Stadnik et al. (1977). McAuliffe (1966, 1971) reported results from the measurement of hydrocarbons dissolved in groundwater.

A major problem with surface prospecting has been interpretation of the results, in particular determining if the gases are biogenic (microbial and near-surface origin) or thermogenic. A partial solution to this problem made use of the concentration of methane relative to the other gases. Biogenic gases typically contain mostly methane, likely the most abundant and widespread of all hydrocarbon gases held within the sedimentary rocks of the crust (Hedberg, 1980). Another approach is to use the isotopic composition of the methane, along with the composition of the light hydrocarbon gases, ethane and propane, to distinguish microbial from thermal gas (Bernard et al., 1976).

Initial attempts at surface prospecting were confined to onshore studies, but in the late 1960s and 1970s similar applications offshore, including the development of various sniffing devices, were developed. Sniffers used various means to strip the gases, typically those in the C_1–C_4 range, from water samples collected close to the sediment/water interface prior to their analyses by GC. One of the advantages of this type of offshore sniffing compared to onshore studies was that background interference from gases coming from plant debris and roots was non-existent; however, as with onshore studies, interference from microbial methane was a potential problem. Offshore sediment samples were also being collected over grid patterns, and gases were isolated and analyzed using many of the same techniques described for onshore sediments. The advantage of this type of sampling was again the lack of background interference compared to that in onshore sampling. In selected cases, gas bubbles from seeps could be observed on the seafloor and collected directly into sample bottles and returned to the laboratory for analyses (Brooks et al., 1973; Bernard et al., 1976).

In many situations, the use of methods to detect indirect surface expression or alteration of surface features resulting from the seep was a more viable option. Such indirect approaches ranged from the extremes of changes in the mineralogy of the overlying soil to changes in the vegetation type as a result of a gas seep. Near-surface carbonate cements can be formed from carbon dioxide produced by bacterial degradation of hydrocarbons seeping to the surface from deep petroleum deposits. Horvitz (1981) noted that ferrous carbonate anomalies, which could be distinguished on the basis of their unusual thermal decomposition pathways, showed high concentrations above the edges of hydrocarbon accumulations. Their origin was verified, in some cases, through determination of their carbon isotope composition (Behrens, 1988). Donovan and Dalziel (1977) measured the isotopic composition of carbonate cements in outcrops and detected anomalous isotopic compositions indicative of hydrocarbon seepage. Donovan (1981) reported anomalous isotope compositions for the carbonates and also noted associated occurrences of pyrite. Other indirect methods of detecting surface anomalies included iron and manganese leaching from surface rocks (Kartsev et al., 1954; Donovan et al., 1975), ions associated with petroleum (Kartsev et al., 1954; Davis, 1967; Hitchon, 1974), helium associated with gas seeps (Dyck, 1976; Roberts et al., 1976), radon 222 (Gates and McEldowney, 1977), and dissolved nitrogen in groundwaters (Zorkin et al., 1976). LANDSAT imagery techniques (Marrs and Kiminsky, 1977) became available at the end of the 1970s. Various microbiological methods have also been reported and involve detection of enhanced levels of methane- and ethane-consuming bacteria in the sediments. Some of the more notable early reviews of this method are Davis (1967), Brisbane and Ladd (1968), Sealey (1974a,b), and Miller (1976).

5. Impact of new analytical techniques

The ability to fractionate crude oils into sub-fractions, or even individual compounds, represented a significant advance in geochemistry and its application to exploration problems. In the early part of the twentieth century relatively little was known about the composition of crude oils, and little if any attention was paid to extracting source rocks and characterizing the source rock extract. API projects, particularly API Project 6, which started in 1927, were responsible for initiating the development of techniques necessary for the fractionation of crude oils. Later, the 1950s saw developments in many of the basic techniques, including liquid–solid chromatography, which are used today for fractionation and identification processes, albeit with increases in sensitivity, specificity, and sophistication.

5.1. Distillation

Distillation was the forerunner of gas chromatography, and while not commonly used in geochemistry today, distillation is still a major part of refinery operations. It has long been known that oils and bitumens can be fractionated by distillation at different temperatures and classified into paraffin base and asphalt base, depending on the content of the asphalt or wax in the petroleum residuum. Within each group, oil correlations were made on the basis of distillation curves; however, many oils did not fall into the end member categories and were classified as mixtures. In the late 1920s, the US Bureau of Mines adopted the Hempel method of distillation for crude oil correlation, and Smith (1940) subsequently developed the correlation index (CI) as a means of evaluating the chemical character of the distillation fractions (Fig. 5). The CI is calculated from the specific gravity and boiling point of the distillation fractions. On the basis of the Hempel distillation data plus the CI, it was possible to distinguish crudes from different sources and to correlate samples from the same source. Although this method is no longer in use today, the US Bureau of Mines (or its contemporary equivalent) maintains about 35 year's of Hempel distillation information.

5.2. Gas chromatography

One of the main concepts of distillation is the degree of separation that can be achieved on the basis of the number of plates in the distillation tower. In gas–liquid chromatography, usually called gas chromatography (GC), a similar concept is applied: in general, the longer the column the greater the resolving capability and degree of separation. Whereas the degree of separation expected from distillation may be of the order 2 to 300 theoretical plates, gas chromatography regularly provides 25,000 or more theoretical plates of separation. Martin and Synge (1941) proposed that compounds could be separated by partitioning between a gas and a liquid; this separation was first achieved by James and Martin (1952) for fatty acids. The technique of gas–liquid chromatography (GC) became commercially available about 1960. A tremendous amount of new information on the composition of petroleum was obtained from GC using thermal conductivity and flame ionization detectors, but it was soon realized that for more complete analyses, GC would need to be coupled to more sophisticated detectors. Several years after the introduction of GC, coupling with a mass spectrometer became practical, giving rise to the powerful analytical technique of gas chromatography/mass spectrometry (GCMS). Other coupled analytical techniques followed, including liquid chromatography/mass spectrometry (LCMS) and gas chromatography/infrared spectrometry (GCIR).

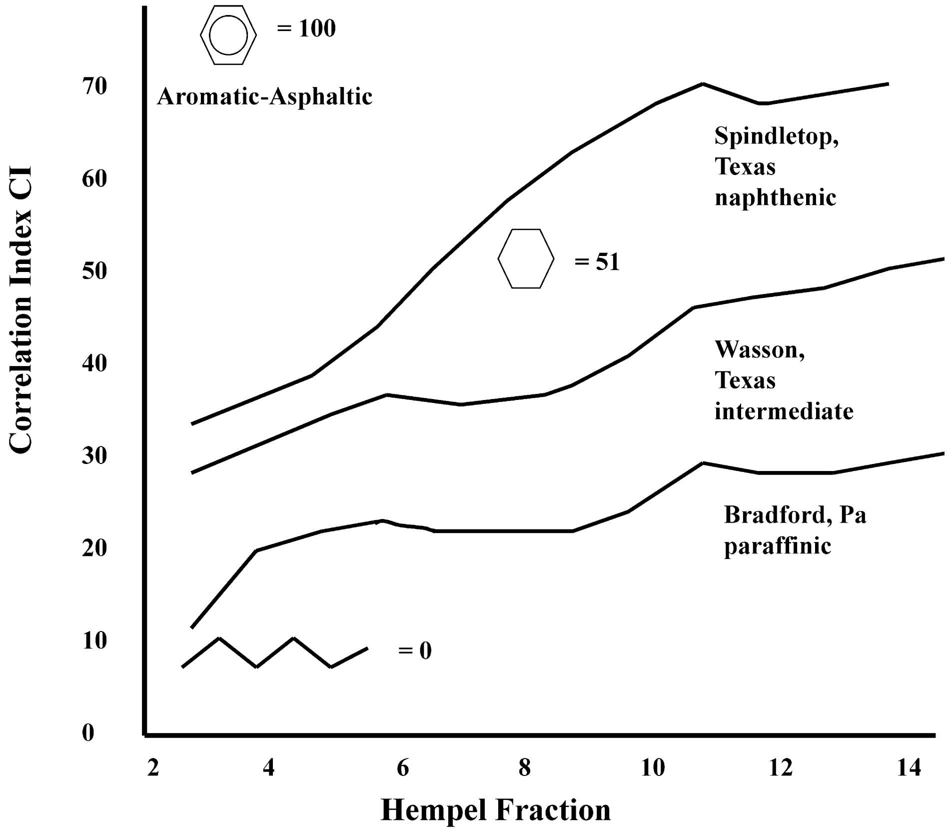


Fig. 5. Crude oils were initially characterized on the basis of Hempel distillation data plus the correlation index (CI). In this diagram three crude oils are characterized in this manner to illustrate the differences between naphthenic, intermediate and paraffinic crudes. (The figure is redrawn from Hunt, 1979, and the data used to construct the original figure are from McKinney et al., 1966.)

Early gas chromatographs consisted of an oven, injector, column and detector. Most significant developments have taken place in the columns used for the separation of individual compounds in complex mixtures. Early columns were short, wide-bore and typically made of glass or copper. As the internal diameter of the columns was reduced and the length increased, the resolution (or number of theoretical plates) increased. The initial columns were "packed" columns containing an inert support coated with a "liquid" film, typically Apiezon grease or a polymethylsilicone polymer responsible for the separation of compounds by partitioning between the gas and liquid phases. The introduction of the "capillary" column, initially stainless steel and then glass, further improved the resolution and degree of separation. Phases improved, solid supports were eliminated, and phases were coated on the inside of the stainless steel, glass, or more recently fused silica, column. The chromatograms in Fig. 6a and b illustrate the significant improvement in resolution obtained as a result of the changes in column technology.

5.3. Gas chromatography/mass spectrometry

Prior to the advent of combined gas chromatography/mass spectrometry (GCMS), it was practically impossible to contemplate the rapid analysis of an organic mixture having more than 20 components. Even the separation and identification of two or three major components could take a year or more using classical analytical methods. The sample size required for such characterizations were many orders of magnitude greater than the sizes required today, and the analysis of individual components at the parts per billion concentration levels was not possible. Whereas such sensitivity is not needed for many petroleum geochemical analyses, it is often required in environmental and biomedical analyses.

Much of the early GCMS work was accomplished using magnetic-sector mass spectrometers. When the quadrupole MS became commercially available in the mid-1970s the popularity of GCMS increased dramatically for a number of reasons. Quadrupole systems,

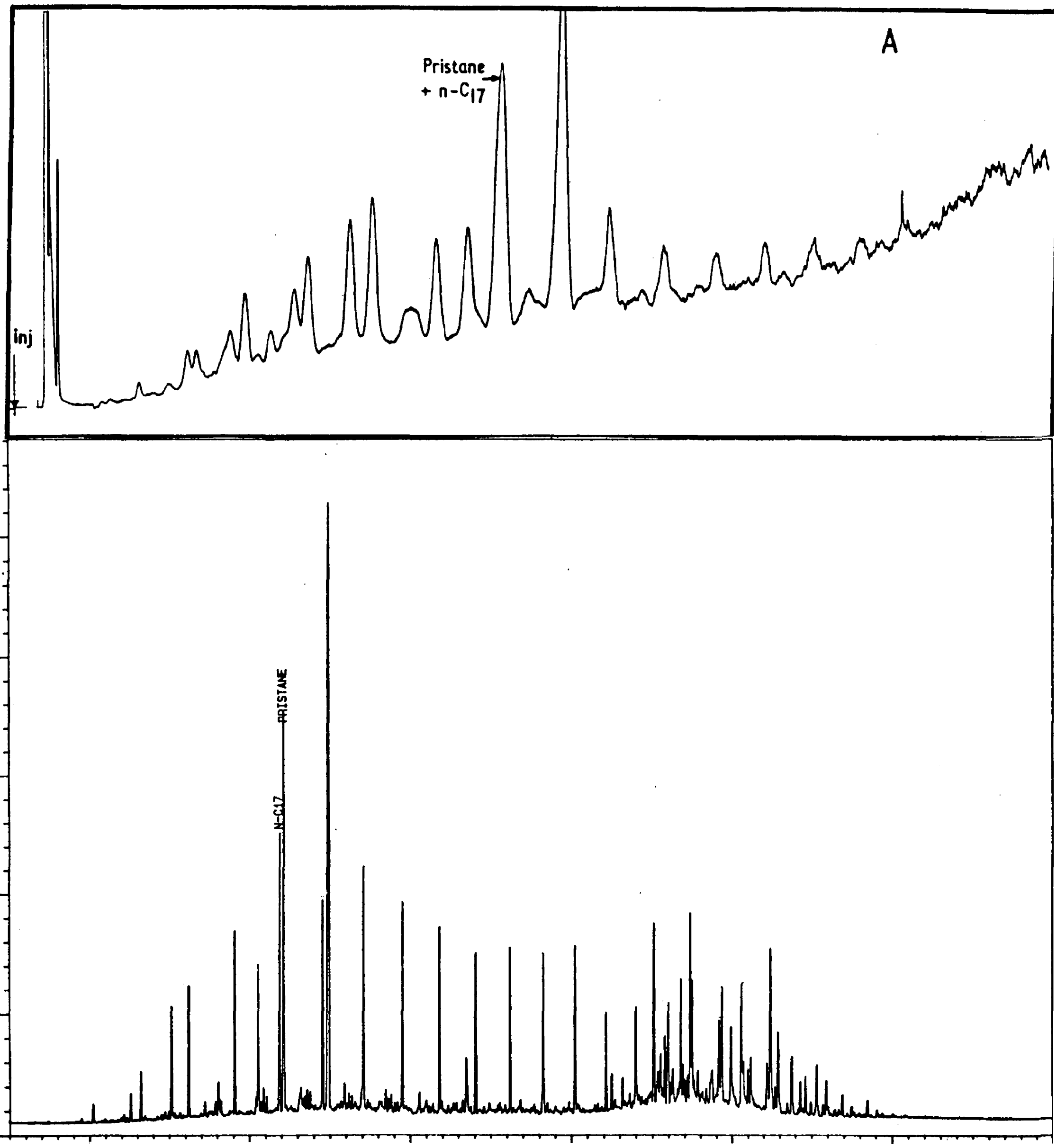


Fig. 6. Short columns (3–6 ft) were initially used in gas chromatography and were packed with an inert solid support coated with a liquid phase. Whereas sufficient resolution necessary to separate *n*-alkanes was readily achievable, many of the less abundant components could not be resolved. The chromatograms shown here, provided by Dr. A.G. Douglas, illustrate (a) the *n*-alkanes from the Marl Slate as determined by packed column GC, and (b) for comparative purposes the same sample analyzed on a contemporary capillary column. The comparison illustrates the far greater resolution obtained by capillary columns.

although lacking the high resolution capabilities of magnetic-sector instruments, were able to scan rapidly, did not have any memory (hysteresis) effects, were sensitive, easy to use, and did not require the elaborate tuning procedures of the magnetic-sector systems.

In the late 1970s and the early 1980s, a large number of novel biomarkers were discovered in crude oils, source rock extracts and other geological samples (Seifert et al., 1972; Kimble et al., 1974). A comprehensive review published by Mackenzie et al. (1982) summarizes advances in sterane geochemistry to about 1980. Hitchon (1974) reviewed the application of geochemistry to the search for oil and gas, covering early days of biomarkers, introducing concepts of basin modeling, discussing ideas on the generation of oil, and serving as a useful stepping-stone between the early analytical techniques and those coupled analytical systems being developed in the early 1970s. Most major instrumental innovations had already occurred by 1980, and since then most developments have involved modification and improvement of existing techniques. Perhaps the only commercial development that had not occurred in one form or another by the late 1970s was the coupling of a GC with an isotope ratio mass spectrometer (IRMS). Mathews and Hayes (1978) were first to describe GCIRMS, but it was not until the late 1980s that commercial systems became available.

5.4. Optical rotation

Optical activity, measured by the degree and direction of rotation of polarized light, has been used for many years to obtain information on the origin of crude oils and possible relationships between different oil samples. Whitmore and Oakwood (1946–1947) described their efforts to establish whether or not the optical activity in petroleum is derived directly from living organisms. It was already recognized by that time that plant hydrocarbons are optically active in the molecular weight range of some of the heavier hydrocarbons in petroleum. Their results make clear that the fraction with the highest degree of optical activity was the hydrocarbon fraction containing steranes and terpanes, a finding confirmed by Whitehead (1971). The use of optical rotation for the purposes of correlations was phased out, but the stereochemistry of chiral biomarkers, using GC, provided a proxy for optical activity (Hills and Whitehead, 1966; Maclean et al., 1968; Maxwell et al., 1972).

5.5. Nuclear magnetic resonance

Nuclear magnetic resonance (NMR), particularly ^{13}C NMR, developed commercially in the 1960s and 1970s, has found limited applications in petroleum exploration. It is used more extensively in the characterization of refinery products, particularly in determining their aromatic content (Bouquet and Bailleul, 1982). The aromatic content is typically measured on the asphaltenes and vacuum residues, and other refinery cuts that generally include the distillates, base stock oils, fuel oils, and cracking effluents. The application of ^{13}C NMR to the structural determination of individual compounds and to the characterization of kerogens and asphaltenes has been limited (Balogh et al., 1973).

5.6. Pyrolysis

Although crude oils and source rock extracts are readily characterized through the use of GC and GCMS, most of the organic matter in a source rock is insoluble in common organic solvents and cannot be analyzed directly by these techniques. Similarly, source rock extracts and crude oils contain an asphaltene fraction which can be isolated by precipitation, but it has limited solubility in most solvents and thus is not directly amenable to GC and GCMS. One method used to characterize asphaltenes and kerogens, however, was through their initial degradation by pyrolysis. Methods of pyrolysis can be classified in a number of ways. Foremost are fingerprinting methods which typically consist of some type of flash pyrolysis or rapid temperature-programmed pyrolysis, with the pyrolysis products being transferred rapidly to a GC column. The same approach can also be used in an off-line mode where the pyrolysis products are trapped and then fractionated, if necessary, prior to analysis by GC or GCMS (Douglas and Grantham, 1974). The development of Rock-Eval, a standardized pyrolysis method for source-rock characterization and evaluation (Espitalié et al., 1977), led to its widespread use in the petroleum industry, where it became a principal analytical tool.

A significant development in pyrolysis techniques was the introduction of hydrous pyrolysis (Lewan et al., 1979; Winters et al., 1983). Unlike flash pyrolysis, hydrous pyrolysis is undertaken in a high pressure vessel in the presence of water. Reactions are typically performed just below the critical temperature of water. By performing a series of reactions at different temperatures one can simulate the fate of the organic matter at different burial depths. Information obtained in this manner can be used for basin modeling purposes, or to determine the nature of the products generated and to correlate them with other oils in the basin. The most significant impact of hydrous pyrolysis is that it permits assessment of the fate of an immature rock as it is matured at greater depths of burial. The technique has become routine, and is now available as a commercial service.

5.7. Stable isotope measurements

Stable isotopes, mainly those of carbon, have played an important role in many aspects of petroleum geochemistry. Commonly the bulk isotope ratio values for the complete oil or source-rock extract are determined. These values represent the weighted average isotopic compositions of all the constituents in the sample under investigation. Early applications of bulk carbon isotope values included a study by Silverman and Epstein (1958) of a number of Tertiary crude oils from different environments. Marine and non-marine oils could be differentiated on the basis of their isotopic compositions. A later study of Carboniferous oils from the Urals, however, did not show the same discrimination (Galimov,

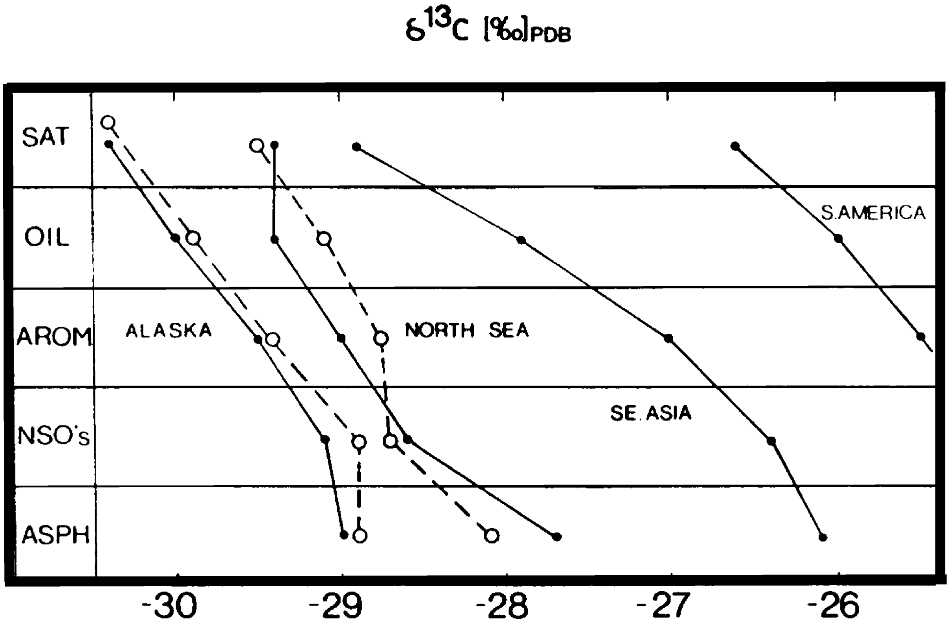


Fig. 7. For many years carbon isotopic data have played an important role in the characterization of crude oils. Stahl (1977) developed a correlation method using the isotopic composition of individual fractions within a crude oil to develop the correlation curves shown above (reproduced with permission from Stahl, 1977).

1973). Other early applications noted a general trend of enrichment of the light ^{12} isotope with increasing age (Welte et al., 1975; Stahl, 1977), possibly caused by variations in intensity of photosynthesis and changes in the isotopic composition of the atmospheric CO_2. Kvenvolden and Squires (1967) successfully used isotopic age trends to relate and distinguish crude oils on a regional basis in west Texas. Fuex (1977) reviewed the application of stable carbon isotopes to petroleum exploration.

Isotopic compositions of crude oils can be plotted on a petroleum type-curve (Galimov, 1973; Stahl, 1977) and used for crude oil correlation studies (Fig. 7). Water washing and microbial alteration tend to alter the shape of the curves, particularly the curves of the saturate fraction, making correlations somewhat more difficult. Stahl (1977) expanded the concept to enable oil/source rock correlations to be undertaken on the basis of the isotopic values.

Silverman (1965) was among the first to recognize isotopic changes during oil migration. He noted a slight depletion in ^{13}C with increasing migration distance, caused by the relative increase in the isotopically light saturates and loss of the isotopically heavy aromatics, polars, and asphaltenes during migration. Bacterial degradation causes the greatest isotopic enrichment to the saturate fraction (Stahl, 1977). Carbon isotopic compositions of methane were also used extensively in exploration studies for natural gas as summarized by Stahl (1977). Many of the trends mentioned above for oils also apply to methane. Increasing maturity and biodegradation result in heavier isotopic compositions of methane.

6. The biomarker revolution

The development of the coupled analytical techniques described above significantly enhanced the importance of petroleum geochemistry. Compounds now referred to as biological markers, biomarkers, molecular markers, chemical fossils, or geochemical fossils were being discovered rapidly in petroleum and sediment extracts through the use of these techniques (Eglinton et al., 1964; Hills et al., 1966; Eglinton and Calvin, 1967; Tissot and Welte, 1984; Maxwell et al., 1971; Blumer, 1973; Whitehead, 1974). Biomarkers are molecular fossils derived from living organisms, typically complex organic compounds composed of carbon, hydrogen and other elements, which show little structural difference from their parent biomolecules, e.g. sterols/sterenes/steranes. The concentration of the biomarker precursor in the living organism may be relatively high, but after diagenesis and thermal alteration, biomarker concentrations in crude oils and source rock extracts are often in the parts per million range.

Biomarkers are typically individual compounds, but a group or homologous series of compounds may also be used to identify a specific source of organic matter in a rock or crude oil. Biomarkers also have many applications in petroleum geochemistry: (1) correlation of oils with each other or suspected source rocks; (2) evaluation of thermal maturity and/or biodegradation; (3) regional variations in the character of oils and source rocks as controlled by organic matter input and characteristics of the depositional environment; and (4) information on kinetics of petroleum generation and basin thermal history. Examples of these applications are described below.

Treibs (1934) was the first to develop the biomarker concept, with his pioneering work on the identification of porphyrins in crude oils and his suggestion that these polyphrins may have originated from the chlorophyll of plants. Later Blumer et al. (1963) and Blumer and Thomas (1965) isolated pristane from Recent marine sediments and concluded that it was derived from the phytol side-chain of chlorophyll. Other workers reported on various classes of organic compounds in sediments without recognizing their biomarker implications. For example, Smith (1952, 1954, 1955) showed that some hydrocarbons were incorporated into recent sediments of the Gulf of Mexico. Kidwell and Hunt (1958) found saturated and aromatic hydrocarbons in Recent sediments of the Perdernales area in the Orinoco delta, whereas Meinschein (1959, 1961) reported saturated hydrocarbons, including steranes, terpanes, and polycyclic aromatic hydrocarbons in sediments of the Gulf of Mexico. Emery (1960) showed that gaseous and liquid hydrocarbons could also be found in sediments of Southern California.

One of the first families of biomarkers discovered and studied extensively was the family of *n*-paraffins or *n*-alkanes. Early work by Bray and Evans (1961), Meinschein (1961), and Kvenvolden (1962), among others, showed the odd/even carbon number predominance of *n*-alkanes in recent sediments (see Fig. 2), reflecting the input of higher plant material. Similarly, Clark and Blumer (1967) and others noted that marine organisms contained *n*-alkanes with a predominance in the C_{15}–C_{19} region. Not only could the distribution of *n*-alkanes be used to indicate the nature of the source material in the sediments, but also changes in the distribution of *n*-alkanes with increasing depth could indicate maturation. The ratio of odd/even carbon numbered *n*-alkanes was used to measure maturity (Bray and Evans, 1961; Philippi, 1965; Scalan and Smith, 1970; Tissot et al. 1977).

Isoprenoid hydrocarbons, particularly pristane (Pr) and phytane (Ph), could be detected by GC, so information was available about the origin and distribution of these compounds before the advent of the GCMS. Blumer et al. (1963) found Pr in zooplankton; Blumer and Thomas (1965) noted the presence of the precursors of Pr and Ph in various zooplankton. At the same time the Pr/Ph ratio was proposed as a measure of the redox potential of the environment in which the organic material was deposited, although these concepts have undergone numerous revisions and modifications since then (Powell and McKirdy, 1973; Didyk et al., 1978). The n-C_{17}/Pr and n-C_{18}/Ph ratios are also widely used as indicators of maturity and extent of biodegradation.

More complex biomarkers such as various groups of terpanes (tricyclic, tetracyclic, and pentacyclic) and steranes were studied extensively (summarized by Tissot and Welte, 1984). After hopanoid hydrocarbons (a class of terpanes) were found in geological samples, the number of them that were identified expanded rapidly. Hopanoid geochemistry was reviewed by Ourisson et al. (1979). Monoaromatic steranes in crude oils were found by O'Neal and Hood (1956) using high resolution mass spectrometry. The commercial availability of GCMS and associated data systems in the mid-1970s, plus the pioneering work of oil company petroleum geochemists such as Seifert and Moldowan (1978, 1979, 1981), led to an explosion in the use of biomarker compounds for a wide variety of geochemical purposes. An example of the GCMS identification of steranes is shown in Fig. 8.

7. Early identification of source rocks

In trying to understand the origin and occurrence of oil, pioneering petroleum geologists made some very perceptive observations. For example, Newberry (1860) described the oil and gas in the Berea sandstone near Mecca, Ohio, as being formed by low temperature heating of organic matter in the Ohio Black Shale. Kentucky's best oil fields were located where the Cumberland Sandstone was immediately overlain by the Ohio Black Shale. Decades later, Snider (1934), in summarizing the general opinion of petroleum geologists, stated that there seemed to be almost universal agreement that organic matter is buried principally in argillaceous mud and to a lesser extent in calcareous muds and marls and in sandy muds. Coarse sands and gravels and very pure calcareous deposits are generally without any notable content of organic material. Consequently, shales and bituminous limestones consolidated from muds and marls are generally regarded as source rocks for petroleum and natural gas. Some shales and carbonates with porous and permeable sections within them can act as both source and reservoir. Most of these early concepts have proved to be correct.

A petroleum source rock may be defined as a fine-grained sediment that has generated and released enough hydrocarbons to form an accumulation of oil or gas. Definitions that include migration and accumulation are needed because practically all fine-grained sediments can form some hydrocarbons. Techniques for recognizing source rocks are usually based on case histories of the type, quantity, and maturation level of organic matter in rocks associated with production. Also, crude oil source rock correlations have helped to establish that a particular rock has charged a particular reservoir. In fact, the genetic relationship between an active source rock and the resulting oil and gas accumulation is the basis of the petroleum-system concept of petroleum exploration developed later and discussed in detail in Magoon and Dow (1994).

Using analytical techniques that are crude by today's standards, Trask (1932) looked for diagnostic criteria for recognizing petroleum source beds. Cuttings and cores were analyzed for carbon content, reduction number (milliliters of 0.4 N chromic acid reduced by 1 g of sediments), nitrogen content, color, and volatility.

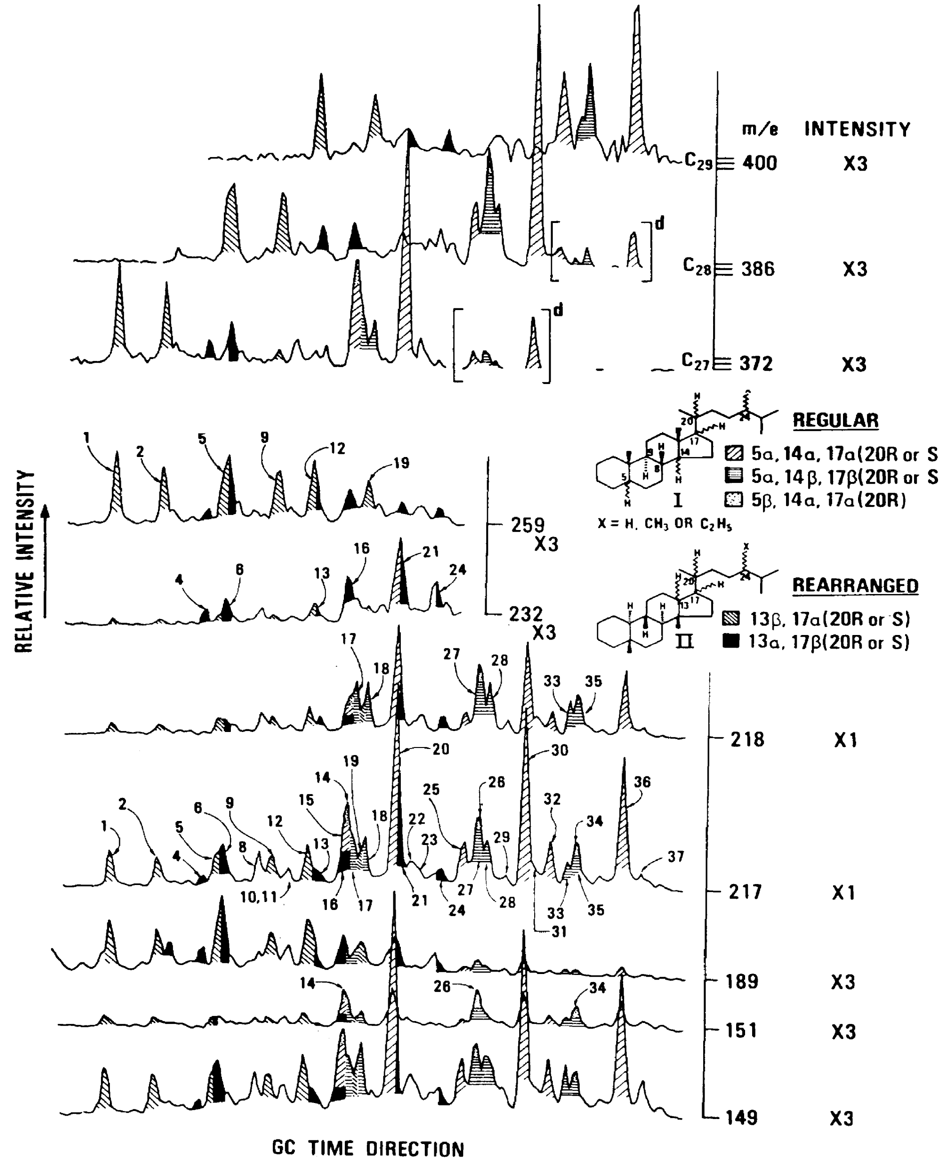


Fig. 8. GCMS and associated ancillary techniques such as multiple ion detection played a key role in the characterization of biomarkers in crude oils and source rock extracts. This diagram from early work by Seifert and Moldowan (1979) illustrates the complexity of the sterane distributions in a typical crude oil. Peaks of the chromatograms are labeled here for illustration only. The peak identities can be found in Table 4 on p. 116 of the original paper (reproduced with permission from Seifert and Moldowan, 1979).

None of these properties were very useful in characterizing source rocks. He also extracted bitumen from rocks likely to contain liquid hydrocarbons, with boiling carbon tetrachloride, but he did not have the advantage of chromatographic separation and analysis techniques to enable him to recognize petroleum in the source rocks.

Hunt and Jamieson (1956) first demonstrated that crude-oil extracts in source rocks have a composition comparable to that of reservoir oil. Pulverized rocks were extracted with a mixture of benzene or toluene and a water miscible organic solvent, e.g., methanol. The extracts were separated by column chromatography on powdered activated alumina, and fractionated on a microstill in order to make direct comparisons between rock extracts and oils from reservoirs in a study area of the Powder River Basin, Wyoming. Their work showed that liquid hydrocarbons, in many cases comparable to reservoir oils, were indigenous to practically all shales and carbonate rocks. Also, since the volume of non-reservoir rocks far exceeded that of reservoir rocks, it was apparent that enormous quantities of oil were still "locked up" in the source beds. Source rocks were classified as good, fair or poor, based on the content of extractable petroleum-like material. Philippi (1965) studied source rock quality in the Los Angeles and Ventura basins of California, and Baker (1962) published a detailed source-rock evaluation of the Cherokee Formation of Oklahoma.

These early studies defined source rocks on the basis of their hydrocarbons, whereas it is now recognized there are three important factors for good source rocks: quantity, quality, and stage of maturation of organic matter.

7.1. Quantity of organic matter

The quantity of organic matter, usually expressed as total organic carbon (TOC), in source beds ranges from greater than 0.5% to about 15%. Ronov (1958) analyzed the TOC in about 1000 samples of Upper Devonian shale from throughout the Russian platform from Kiev in the west to Ufa in the east. Although the Russian platform has good structures and good sandstones with high porosity and permeability throughout the area, all the oil fields are concentrated in an area near Ufa where TOC values range from 0.5 to 5 wt.%. No oil or gas was found in the northern part of the Russian platform where TOC values are generally less than 0.25%. In a detailed study of the Cherokee shales of Kansas and Oklahoma, Baker (1962) found TOC values as low as 0.1% in greenish gray, non-source shales and as high as 17% in one black shale unit. A minimum of 1.5–2% TOC has been generally accepted for defining good source rocks (Hunt, 1996).

7.2. Quality of organic matter

Kerogen is the disseminated organic matter in sedimentary rock that is insoluble in non-oxidizing acids, bases and organic solvents; understanding the chemistry of kerogen (and coal) was critical to understanding the origin of petroleum and to the development of petroleum generation models (Durand, 1980). After the role of kerogen in petroleum formation was clearly recognized and accepted (Abelson, 1963), much effort was expended between 1960 and 1980 in developing ideas on the time–temperature histories of petroleum generation from kerogen in various petroleum-bearing basins (Philippi, 1965; Tissot et al., 1971; Connan, 1974). From these studies came an understanding of the geologic zone of intense oil generation, now often called the oil window.

The organic matter (OM) initially deposited with unconsolidated sediments is not kerogen, but a precursor that is converted to kerogen during diagenesis. The most important factor controlling the generation of oil and gas is the hydrogen content of the (OM). The quantity of petroleum generated and expelled increases as the atomic hydrogen to carbon (H/C) ratio of the OM increases. Nearly all OM may be classified into two major types, sapropelic and humic (Potonie, 1908). The term *sapropelic* refers to the decomposition and polymerization products of lipid-rich organic materials such as spores and planktonic algae deposited in sub-aquatic muds (marine or lacustrine), usually under oxygen restricted conditions. Sapropelic OM, like resins and waxes, shows high atomic H/C ratios in the 1.3–2.0 range. *Humic* usually refers to products of peat formation, mainly to land plant material deposited in swamps in the presence of oxygen. The organic matter in sedimentary rocks was first classified by coal petrologists. Stach et al. (1982) provide details on the classification of organic matter, H/C ratios, and a description of the origin and deposition of both sapropelic and humic materials.

7.3. Maturation of organic matter

D. W. van Krevelen (1961) published a simple and rapid method for following the chemical processes that occur during coal maturation (coalification). He plotted the atomic H/C versus O/C ratios as shown in Fig. 3a. This plot had the advantage of showing both the quality of OM (high atomic H/C compared to low H/C) as well as the pathway that would be followed by the coals during maturation. Tissot et al. (1974) plotted the atomic H/C to O/C ratios for a whole series of sedimentary rocks of different ages, and classified their kerogen into three distinct types. The popularity of this chart soon led to identification of four types (I, II, III, IV), as shown in Fig. 3. The charts were also modified to accommodate increasing information obtained from other sedimentary rocks over the years. With time and increasing thermal stress, all the samples shown in Fig. 3a gradually move toward the lower left corner of the chart, which represents pure carbon.

Although the van Krevelen diagram is still widely used today, it takes time to construct because the kerogen has to be isolated from each sample and analyzed for carbon, hydrogen, and oxygen. Espitalié et al. (1977) developed the hydrogen and the oxygen indices through simple pyrolysis of sediment samples. These indices are proxies for the atomic ratios (Fig. 3b) and can be used to "mimic" the van Krevelen diagram. The indices have the added advantage of being obtained in about 20 min per sample, compared to hours for the ratios used in van Krevelen diagrams. Espitalie's research led to the commercial development of the Rock-Eval pyrolyzer which enabled geologists to obtain data on the quantity, quality and maturation state of the kerogen at the wellsite while drilling.

Meanwhile, organic petrographers had developed a series of maturation indicators, the most reliable of which is vitrinite reflectance. The use of vitrinite reflectance as a technique for determining the maturity of oil in sedimentary rocks was first described by Teichmuller (1958). She had observed the same relationships between coal rank and oil as described by White (1915) in his carbon ratio theory. Teichmuller had been using the reflectance of vitrinite, a maceral of coal, to measure coal rank. It occurred to her that in sediments where coals were not readily available, as in northwest Germany, it should be possible to measure the reflectance of the small vitrinite inclusions that occur in many of the carbonates and shales. She used this technique to classify petroleum regions that did not possess deposits of coal. Today vitrinite reflectance is a widely used indicator of thermal stress because it extends over a longer maturity range than any other indicator, and a skilled organic petrologist can make a large number of analyses in a relatively short time.

By the 1970s, most petroleum geochemists had agreed that the origin and maturation of petroleum occurs in three stages: diagenesis, catagenesis, and metagenesis (Hunt, 1979). Diagenesis represents the stage of the accumulation of hydrocarbons from organisms and bacterial activity during low temperature chemical reactions on OM, leading to an increase in H/C ratios. Diagenesis ends at about 50 °C when lithification of the rock matrix begins. Catagenesis is the stage where bitumen forms from kerogen and petroleum forms from bitumen. By this stage the rocks are well lithified, and oil and gas are being generated. Metagenesis starts around 200 °C, and pyrobitumens and increasing quantities of gas are formed; oil that is present at this stage is altered and ultimately converted to gas or carbon.

An early indicator of organic maturation was observed by Bray and Evans (1961), who discovered that the odd/even carbon number periodicity of *n*-paraffin chains decreases with increasing depth of burial. Their discovery led to a maturation index, called the carbon preference index (CPI) which has been widely used. Fig. 9 shows approximate relationships among maturity parameters.

8. Oil–oil and oil–source correlations

Prior to the development of GCMS and the biomarker concept, virtually all correlations were based simply on geological inference with little or no geochemical data (e.g. Barbat, 1967). Hunt et al. (1954) carried out oil–source correlations on commercial liquid and solid oil deposits from the Uinta Basin using infrared spectrometry, refractive indices, solvent extractable organic matter, compound class distributions, and elemental analyses. Application of these techniques showed that these deposits are related to adjacent lacustrine source beds.

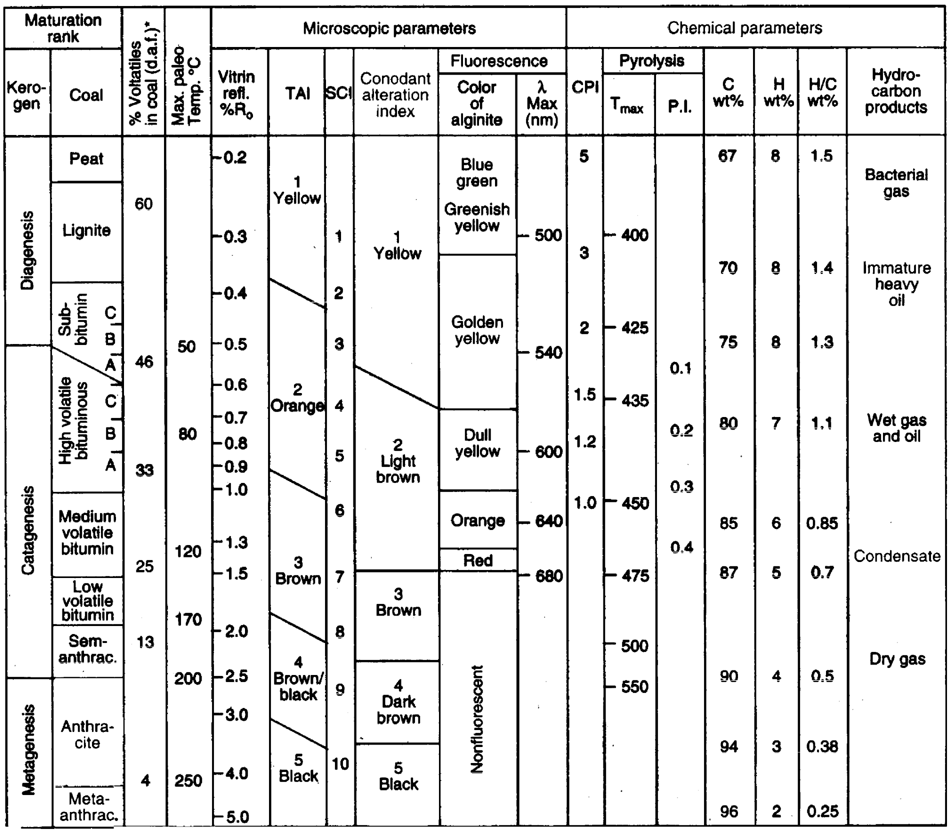
In the late 1960s and early 1970s geochemists began to utilize (a) *n*-alkane distributions, determined initially by MS, then GC, and later (b) biomarker distributions as determined by GCMS, for exploration purposes. Prior to the availability of data systems, biomarker profiles were printed on light sensitive UV paper and produced poor quality chromatograms compared to today's standards (Fig. 10a). The development of data systems for use with GCMS provided a major step forward, as can be seen in Fig. 10b illustrating a typical early example of an oil–source rock correlation on the basis of biomarker distributions. The development and commercial availability of GCMS instruments quickly led to the routine use of this approach to undertake oil/source rock correlations (Seifert and Moldowan, 1978; Barker, 1981). Curiale (1993) pointed out the importance of the development of GCMS in that it permitted detailed molecular correlations to be made between both light (Young and McIver, 1977) and heavy hydrocarbons (Welte et al., 1975; Seifert, 1977; Leythauser et al., 1977). Seifert (1977) introduced the concept of molecular correlation involving kerogen pyrolysates and crude oils, successfully showing that the insoluble fraction of the source organic matter could be used as a matching parameter. The first integrated correlation work, combining both geochemical data and the geological framework, was by Williams (1974) and Dow (1974) in their studies of the Williston Basin.

The discovery of biomarkers in crude oils and source rock extracts led to the idea that if these complex component mixtures were present in each sample, they could be used as fingerprints for correlation purposes. In other words, if two oils were derived from the same source rock at similar maturities, they should have similar distributions of biomarkers. The complexity of the biomarkers enhanced their utility. If the oils and the source rock extracts contained only one compound, there could be little confidence in the correlation. However, if the fingerprints had similar distributions of 30 or 40 compounds in different classes, a higher level of confidence could be assigned to the correlations. A similar approach was used to examine correlations between source rocks and crude oils.

Correlations were originally based upon bulk parameters, including properties such as API gravity or possibly color. When GC was developed and used routinely for monitoring the distribution of *n*-alkanes in crude oils and source rock extracts, more specific modes of correlations became available. In parallel with the development of GCMS came the biomarker revolution. Although the initial attempts and outputs were rather crude, as time progressed, computerized data systems led to higher sensitivity. As the general knowledge of biomarkers increased, the quality and accuracy of the correlation greatly improved. Stable isotopes were also widely used as correlation tools in the 1960s and 1970s (Silverman and Epstein, 1958; Fuex, 1977), and the combination of biomarkers and stable isotopes provide a powerful tool in petroleum geochemistry.

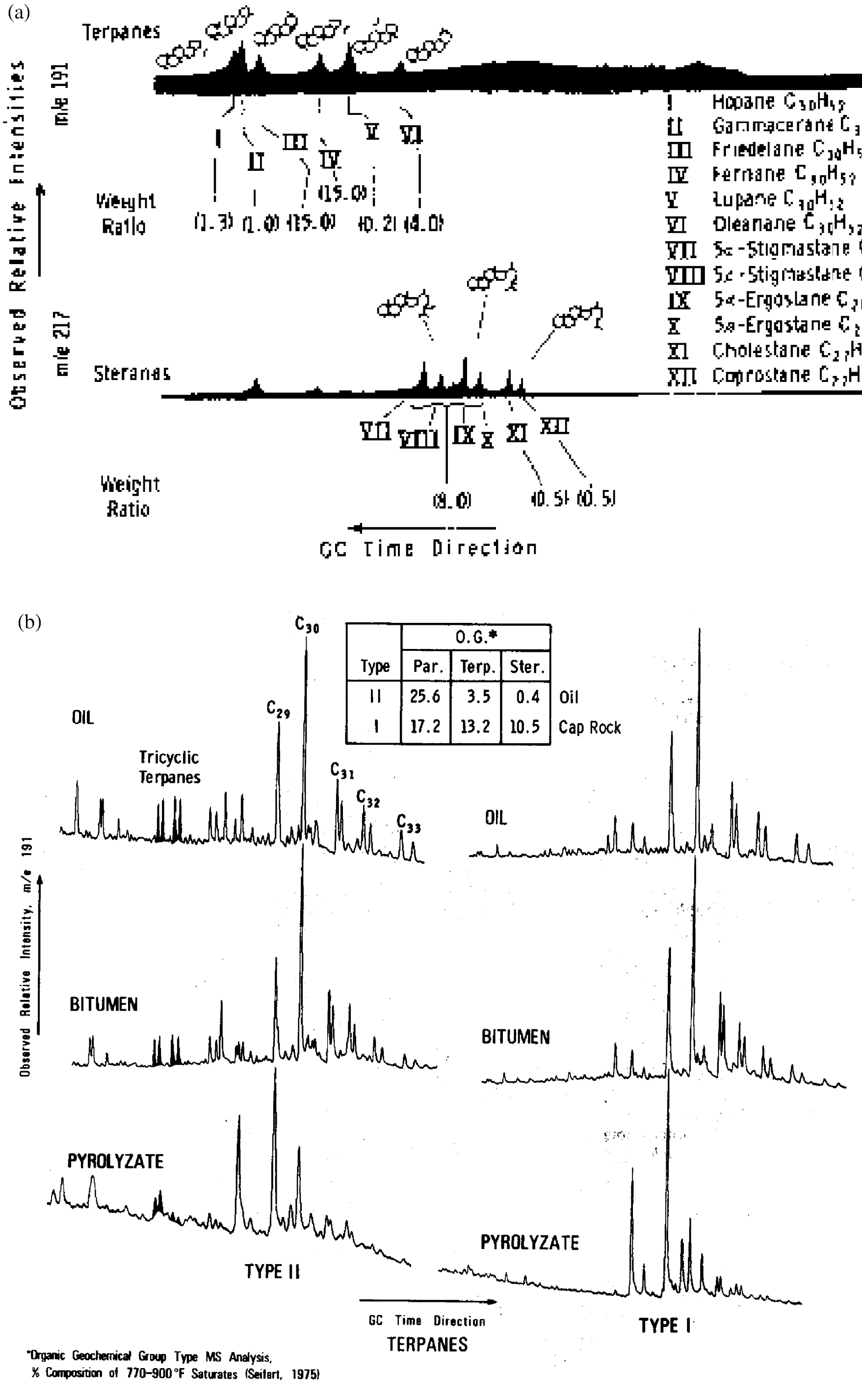
9. Geochemistry applied to migration and accumulation of petroleum

Petroleum migration has been classified as primary and secondary (Illing, 1933). The former is movement of oil and gas within and out of non-reservoir source rocks into permeable rocks, whereas secondary migration is the movement within permeable carrier and reservoir rocks leading to petroleum accumulations. Today the process is recognized as being more complex, because there is extensive movement through fractured source rocks which may act as both source and reservoir.



*Dry ash free

Fig. 9. A wide variety of maturation parameters for both source rocks and crude oils has been developed over the years. This chart shows a comparison of some of the more commonly used chemical and petrographic maturation parameters. R_o = reflectance with oil immersion objective; CPI = carbon preference index; PI = production index, TAI = thermal alteration index; SCI = spore coloration index. (This table was reproduced with permission from Hunt, 1996, and is actually based on data from a variety of sources including early studies by Staplin, 1969, and Teichmuller, 1974.)



Type	O.G.* Par.	O.G.* Terp.	O.G.* Ster.	
II	25.6	3.5	0.4	Oil
I	17.2	13.2	10.5	Cap Rock

*Organic Geochemical Group Type MS Analysis,
% Composition of 770–900°F Saturates (Seifert, 1975)

Fig. 10. (a) Prior to the availability of computers, chromatograms from GCMS systems were recorded on light sensitive paper. This figure illustrates early chromatograms showing sterane and terpane distributions obtained in this manner (courtesy of Chevron and also published in Seifert, 1977). (b) It was recognized that relationships between oils and suspected source rocks could be established by comparison of biomarker fingerprints. Pyrolysis of the source rock produce an additional fraction which could also be analyzed in the same manner to provide supporting evidence for the relationship between a particular oil and its source rock. The carbon numbers above the peaks in the top left chromatogram refer to the carbon numbers of the hopanes (reproduced from Seifert, 1978).

Methane is widely distributed in the subsurface because it is soluble in pore fluids and also migrates. Higher carbon number molecules are much less soluble in pore fluids, making it much less likely that these compounds migrate in solution (McAuliffe, 1966). Blount et al. (1980), McAuliffe (1966) and Zhuze et al. (1971) noted that temperature was the most important factor for increasing the solubility of lower molecular weight hydrocarbons. However, Zhuze et al. (1971) also noted that water saturated with gas would decrease solubility and cause exsolution of hydrocarbons such as benzene, toluene and methylcyclohexane. Increasing salinity and decreasing pressure and temperature would also cause a decrease in the solubility of hydrocarbons in pore waters (Price, 1976). As a result of these findings, it was recognized that solution in pore fluids was of minor importance in petroleum migration.

The two most important mechanisms of migration are gas-phase and oil-phase migration. Early studies demonstrated that subsurface gases can dissolve large amounts of liquid hydrocarbons under temperature/pressure conditions corresponding to depths of 6000–10000 ft (1830–3050 m) (Sokolov and Mirnov, 1962; Sokolov et al. 1963). Neglia (1979) had noted that the Malossa field in Italy contained a condensate with heavy liquid components dissolved in the gas phase and, using data from Rzasa and Katz (1950), showed that hydrocarbons up to C_{18} would dissolve in the gas phase under these conditions. Rumeau and Sourisse (1973) also concluded that hydrocarbons in the SW Aquitane Basin probably entered the reservoir in the gas phase, because fluid flow from compaction ceased very early in the history of the reservoir. Gas phase migration along vertical faults through Tertiary sandstones explains the presence of aromatic rich condensates in the Pleistocene of the Gulf Coast (mentioned in Hunt, 1996), Western Canada Basin (Hitchon and Gawlak, 1972), and East Turkmen (Gavrilov and Dragunskaya, 1963).

Oil generation will be followed by migration from the source rocks into the carrier beds, where the oil will migrate until it reaches an appropriate trap. During and after generation and expulsion, the oil will undergo changes, and the composition of the oil arriving in the reservoir will differ considerably from the oil originally generated in the source rock. Polar and asphaltene contents of oils that are considerably lower in concentration than those in the source rock bitumens provide evidence for the phenomenon of geochromatography, in which the more polar compounds are adsorbed by clay minerals and migrate at a much slower rates than the saturate and aromatic hydrocarbons (Hunt, 1979).

The interpretation of some early biomarker parameters changed as more information was obtained. A good example is the diasterane/sterane ratio. Originally it was thought that variations in this ratio reflected the relative amount of clay minerals in the original depositional environment, based on results from laboratory studies (Rubinstein et al., 1975). This idea was widely accepted, and many samples with a relatively high diasterane content were postulated to be derived from a depositional environment with a high clay mineral content. If the sample came from a pure carbonate environment, yet contained diasteranes, it would be interpreted that the carbonate was "dirty" and contaminated with clay minerals (Palacas et al., 1984). Moldowan et al. (1985) suggested, however, that the reason for this anomaly was more likely related to changes in oxicity of the depositional environment. In a highly reducing environment the intermediate sterenes would be rapidly hydrogenated to steranes, eliminating the possibility of diasterane formation. In a more oxic environment, the sterenes would not be hydrogenated and could therefore be preferentially converted to diasteranes. Understanding the geochemistry of biomarkers is still, in many ways, in its infancy.

10. Alteration of petroleum in the reservoir

Once oil arrives in the trap, it can be subject to a number of processes which may dramatically modify its original properties even more than did the migration processes. The major processes leading to compositional changes may result from temperature and pressure changes (in-reservoir maturation), moving water (waterwashing and biodegradation), or an influx of natural gas (deasphalting causing precipitation of solid bitumen within the reservoir). Numerous pre-1980 reviews cover this topic (Milner et al., 1977; Tissot and Welte, 1978; Hunt, 1979).

Very high molecular weight hydrocarbons in crude oils are relatively resistant to biodegradation. These compounds can be responsible for many problems occurring in reservoirs. A severely biodegraded oil may appear to have had all of its *n*-alkanes removed when characterized by conventional GC; however, Winters and Williams (1969) recognized the presence of high molecular weight waxes in certain heavily biodegraded oils, and referred to them as biowaxes. They documented for the first time the effects of biodegradation in the laboratory. Similar laboratory effects were demonstrated by Jobson et al. (1972) using a sample of Saskatchewan crude oil incubated at 30 °C with a mixed culture of bacteria. The quantities of heavy oil discovered worldwide prior to 1980 demonstrated the importance of this process as a means of altering crude oil composition (Demaison, 1977).

Major requirements for crude-oil biodegradation in a reservoir were summarized by Philippi (1977) and Connan (1984). Based on the understanding at that time, the main requirements were: (a) moving water, preferably fresh water having a high sulfate content with degradation occurring, not within the bulk oil, but at the oil/water interface; (b) a supply of nutrients (nitrates and phosphates); (c) microbes; and (d) temperatures typically below about 88 °C. The effects of biodegradation have been recognized and well-documented (Volkman et al., 1984). After initial loss of the low-molecular-weight hydrocarbons, bacteria begin to remove the *n*-alkanes, proceeding from the lower to the higher carbon numbered molecules. Once the simpler molecules have been removed, microbes proceed to the more complex molecules removing isoprenoids and then the complex polycyclic molecules. For the most part the general order of removal of these different compounds classes follows a fairly similar pathway in all oils. The pathway is frequently used to indicate the relative extent of biodegradation of crude oil. Changes in the bulk composition of crude oil, as well as in the aromatic components specifically, have been well documented by Connan (1984). Changes in composition can also lead to changes in the way oils are characterized, if the classifications of Tissot and Welte (1978) are used. Early examples of the changes to crude oils caused by biodegradation can be monitored by GCMS, as illustrated in Fig. 11.

11. Early modeling of geothermal histories

It has been recognized for some time that as organic matter is buried, thermal degradation of the kerogen occurs to yield petroleum range hydrocarbons under reducing conditions. Over the years these reactions have been demonstrated many times in the laboratory, and observed in the natural environment. Among the earliest experiments demonstrating these effects were those of Engler (1913), who heated oleic acid and other organic matter to produce a range of petroleum hydrocarbons and by Jurg and Eisma (1964) who heated behenic acid to produce hydrocarbons. Hunt (1979) described a number of additional experiments that involved heating various types of organic matter to produce petroleum hydrocarbons; it is now generally accepted that the major mechanism for the formation of most oil is the following reaction derived from these early laboratory experiments:

$$\text{Kerogen} \rightarrow \text{bitumen} \rightarrow \text{oil} + \text{gas} + \text{residue}$$

Confirmation of the above reaction was extremely important, but equally important was the need to evaluate when oil generation started, how long it lasted, and at what depth it occurred. Timing of petroleum generation is particularly important in relation to the formation of structures, stratigraphic traps, and faults which act as migration pathways. This information can be obtained by modeling the time–temperature history of the source rock.

Hilt (1873) recognized that carbonization of coal increased with time, temperature, and depth, and White (1915) subsequently noted the relationship between the occurrence of oil and gas, and the rank of coals in the eastern United States. Habicht (1964) made the first attempt to model petroleum generation. A burial history curve was constructed for a Jurassic source rock, and Arrhenius equation kinetics were used to determine the time and depth of oil generation in the Gifhorn trough of northwest Germany. Subsequently, Philippi (1965) documented the increase in the yield of hydrocarbons from source rocks with increased time and temperature in the Los Angeles and Ventura Basins of California. Later, Poulet and Roucache (1969) used a series of source rock burial history curves to describe the origin of hydrocarbons in the Northern Sahara Hassi Messoud area (Algeria). The main finding of these early studies was that temperature alone is not sufficient for the generation of hydrocarbons, but that time also needs to be taken into account. In other words, rapid burial with high geothermal gradients does not result in the same level of maturation as does slow burial with low geothermal gradients.

The first mathematical model, using the Arrenhius kinetic theory and a source rock burial curve, was published by Tissot (1969). At the time these studies were taking place, Teichmuller (1958) demonstrated for the first time the relationship between vitrinite reflectance and the occurrence of oil. The reflectance of vitrinite increases exponentially with a linear increase in temperature, and generally plots as a straight line on a semilog plot (Dow, 1977). Hood et al. (1975) developed a simplified method of predicting oil generation from a source rock by combining maximum temperature and effective heating time. The latter was defined as the time during which a specific rock has been within 15 °C of its maximum temperature, which is where most of the generation occurs. This level of organic maturation (LOM) was correlated with vitrinite reflectance.

Larskaya and Zhabreb (1964) were the first to demonstrate that generation of oil from kerogen of shales increases exponentially with temperature. This intense generation zone was called by Vassoevich et al. (1969) "the principal phase of oil formation." Connan (1974) called it "the threshold of intense oil generation" (Fig. 12), and he developed a method of using these depth–yield data in a practical manner by constructing a time–temperature Arrhenius plot to define the threshold of intense generation for several sedimentary basins (Fig. 13).

Lopatin (1971) developed a model, based on the empirical relationship between vitrinite reflectance and petroleum formation, which was simpler than the model proposed earlier by Tissot (1969) for using time and temperature to calculate the thermal maturity of organic matter in sediments. Lopatin (1971) also developed the

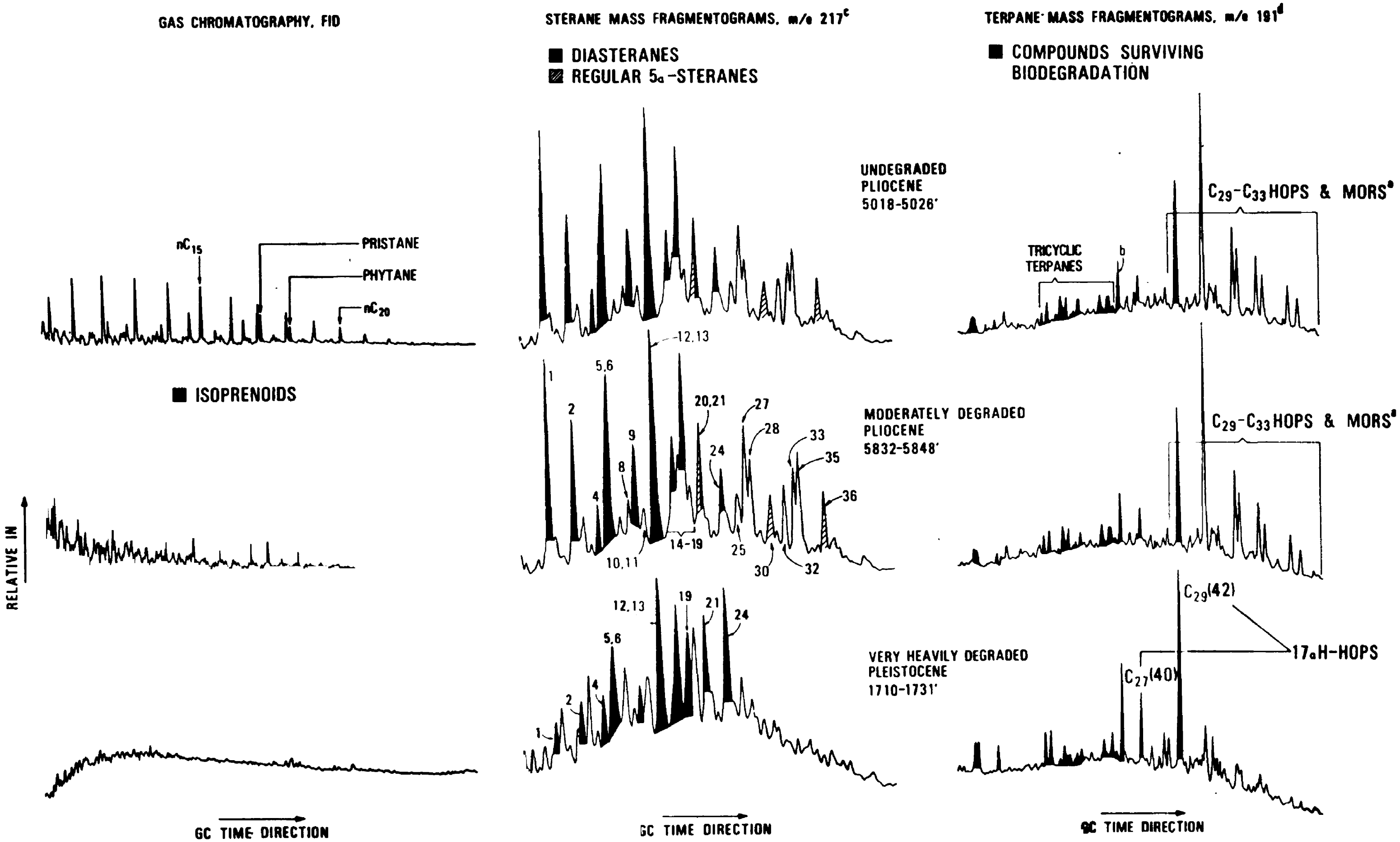


Fig. 11. Early examples of GCMS data used to study progressive effects of biodegradation of crude oils and selective removal of various biomarkers. The chromatograms on the left hand side indicate progressive changes in the level of biodegradation. Corresponding changes were noted in the biomarker distributions. The numbers on the sterane peaks are shown here for illustration only, but are identified in Table 4 on p. 116 of the original paper (reproduced with permission from Seifert and Moldowan, 1979).

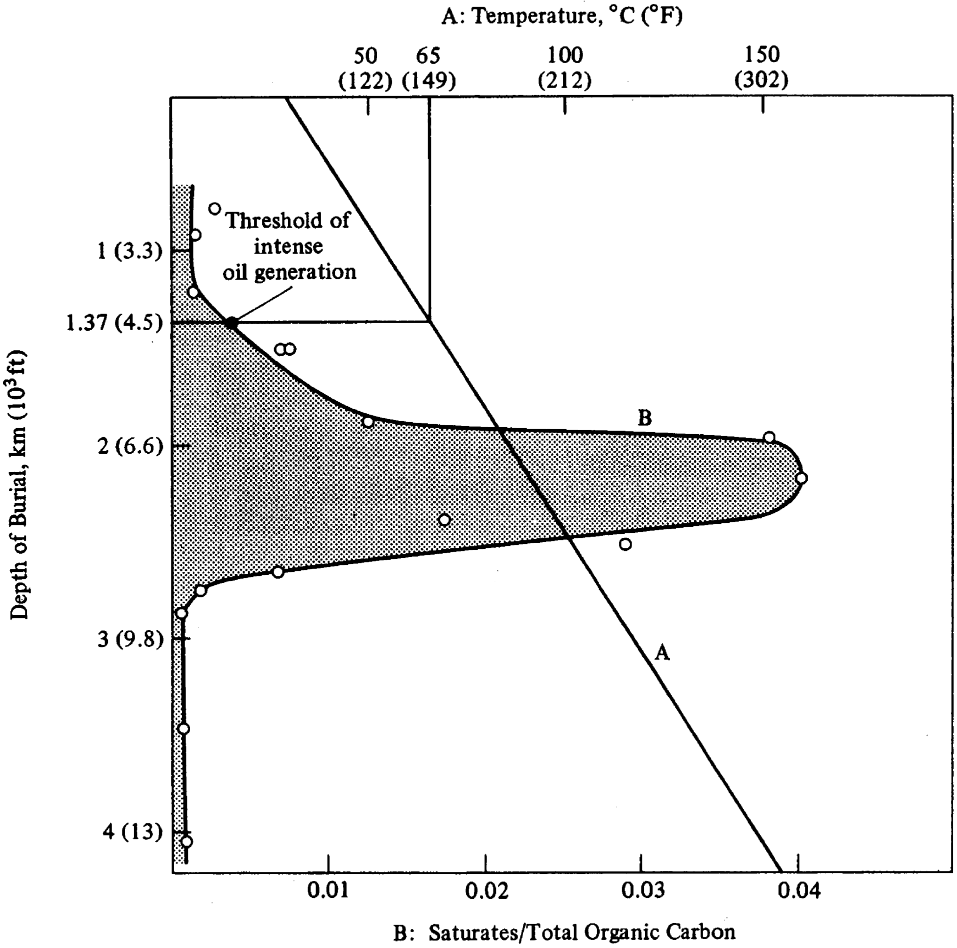


Fig. 12. The roles of temperature and depth of burial were recognized as important factors in the generation of crude oils. Vassoevich et al. (1969) initially described the principal phase of oil generation and Connan (1974) first introduced the term "threshold of intense oil generation" illustrated in this diagram for the Douala Basin, Cameroon (reproduced with permission from Hunt, 1979).

time temperature index (TTI), a measure of the total thermal exposure of a source rock after it was deposited (Waples, 1985). This measure was based on the old chemical rule that reaction rates double for each 10 °C rise in temperature (Bergius, 1913). However, subsequent applications found that the Lopatin method tended to underestimate maturity at higher heating rates. This observation led to the development of models that combined the Lopatin approach with Arrenhius kinetics. Because these developments took place after 1980, they are not discussed here. The important point is that these pioneering modeling methods ultimately gave rise to very sophisticated models which, when combined with data on evolution of migration pathways, traps, and structures, permitted a better evaluation of the risk in prospecting for economic hydrocarbon accumulations.

12. Summary of early developments

Petroleum geochemistry has come a long way since 1860. Many of the most significant advances have developed in parallel with the evolution of sophisticated analytical techniques. Other major advances have resulted from the close liaison between exploration geologists and petroleum geochemists. Petroleum geochemistry is now a routine part of virtually all exploration efforts by major and smaller companies, although it is disappointing that there is not more emphasis on petroleum geochemistry in the academic curriculum of earth sciences.

The past 60 or 70 years have seen advances from characterizing oils on the basis of bulk properties such as API gravity or optical rotation, to extremely detailed characterization of crude oils at the molecular level. The

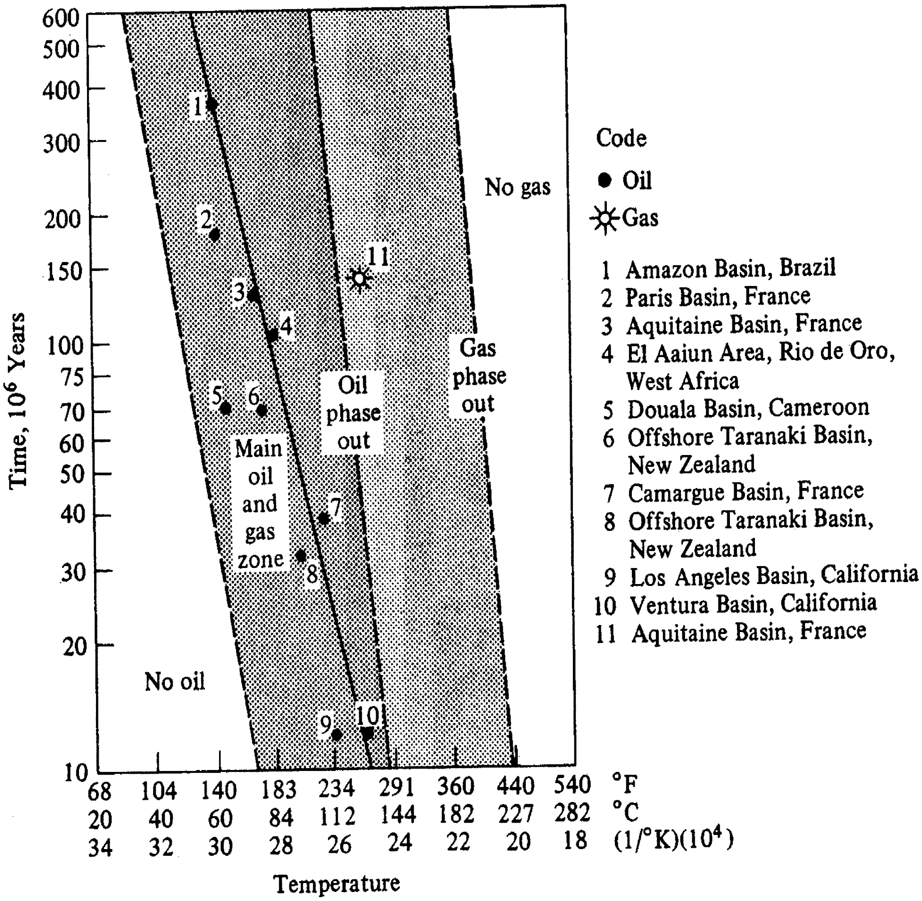


Fig. 13. Time–temperature of petroleum genesis used to evaluate drilling prospects. The prospective areas for oil are within well-defined time-temperature limits as shown by the dark shading. Prospectivity will vary with geothermal gradient and rate of deposition of organic matter (reproduced with permission from Hunt, 1979).

field has gone from the recognition of the significance of the odd/even periodicity of *n*-alkanes in recent sediments to the identification of specific compounds used to predict the source, depositional environment, and in some cases the age of the oil's source rock. Ideas have evolved from the possibility of oil being generated from recent organic material as it is deposited in aquatic environments, to a detailed understanding of the thermal reactions necessary to generate hydrocarbons via kerogen buried deeply within a basin.

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