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Some Geochemical Aspects of Petroleum Genesis

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Abstract

Confirmation of the theory of an organic origin of petroleum is given by the analysis of the hydrocarbon constituents which can be demonstrated to have a structure similar to compounds produced by modern organisms. These hydrocarbons are formed at depth, under the influence of an increase in temperature from the lipid components of dead organisms, although it is not yet clear whether the hydrocarbons are formed directly from the lipids or via the intermediate formation as asphaltic and kerogenous materials. Source material for petroleum has, traditionally, been regarded as of marine origin, but there is increasing evidence that terrestial organic material may play a significant role in petroleum genesis. Migration is perhaps the least understood aspect of the processes leading to petroleum accumulation~~s~~. The most realistic explanation so far proposed requires the migration of petroleum, as a colloidal form, in waters released from shal~~y~~ey sediments during diagenesis.

SOME GEOCHEMICAL ASPECTS OF PETROLEUM GENESIS

INTRODUCTION

Despite the importance of petroleum in the economy of modern society the origin and formation of petroleum in the earth has, until recently, been largely a matter for conjecture. Over the years, a great deal of information has accumulated on the composition of petroleum, largely as a result of the investigations sponsored by the American Petroleum Institute; these include API Research Projects 6, 48 and 52, concerned with the hydrocarbon, sulphur and nitrogen components of petroleum respectively. However, it is only recently, with the advent of modern analytical techniques, that analyses of the organic residues in rocks have been possible and have led to the formation of tentative theories of petroleum genesis.

Crude oil has been defined as a naturally occurring complex mixture of hydrocarbons containing small amounts of oxygen-, sulphur- and nitrogen-bearing compounds and some metallic constituents, particularly vanadium, nickel, iron and copper. The relative proportions of these chemical types may vary considerably from one crude oil to another. Thus the purely hydrocarbon content may be as high as 98% for some petroleums, but as low as 50% in others. The non-hydrocarbons are essentially hydrocarbon in character since they contain only one or two atoms of elements other than carbon and hydrogen.

Over 250 hydrocarbons are known to occur in various crude oils (WHITHEAD and BREGER 1963, MAIR 1964, BESTOUGEFF 1967), ranging in carbon number up to C_{36} and beyond, but in general at least 50% of petroleum is made up of hydrocarbons in which the number of carbon atoms falls in the range C_3 - C_{14}. The distribution of hydrocarbon classes in a medium crude oil is illustrated in Fig. 1 (after Bestougeff).

In any consideration of the origin of petroleum we must allow for the accumulation of locally important concentrations of organic materials of which the greater part is made up of hydrocarbons of low molecular weight. This problem may conveniently be resolved into three parts; the chemical origin of petroleum hydrocarbons, the recognition of source material and the migration and accumulation of petroleum.

CHEMICAL ORIGIN OF PETROLEUM HYDROCARBONS

An organic origin for petroleum. On the basis of the chemical and geological evidence currently to hand there can be little doubt that petroleum has a biogenic origin. Geologically, the evidence in favour of an organic origin for petroleum is based on the association of petroleum pools and organic residues with sedimentary sequences and their particular association with sediments in which biological remains abound. In contrast, igneous and metmorphic rocks have only rarely yielded petroleum and frequently in those exceptional cases the petroleum has been shown to have migrated into these rocks. Chemical evidence for an

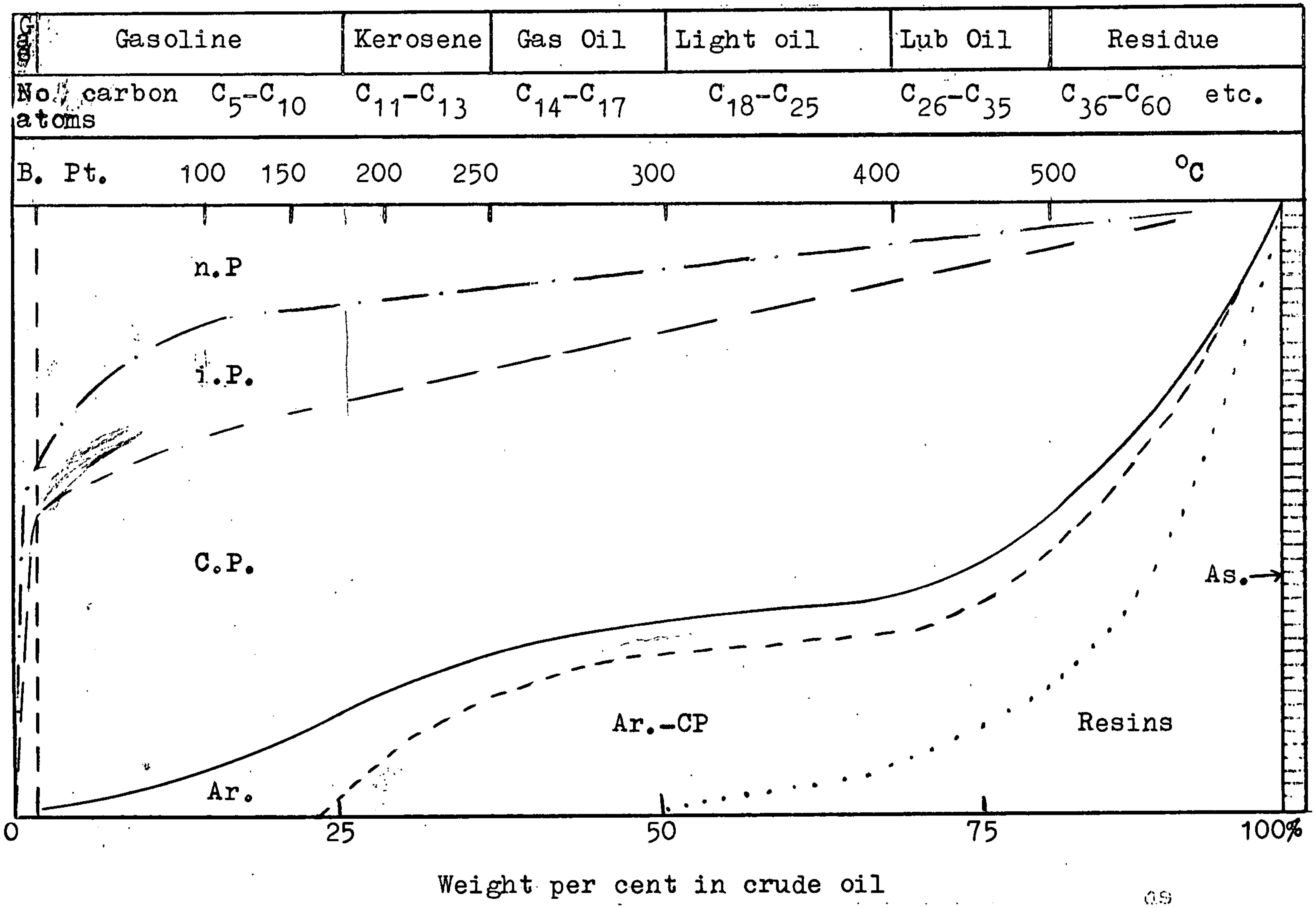


Fig. 1. Distribution of hydrocarbon classes in a medium-crude oil. n.P. = normal paraffins; i.P. =isoparaffins; C.P.=cycloparaffins; Ar.=aromatics; Ar.-CP=naphtheno-aromatics; Resins = heterocyclic compounds; As.=asphaltenes. (after BESTOUGEFF 1967)

organic origin of petroleum with the components of modern organisms and can be summarised as follows:-

1. The occurrence in both petroleums and sediments of polyisoprenoid hydrocarbons e.g. phytane, pristane, steranes and triterpanes (Fig. 2) which have carbon skeletons characteristic of a biological origin (DEAN and WHITHEAD 1961, BENDORATIS _et al_ 1962, CUMMINS and ROBINSON 1964, HILLS _et al_ 1966, 1970, MURPHY _et al_ 1967, DANIELI _et al_ 1968, HENDERSON _et al_ 1968, 1969).

2. The presence in petroleums of porphyrins related to the chlorophyll and hemin of modern organisms (TREIBS 1936, HODGSON _et al_ 1967).

3. The optical rotary capability of petroleum which is generally confined to compounds of biogenic origin (HULME 1938, MAIR _et al_ 1938, ROSENFELD 1967).

4. The similarity of the carbon isotope ratios of modern organisms to petroleums and the marked difference of these ratios to those of inorganic minerals, (PARK and EPSTEIN 1960, 1961, SILVERMAN 1967).

5. The occurrence in some petroleums of _n_-alkane distributions in which the carbon preference index (CPI, defined as the ratio of odd to even carbon numbered _n_-paraffins) is greater than unity, similar to the distribution found in many modern organisms (MARTIN _et al_ 1963).

However, the complexity of composition of the hydrocarbons occurring in the gasoline range has led some authors to suggest an abiotic origin for this fraction. Thus, FRIEDEL and SHARKEY (1963) have compared the distribution of low molecular weight hydrocarbons (range up to C_8) in petroleum with that obtained from the Fischer Tropsch process. Similarly, ROBINSON (1963) has suggested an abiogenic origin for these lower molecular weight hydrocarbons. However, it is difficult to envisage how such hydrocarbons, which must be generated at depth below the normal expected level of hydrocarbon production, become mixed with hydrocarbons generated from a biogenic source. Degasification of the interior of the earth is perhaps a means by which this might be achieved (RUDAKOV 1967), but there is very little evidence to suggest that this might have taken place.

Alteration of biological debris. Although petroleum is considered to have a biogenic origin it is evident that the biological remains must have undergone considerable alteration to yield the various hydrocarbons that constitute petroleum. Thus the hydrocarbons of low molecular weight which form such a large part of petroleum, can only be found as traces in recent sediments and are not produced in modern organisms. The conclusion must be that hydrocarbons in the range C_3 to C_8 must have been formed at some time after the burial of the sediments (HUNT 1962). In addition, the normal paraffins of crude oils and ancient sediments are evenly distributed between odd and even carbon numbered chains, whereas in recent muds there is a predominance of odd over even carbon numbered paraffins (SMITH 1954, STEVENS _et al_ 1956, MEINSCHEIN and KENNY 1957, BRAY and EVANS 1961, KVENVOLDEN 1966, CLARKE and BLUMER 1967). HENDERSON (1968) has summarised the evidence which indicates that biological debris, as it is laid down in sediments, undergoes considerable alteration during the course of geological time:-

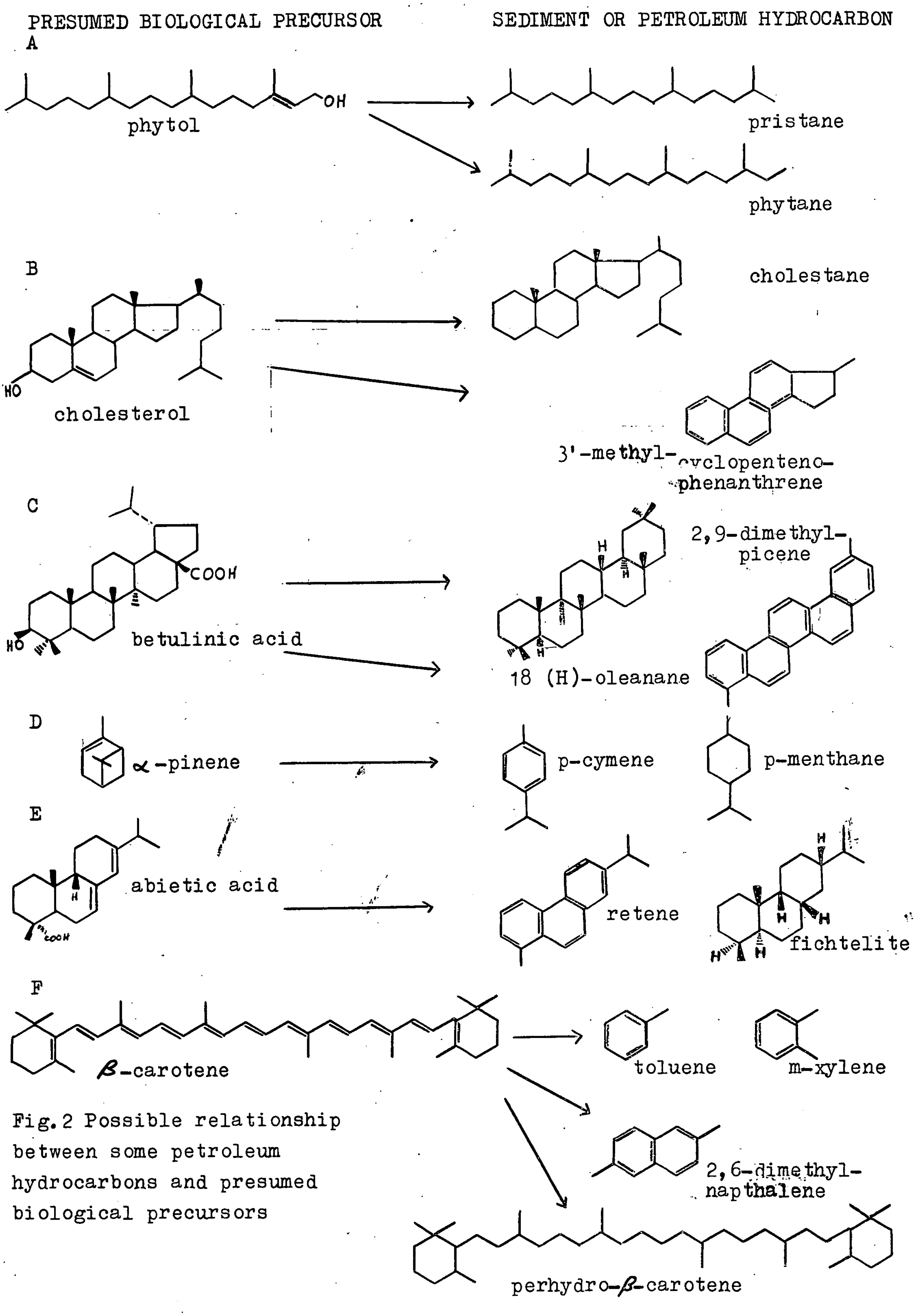


Fig. 2 Possible relationship between some petroleum hydrocarbons and presumed biological precursors

1. The presence of low molecular weight hydrocarbons in the range C_3 to C_8 in ancient sediments and petroleums which are usually absent in recent sediments (EMERY and HOGGAN 1958, DUNTON and HUNT 1962).

2. The decrease in the ratio of odd to even carbon numbered n-alkanes in petroleums and sediments with increasing age (BRAY and EVANS 1961).

3. The overall increase in the concentration of alkanes in sediments with increasing age (HUNT 1961, BRAY and EVANS 1961).

4. There are less fatty acids in sediments than would be expected from their abundance in nature (PARKER 1967).

5. Unsaturated fatty acids are not found in sediments, but are abundant in modern organisms (PARKER and LEO 1965).

6. The differences in the ratio of even to odd n-fatty acids between modern and ancient sediments and petroleums (COOPER 1962, KVENVOLDEN 1966).

7. The increase in the amount of branched fatty acids and branched alkanes in sediments with increasing geological age (PARKER 1967, HUNT 1961)

8. The decrease in optical activity exhibited by petroleums with increasing age (ROSENFELD 1967).

Thermal alteration of organic materials. Early work by ZOBELL et al (1945, 1947) concentrated on the possibility of bacteria being able to convert organic matter into hydrocarbons or to cause concentration of hydrocarbons indigenous to organisms, in sufficient quantities to form petroleum. The effect of radiation on complex organic materials was examined by WHITHEAD et al (1951, 1954). In both cases the proposed mechanisms were concluded to be quantitatively inadequate to explain the origin of commercial amounts of crude oils in known reservoirs, though radiation may alter the character of a crude oil at some stage during its history (COLOMBO et al 1964) and the activities of bacteria may lead to some modifications in crude oil composition. (WINTERS and WINTERS 1969).

The physical agency by which biological material is converted to petroleum-like materials appears to be heating associated with burial of the sediments. PHILIPPI (1965) and LOUIS and TISSOT (1967) have related the production of alkanes to an increase in temperature with burial of the sediments. There is an increase in gross hydrocarbon content, loss of odd to even predominance in the n-alkane range C_{25} - C_{35} and an increase in the ratio of hydrocarbons to total organic carbon with depth. Philippi examined two sequences in the Los Angeles and Ventura Basins and found that oil was being formed at different depths in the two basins, which he attributed to the differing geothermal gradients in the two basins. ALBRECHT and OURISSON (1969) have reported similar changes associated with burial of the sediments in the Douala Basin, Cameroons, but in this case, with increasing depth, the hydrocarbon content reaches a maximum and then diminishes. They attribute this to catalytic cracking and migration of the hydrocarbons. In addition to a change in the distribution of n-alkanes they observed an increase in the proportion of non-isoprenoid branched hydrocarbons.

They suggest that these changes are also a result of the effects of thermal alteration. ROBINSON et al (1965) have demonstrated a decrease in CPI n-alkane values with depth in the Green River Shale Formation and associated it with an increase in temperature. Changes, similar to those recorded by Albrecht and Ourisson were observed in the branched and cyclic alkane fraction of the Green River Shale. BROOKS and SMITH (1967) have demonstrated a decrease in the CPI n-alkane values of coal with increase in rank, which is thought to be predominantly a temperature controlled process (TEICHMULLER and TEICHMULLER 1968).

Experimental evidence for the generation of hydrocarbons by the action of heat on sediments has been obtained by several workers. Thermal alteration experiments have been carried out on recent sediments (MITTERER and HOERING 1967), an Eocene sediment (DOUGLAS et al 1966) and its associated kerogen (HOERING and ABELSON 1963), coal (BROOKS et al 1969a and b), a fatty acid (JURG and EISMA 1964, 1967) and a normal alkane (HENDERSON et al 1968). The general conclusion is that hydrocarbons can be readily generated from the organic material in sediments at geologically viable temperatures.

Catalysis has been long regarded as having an important role in petroleum genesis (BROOKS 1948, 1949, 1952, 1959) and recently certain reactions postulated to occur in petroleum formation have been found to occur more readily in the presence of clay minerals. Thus JURG and EISMA (1964, 1967) have demonstrated that decarboxylation of fatty acids occurs more readily in the presence of clay minerals and BROOKS and SMITH (1969b) have shown that the insoluble portion of coal is an effective decarboxylation catalyst. GALWEY (1969) has suggested that heterogeneous catalysis may play an important part in petroleum formation and has presented data for the conversion of alcohols to hydrocarbons as an example. HENDERSON et al (1968) have stressed the importance of catalysis in the cracking of alkanes under geological conditions, but since olefins are not significant constituents of petroleum a source of hydrogen is required to convert the olefins to paraffins if this process is to be a significant one in petroleum genesis.

Precursors for petroleum hydrocarbons. Although the general principle of hydrocarbon formation, through the alteration of biological debris, is now widely accepted, the precursors and precise mechanism by which these changes have taken place is a matter of controversy. Quite apart from the contribution made by naturally occurring alkanes, various lipids have been proposed as possible precursors of the hydrocarbons found in sediments and petroleum. The processes involving the increase with time of even carbon-numbered n-alkanes and odd carbon-numbered fatty acids have been thought to be related. COOPER and BRAY (1963) postulated a role for fatty acids in petroleum generation in which each acid lost carbon dioxide to form intermediates which reacted to give n-alkanes and n-fatty acids both having one carbon less than the parent acid. LAWLOR and ROBINSON (1965) and KVENVOLDEN (1966) have shown a parallelism of distribution of normal fatty acids and normal alkanes of one carbon or less, in the Green River Shale and in some Mowry and Thermopolis Shales respectively. They proposed a genetic relationship between the n-alkane and fatty acid distributions invoking the scheme of Cooper and Bray as a possible explanation of their findings.

However in the case of the Green River Shale there appears to be no relationship between the isoprenoid fatty acids and isoprenoid alkanes (EGLINTON et al 1966) Phytanic acid (C_{20}) is the predominant isoprenoid acid and if there were any genetic relationship between the acids and the alkanes one would expect pristane (C_{19}) to be the dominant isoprenoid alkane and not phytane as is found.

MARTIN et al (1963) found a predominance of odd carbon numbered n-alkanes in specific molecular weight ranges in some Palaeozoic and Tertiary crude oils: thus n-alkanes with 11, 13, 15, 17 and 19 carbon atoms were slightly more abundant than the even carbon numbered neighbours in the Palaezoic oils. Fatty acids in fats are most commonly C_{12}, C_{14}, C_{16}, C_{18} and C_{20} and these fatty acids were suggested as precursors for the odd carbon-numbered alkanes. Uinta Basin oils, of Tertiary age, contain n-alkanes with a predominance of odd-carbon-numbered members in the range C_{23} - C_{33} and Martin et al suggested that the fatty acids of waxes may be precursors of these n-alkanes. The generation of n-alkanes from esters has recently been demonstrated to take place in coals by BROOKS and SMITH (1969b). Experimental work showed that n-alkanes were formed in coal with increasing rank from the ester waxes which form part of the plant cuticles incorporated into the coal. The alcohol moeities of these ester waxes yielded even numbered n-alkanes, apparently via intermediate formation of olefins, but the acid fragments gave odd numbered alkanes by decarboxylation.

Experimental evidence for the formation of alkanes from fatty acids by decarboxylation has been obtained by JURG and EISMA (1964, 1967). They found that n-fatty acids can be decarboxylated under the influence of heat to give n-alkanes with one carbon less than the original acid and, in addition, hydrocarbons and fatty acids of both shorter and longer chain lengths than the original acid are formed. However, decarboxylation may not be the sole process for the generation of alkanes from fatty acids. Thus BLUMER (1965) found that decarboxylation of modern pigments could not always account for the molecular structure of fossil porphyrins and suggested that reduction of carboxyl groups to methyl groups must have occurred. Recently WELTE and EBHARDT (1968) have reported a parallel distribution between the n-alkanes and n-fatty acids in the range C_{14} - C_{22} from recent sediments in the Persian Gulf, indicating that these may have been formed by reduction of the corresponding acids.

Although pristane and phytane are relatively minor constituents of petroleum they are relatively major constituents of the saturated hydrocarbon fractions obtained from rocks and their origin has been extensively discussed. It is widely held that the pristane and phytane found in sediments and petroleum could be derived from the phytol side chain of chlorophyll (Fig. 2A) (BENDORATIS et al 1962, EGLINTON and CALVIN 1967). Pristane could be formed by decarboxylation of phytanic acid, derived from phytol by oxidation, whilst phytane could be formed from phytol either by dehydration and hydrogenation or reduction of the hydroxyl group. The occurrence of C_{19} and C_{20} isoprenoid compounds in zooplankton (BLUMER et al 1963) and bacteria (KATES et al 1965) suggests an alternative source for the pristane and phytane occurring in petroleum and sediments (EGLINTON and CALVIN 1967). The presence of higher molecular weight isoprenoid hydrocarbons (C_{22} - C_{25}) and acids in crude oil and sediments respectively requires parent isoprenoid compounds with more than twenty carbon atoms (HAN and CALVIN 1969, DOUGLAS et al

1966, BURLINGAME et al 1969). Possible precursors have been listed by DOUGLAS et al (1966) and HAN and CALVIN (1969) and include isoprenyl alcohols, e.g. solanosol (C_{45}), squalene (C_{30}) and lycopene (C_{40}). Farnesol (C_{15}), the esterifying isoprenoid alcohol in certain bacteriochlorophylls, has been suggested as an alternative source of the farnesane found in sediments (DOUGLAS et al 1966).

The cyclic alkanes and aromatic compounds form a large portion of petroleum and it is generally considered that terpenoids are probably the precursors for the simple saturated and aromatic consitiuents (MAIR 1964b, ERDMAN 1967). DOUGLAS and MAIR (1965) have shown that sulphur can react with terpenoids and steroids at relatively low temperatures to give aromatic hydrocarbons. HILLS et al (1970) have suggested that cholesterol might undergo isomerisation and disproportion reactions to form cholestane and an aromatic equivalent (Fig. 2B). Similar processes have been observed at different stages during the fossilisation of pine stumps. The principal component of turpentine, α-pinene, changes in a gradual way to give an aromatic hydrocarbon, p-cymeme, and a cycloparaffin, p-menthane, by isomerisation and disproportionation reactions (SKRIGAN 1951) (Fig. 2D). When resin acids become fossilised they can lose their acid moiety and the resulting hydrocarbon may later be subjected to changes analagous to those mentioned for pinene. Thus acids of the abietane type have been shown to form both retene and fichtelite (SKRIGAN 1963) (Fig. 2E).

BREGER (1960) suggested that simple aromatic compounds, such as toluene and 2, 6, dimethylnaphalene could be formed by thermal degradation of B-carotene (Fig. 2F). Thermal degradation experiments of carotenoids in aqueous systems have substantiated this suggestion (MULLIK and ERDMAN 1963, ERDMAN 1967). ERDMAN (1967) has discussed the possible means of formation of the C_1 - C_{10} hydrocarbons in petroleum and natural gas. The type of reactions for the genesis of methane and lower compounds include aromatisation of unsaturated compounds, such as terpenoids and steroids, the decarboxylation and deamination of amino acids, reduction of alcohols, decarboxylation of low molecular weight acids, maturation of heavy fractions of crude oils and cracking of paraffins.

Kerogen as a source of petroleum hydrocarbons. Kerogen is the term used to describe the insoluble organic material found in sediments. The mode of formation of kerogen and the heavier asphaltic materials in sediments is unknown, but it is thought that they are formed as a result of the 'polymerisation' of the labile constituents of the biological remains.

Kerogen has been variously suggested as a presursor for petroleum hydrocarbons and in particular the lighter hydrocarbons. Thermal alteration experiments performed on kerogen and sediments have yielded hydrocarbons far in excess of the indigenous alkanes (HUNT 1962, HOERING and ABELSON 1963, DOUGLAS et al 1966, MITTERER and HOERING 1967, LOUIS and TISSOT 1967, McIVER 1967) suggesting that alkanes could be generated at depth at relatively low temperatures.

Experimental evidence for the suggestion that asphaltenes are an intermediary product in the formation of hydrocarbons from kerogen has been obtained by LOUIS and TISSOT (1967). They carried out a series of thermal alteration experiments on unaltered samples of Toarcien Shale from the Paris Basin at 180°C for periods up to a year.

Samples were analysed at regular intervals and showed that heavy asphaltenes increased in concentration to a maximum and then decreased in concentration with time. Corresponding with the decrease in asphaltene content the hydrocarbon content increased, suggesting that the asphaltenes are an intermediary product in the formation of hydrocarbons from kerogen. Additional evidence is provided by the work of SILVERMAN (1964). He determined the $^{13}C/^{12}C$ ratio of the distillation fractions of a crude oil from the Murphy Coyote field in California. The isotope ratio was lowest for methane and highest for the fraction with a boiling point of around 230°F. Silverman has explained this difference in isotope distribution by assuming that in the maturation of petroleum the lower molecular weight hydrocarbons were formed by decomposition of higher molecular weight components. The lighter components are enriched in ^{12}C since thermal decomposition experiments have indicated that the $^{12}C - {}^{12}C$ bonds are ruptured about 8% more frequently than $^{13}C - {}^{12}C$ bonds (BRODSKII et al 1959).

THE RECOGNITION OF SOURCE MATERIAL

The source rock concept. Theories of petroleum genesis have been conditioned in the past by the concept of source rocks. It is regarded that petroleum is not indigenous to the resevoir rock where it is found, but must have migrated into the reservoir from other beds where it is formed. This presupposes that in a petroleum-bearing basin there are some beds which either have yielded or will yield petroleum, while others have not and never will yield petroleum. This concept has been criticised since it is practically impossible to draw a definite border line between hypothetical source rocks and non-source rocks (COLOMBO 1965). However, various criteria have been suggested to distinguish between possible source and non-source material. According to PHILLIPI (1957) the source quality of a sedimentary rock can be established on the basis of the amount of residual hydrocarbons generated per unit weight of dry rock. It is very difficult, however, to prove that the residual hydrocarbons in the rock are actually indigenous to the rock itself and did not migrate there, at least in part, some time after the deposition of the sediments. ERDMAN (1961) has suggested as a criterion for genesis that certain petroleum fractions must be present in a source rock and in appreciable quantity, namely:

a. the light aromatic hydrocarbons, consisting of benzene, toluene, xylenes and napthalenes.

b. the light aliphatic hydrocarbons consisting of methane, ethane through to pentanes.

c. the intermediate and heavy aliphatic, napthenic and aromatic hydrocarbons.

d. the asphaltics constituents.

However, Erdman considers that the proportion of organic material converted to petroleum in the rock is more significant than the absolute amount formed since the retentivity of the sediment for the petroleum constituents is a function of the solid carbonaceous material. BRAY and EVANS (1961) have used the carbon preference index of n-alkanes to distinguish between source and non-source rocks. Since in the majority of petroleums, there is no odd to even predominance they suggested that only those rocks whose n-alkanes had no odd to even predominance were potential source rocks. Those rocks which had a substantial odd to even predominance presumably had not generated sufficient hydrocarbons to become source beds.

Types of organic material and degree of maturation. The composition of kerogen varies considerably with the source of the organic material and the temperature history of the sediment. On the basis of elemental composition, FORSMAN (1963) has divided kerogens into three types - coaly, non-coaly and intermediate. Oxidative studies also indicated variations in type, thus coals and coaly-type kerogens yielded benzenoid acids on oxidation whereas non-coaly kerogens yield aliphatic acids. None of the oil shales chosen by Forsman are coal-like, but kerogens from four marine rocks had compositions similar to coals. The kerogens from the oil shales, which were deposited in both marine and non-marine environments, were richer in hydrogen than the coals and were mostly thought to be algal in origin. A third group appeared to have properties intermediate between the coaly and oil shale types. The oil shales which yielded benzenoid acids on oxidation fell within this group and may be a mixture of lignin-derived material and algal or spore remains. As in coals, during maturation, the carbon content of kerogens increases but the distinction between the different types of kerogen is maintained throughout the range.

McIVER (1967) has made a similar study of a number of kerogens of varying ages and environments and found that kerogens from more marine environments contain more hydrogen than kerogens from more brackish or near-shore environments. Maturation effects are superimposed on the environmental and source controls of kerogen composition and their chief products probably include large quantities of carbon dioxide, water and hydrocarbons. BREGER and BROWN (1963) have determined the elemental analyses of a number of kerogens from the Chattanooga Shale. They have used the analyses to distinguish between humic material of terrestrial origin and sapropelic material of marine origin, relating the distribution to the palaeoshoreline. They conclude that the Chattanooga Shale is not a petroleum source rock, dispite its relatively high organic content because the organic material is predominantly of the humic type.

Various methods have been developed in an attempt to characterise source rock by means of the kerogen present in sediments. KHALIFEH and LOUIS (1961) applied an oxidative method to measure the state of reduction, 'pouvoir reducteur', of the insoluble material in sedimentary rocks and reported differences between marine and non-marine organic matter and differences between alleged source and non-source rocks. ERDMAN and RAMSEY (1961) have measured the rate of oxidation of kerogen, petroleum asphaltenes and a coal by an automatic titrimetric method. They found a marked difference between the oxidation rate of petroleum asphaltenes and coal, and also between kerogen from the La Luna Limestone, which is a known petroleum source rock, and kerogen from the Green River Shale. The difficulties associated with the isolation of kerogen in a pure form led GRANSCH and EISMA (1966) to characterise the insoluble organic material present in shales by a pyrolitic method, closely related to the method for the determination of fixed carbon in coals. Total organic carbon (C_T) was determined and the fixed carbon (C_R) was determined after pyrolysis at 900°C. The ratio C_R/C_T was then obtained. They found that the ratio could be related to the type of organic material present, provided the temperature history of the sediments being examined was similar. Alternatively, providing the type of organic material was the same, the ratio could be used to distinguish between samples with different temperature histories.

STAPLIN (1969) has recently summarised the approach used by Imperial Oil of Canada to the characterisation of organic materials in sediments. Kerogen concentrates are prepared and examined microscopically and plant cuticles, spores, pollen, lignified wood fragments, mineral charcoal, resins and algae have been identified from terrestrial sediments. Material obtained from marine sources include phytoplankton and benthic algae and fungi. A measure of the degree of alteration is provided by the change in colour of plant cuticles and is measured on a scale 1-5. This thermal parameter, in combination with a knowledge of the type of organic material in the rock, has been used to assess the hydrocarbon potential of a particular sequence. Thus a high thermal index, in combination with organic material of primarily terrestrial origin, would indicate a potential for only dry gas.

Traditionally, petroleum has been considered to be of marine origin with few exceptions, but increasingly there is evidence that oils derived from a terrestrial source may be more common than had previously been thought. HEDBERG (1968) has suggested that high wax oils may be derived from terrestrial organic material deposited in near shore and paralic environments and the general principal has recently been confirmed by REED (1969) in a study of the source and environment of some oils from the Niger Delta. BROOKS and SMITH (1969b) have shown that oil occurring in the Gippsland Basin, Australia, may well have been derived from organic material of terrestrial origin. There is little doubt that terrestrial organic materials may make a significant contribution to the organic materials deposited in near shore environments. Numerous authors have shown that the *n*-alkane distribution found in many recent marine sediments closely follows the distribution found in many terrestrial higher plants in having a pronounced odd to even ratio of carbon atoms in the range C_{25} - C_{35} (SMITH 1954, STEVENS *et al* 1956, EVANS *et al* 1957, MEINSHEIN and KENNY 1957, BRAY and EVANS 1961, KVENVOLDEN 1966, CLARKE and BLUMER 1967, EGLINTON and HAMILTON 1963, ORO *et al* 1965, DOUGLAS and EGLINTON 1966, STRANSKY *et al* 1967, 1969, MAZLIAK 1969). In contrast, the limited evidence available for the distribution of *n*-alkanes in algae and bacteria of both marine and non-marine origin, shows that there is usually no odd to even predominance and the distribution ranges C_{12} - C_{23} reaching a maximum at *n*-C_{17} (STRANSKY *et al* 1967, ORO *et al* 1967, CLARKE and BLUMER 1967, STRANSKY *et al* 1968, HAN *et al* 1968, WINTERS *et al* 1969, GELPI *et al* 1970). CLARKE and BLUMER (1967) have examined the *n*-alkane content of twelve species of benthonic algae and an associated sediment from the North East coast of the United States.

The n-alkanes obtained from the algae had no odd to even predominance whilst n-alkanes obtained from the sediment had a marked odd to even predominance suggesting a contribution of terrestrial plant material.

Recognition of different contributory sources in ancient sediments is made more difficult in some instances by the confusing effects of maturation. In the case of the Green River Shale, the organic matter is considered to be largely algal in origin (BRADLEY 1966). The n-alkanes range from C_{13} to C_{33} and have a marked odd to even predominance, particularly in the range C_{25} - C_{35} (CUMMINS and ROBINSON 1964, EGLINTON et al 1964, ROBINSON et al 1965). The very large concentration of n-C_{17} is consistent with an algal origin, but n-C_{29} and n-C_{31} are equally prominent and are suggestive of a large land-derived component. Steranes, penta-cyclic triterpanes and perhydro-B-carotene have been identified, suggesting a plant origin for the Green River Shale bitumen (BURLINGAME et al 1965, HILLS et al 1966, MURPHY et al 1967, HENDERSON et al 1968a and b, ANDERSON et al 1969). The n-alkanes obtained from brown coals, as might be expected, have a distribution similar to that obtained from modern land plants (EDWARDS et al 1963, WOLLRAB and STREIBL 1969) but in coals of higher rank the pronounced odd to even predominance diminishes although n-alkanes in the range C_{25} - C_{31} are still the dominant members. (BROOKS and SMITH 1967).

POWELL et al (1970) have made a study of the effects of environment on organic deposition in some Carboniferous sediments. An attempt was made to eliminate the effects of maturation by selecting samples which had similar temperature histories as determined by measurement of the rank of associated coals. A combination of microscopical and geochemical techniques was used to assess the relative contribution of terrestrial and non-terrestrial organic materials in a series of sediments ranging from freshwater to marine. Microscopical examination revealed the presence of woody fragments and spores in all of the sediments examined, even those deposited in a marine environment. In general, the quantity of extract obtained was related to the terrestrial plant content. Those sediments which contained large quantities of spores and woody materials had n-alkane distributions in which the heavy members, C_{25} - C_{31} were predominant and as such resembled the n-alkanes obtained from coals. Those samples which had a relatively low content of terrestrial plant material showed distributions ranging C_{12} - C_{30} with n-C_{17} predominating similar to those found in modern lower organisms, but with some contributions from a terrestrial source.

The possibility of the contribution of terrestrial organic materials to near shore environments requires further investigation before any assessment of its role in petroleum genesis can be made. However, at this stage it would appear that since the development of a land flora in Devonian times, terrestrial organic material may contribute in some part to the source material of petroleum with the possible exception of petroleums derived from carbonate sequences in which the contribution form terrestrial plant material may be relatively small.

MIGRATION AND ACCUMULATION OF PETROLEUM

The migration and accumulation of petroleum is perhaps the least understood aspect of the origin of petroleum, but current theories are usually discussed under two headings:-

A. Primary migration (the transfer of petroleum from the preserved source rock into a permeable reservoir rock).

B. Secondary migration (the segregation of oil and gas in a resevoir resulting ultimately in accumulation).

This division is rather arbitrary and in fact it is rather difficult to separate the migration process into these two stages.

Compaction has long been regarded as a possible means by which petroleum could be transported out of a source rock. Muddy sediments, as they are laid down on the sea floor, are saturated with water and have a pore volume of the order of eighty of ninety per cent. HEDBERG (1936) recognised four phases of mud compaction, outlined as follows:-

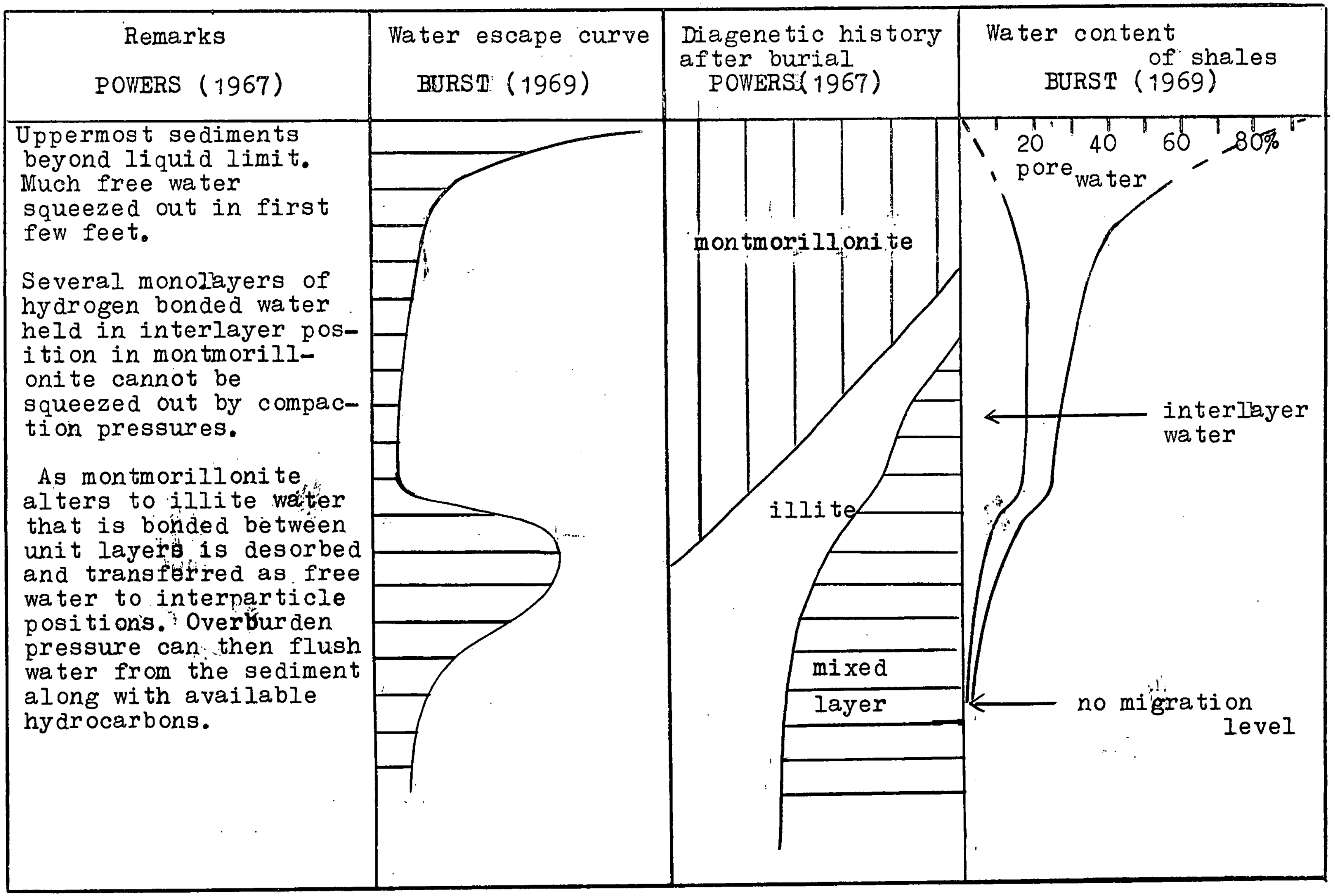
1. Mechanical adjustment of the mineral components and decrease in porosity from 90 to 75%. This occurs with a sediment cover of 0 to 0.1 metres.

2. Reduction of the porosity from 75 to 35% is accompanied by a strong reduction in water content and probably is accomplished at a depth of 200-300 metres. It ends when the clay minerals are in contact and as a result only a relatively small amount of free water remains.

3. With mechanical deformation of the mineral components, porosity decreases from 35 to 10%, probably between 300 and 2000 metres.

4. Recrystallisation takes place within the rock. Decrease in porosity below 10% is accomplished very slowly.

More recent work has confirmed the general trends established by Hedberg. (BROWN 1969). It is evident from this compaction scheme that the bulk of the water is expelled from muddy sediments at relatively shallow depth. Current theories of hydrocarbon genesis require that hydrocarbons be generated at depth which would be outside the zone of maximum water expulsion. Recently, POWERS (1967) and BURST (1969) have suggested a means by which deep flushing of potential source rocks might occur. They have shown that conversion of montmorillonite to illite is a diagenetic process which is related to the depth of burial of a sediment. It is accompanied by expulsion of water from the clay lattice, representing maybe as much as 10 to 15% of the bulk volume of the sediment. Thus in their compaction scheme (Fig. 3), a muddy sediment, undergoing burial, rapidly loses a large proportion of the free water within the first few feet of burial. Water loss, with increasing burial, decreases rapidly and becomes more or less constant until the montmorillonite - illite transformation zone is reached, when there is a rapid increase in water loss associated with the removal of bound water layers from the montmorillonite lattice. There is, then, a gradual decline in the rate of



Uppermost sediments beyond liquid limit. Much free water squeezed out in first few feet.

Several monolayers of hydrogen bonded water held in interlayer position in montmorillonite cannot be squeezed out by compaction pressures.

As montmorillonite alters to illite water that is bonded between unit layers is desorbed and transferred as free water to interparticle positions. Overburden pressure can then flush water from the sediment along with available hydrocarbons.

Fig. 3 Compaction history of clayey sediments containing monmorillonite as principal clay mineral. Modified after POWERS (1967) and BURST (1969) water loss with increasing depth. Burst has demonstrated that this transformation is controlled by temperature rather than overburden pressure and hence the depth of transformation is related to the geothermal gradient. Burst considers that the temperature of conversion can be limited to the range 182-232°F.

BURST (1969) has applied this theory to the occurrence of crude oils in the Gulf Coast area of the United States and has related the depths of petroleum pools to the levels of montmorillonite-illite transformation. He found that although the illite-montmorillonite transformation depths range from 4,000 to 16,000 feet, hydrocarbon occurrences are distributed about a mean 1,500 feet above the theoretical montmorillonite-illite transformation level. This is explained by a model in which water derived from the montmorillonite-illite transformation process, initiated hydrocarbon movement in an upward direction. A prerequisite of this theory is that, initially, the source rocks should have a substantial proportion of their clays composed of montmorillonite. POWERS (1967) has in fact suggested that organic rich rocks, in which illite is the dominant clay mineral, are not destined to become source rocks with diagenesis, but will become oil shales.

Although movement of water out of the source rock is regarded as the driving force for primary migration, the physical state in which oil moves from the source rock has been extensively debated. Various authors (HOBSON 1954, ROOF and RUTHERFORD 1958; SILVERMAN 1964) have suggested that oil migrates as a discrete phase through water wet pores. This theory has been criticised since migration of this type through fine grained rocks would require forces several times greater than those produced by normal hydrodynamic gradients (BAKER 1967, WELTE 1965). Other authors (BAKER 1960, 1962, 1967, MEINSHEIN 1959, 1961) suggest that oil is moved out of the source rock dissolved in the waters released during compaction. The low solubility of hydrocarbons in water and brines has always been regarded as a stumbling block to the total acceptance of this theory. However, BAKER (1960, 1962, 1967) has indicated how an increase in hydrocarbon solubility could be achieved. He has shown that salts of organic acids, and possibily *n*-alkanes, can form micelles in formation waters and, in their turn, can group to form colloidal particles. These colloidal particles increase the water solubility of the hydrocarbons by providing hydrocarbon-like regions in which other hydrocarbons can selectively dissolve. Baker considers that there can be two types of micelles and has related the distribution of hydrocarbon groups (paraffins, napthenes and aromatics) in oils to the specific solubilities of these groups in the types of micelles available for transport. In addition, he has related the distribution of *n*-paraffins in some Venezuelan crude oils to their possible migration in a colloidal system in which there are two types of micelles. Thus, the distribution of *n*-alkanes in a petroleum need not necessarily resemble that of the source, since as long as the supply of *n*-alkanes exceeds the absorption capacity of the formation waters the *n*-alkane distribution in the oil will be dependent of the solubilities of the *n*-alkanes. A similar distribution between oil and source will only be attained if the supply of alkanes is less than the absorptive capacity of the formation waters. Some supporting evidence for this theory has been obtained by WELTE (1965).

He extracted two rock samples of Tertiary age, partly in the conventional manner with an organic solvent and partly by stirring with an oilfield water 60°C: the oilfield water had previously been cleaned of hydrocarbon by extraction with ether. The conventional extract of the samples showed a clear preference in the higher n-alkanes for odd carbon numbers whereas the n-alkanes extracted with the oilfield water had an even carbon number distribution.

Various mechanisms have been suggested whereby oil may separate out of solution and accumulate to form a deposit. HOBSON (1961) has criticised these mechanisms which depend on changes of pressure and temperature to achieve phase separation. BAKER (1967) has suggested that oil may separate out as a result of the exclusion of salt from oil bearing water re-entering fine grained sediments. This theory is based on the work of DESITTER (1947) who suggested that confining layers between more permeable formations may act as semi-permeable membranes which allow water to pass out of the formation whilst retarding salt ions.

SOKOLOV et al (1963) consider that various types of migration may occur in different cases or at different stages and include:-

a. Filtration of gas oil due to pressure differences between pores.

b. The bouyancy of gas and oil in the reservoir waters.

c. The movement of free and dissolved gas and oil by underground waters.

d. Expulsion of gas and oil along with water during compaction.

e. The diffusion of gas and oil.

The movement of oil as a discrete phase within a reservoir rock has been extensively discussed by LEVORSEN (1967).

NAGY (1960) proposed that movement of oil through a system of water wet rocks would result in some chromatographic effects resulting in the selective removal of some petroleum components by solution in water or absorption on mineral grains. The possibility of chromatographic effects has been recognised by other workers, BONHAME (1956), HODGSON and BAKER (1959), D.R. BAKER (1962), COLOMBO and SIRONI (1961), RIEKER (1962). Laboratory studies by THOMPSON (1961) have shown that montmorillonite and illite are capable of producing large chromatographic effects whilst pure sands and carbonates produce only slight effects. The polar constituents, e.g. asphalts and napthenic acids are more susceptible to chromatographic effects. This may also result in differences in the ratio of stable carbon isotopes following migration through absorptive media. Since aromatics have a slightly higher $^{13}C/^{12}C$ ratio than do the aliphatic hydrocarbons from equivalent boiling ranges, it is to be expected that if chromatographic effects do occur there should be a slight decrease in $^{13}C/^{12}C$ ratio of petroleum with increasing distance of migration (SILVERMAN, 1965). SILVERMAN (1965) has summarised the effects that might be induced by migration, namely,

1. Increase in paraffin content.

2. Decrease in content of asphalts, resins, porphyrins, non hydrocarbons and heavy metals.

3. A slight decrease in C^{13}/C^{12} ratio.

The net effects of these changes would be an increase in the A.P.I. gravity of the petroleum. Silverman has applied these criteria to a study of migration in the Quinquire Oil Field, Venezuela and has shown that slight chemical differences do occur between oils which are thought to have a common source, and suggests that migration had occured in an up-dip direction.

SILVERMAN (1964) has pointed out that petroleums occurring in limited geographical areas, although showing some evidence of a common source, frequently differ markedly in chemical composition. He suggested that these petroleums may have undergone a separation during the course of migration as a result of changes in pressure and temperature. He envisages petroleum existing at depth as a single phase system. Pressure reduction occurring as a result of faulting or erosional unloading may cause the single phase fluid to separate into gas and liquid phases which may then separate during migration. Such a process occurring during migration may result in the separation of fluids of differing composition in different traps.

SUMMARY

As petroleum occurs in such a diversity of geological situations (HEDBERG 1964) it would appear that a single unified theory of petroleum genesis, which is applicable to all cases, may never be achieved. However, the outlines of a general theory are beginning to emerge, although there still remain areas in which data are inadequate.

In general terms, it can be stated that petroleum hydrocarbons are generated at depth, under the influence of an increase in temperature, from the lipid components of organisms incorporated into the sediments. Decarboxylation of fatty acids is regarded as the principal mechanism for the formation of aliphatic hydrocarbons, whilst cyclic alkanes and aromatic compounds are thought to be formed from terpenoids by isomerisation and disproportionation reactions. There is considerable evidence to show that lipids react with other cell components to form the complex polymer 'kerogen', which on maturation may yield a variety of hydrocarbons by cracking reactions. This maturation process results in a decrease in the ratio of odd to even carbon numbered n-paraffins in sediments. However, this may only apply in the case of organic material of terrestrial origin in which there is initially a high ratio of odd to even n-paraffins. The n-alkanes obtained from bacteria and algae usually show this preference and the effect of maturation on the hydrocarbon distribution of marine organic material remains to be fully explored.

The occurrence of petroleums in non-marine sequences invalidates the once widely held view that petroleum is of marine origin though it is by no means accepted that coal is the source material for these hydrocarbons. Rather, it is more likely that the spores, cutins and resins derived from land plants are the source for these oils.

The migration of petroleum hydrocarbons from the source rock into the trap remains the most controversial aspect of petroleum genesis, and it is quite possible that migration incorporates many of the features of the theories previously discussed. Despite the difficulties, the micellar theory of BAKER (1967) in association with the deep-flushing mechanism suggested by POWERS (1967) and BURST (1969), probably represents the most realistic method for the movement of oil from the source rock. Ultimately, a discrete oil phase must be formed in the reservoir rock and it is at this stage that globular migration, with its associated features, might be expected to occur. However our understanding of this phase of petroleum formation is far from complete and more data on the physico-chemical relationship of hydrocarbons in source rocks is required.

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