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THE COMPOSITION OF PETROLEUM

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Petroleum has a complex chemical composition. It consists mainly of hydrocarbons; compounds containing oxygen, nitrogen and sulphur are usually of minor importance, while metals are even less abundant.

The hydrocarbons vary widely in boiling point, molecular size and structure. Although relatively few individual compounds have been identified, several types of compounds can be distinguished.

Crude oils differ considerably in composition, depending on the source matter, the thermal history of the source matter and alteration processes in subsurface reservoirs.

INTRODUCTION

The composition of petroleum is extremely complex (Speers and Whitehead, 1969). It would go beyond the scope of this paper to give a complete review of what is known in this field. The paper will cover only the most important aspects of the composition of petroleum and also try to illustrate how this composition came about by discussing briefly the origin of petroleum and the alterations that may take place in subsurface accumulations.

The main elements in petroleum are carbon and hydrogen, while sulphur, nitrogen and oxygen usually occur in subordinate quantities. The elemental composition of most crude oils generally varies between the following limits (% weight): carbon 80-87, hydrogen 10-15, sulphur 0-10, nitrogen 0-1 and oxygen 0-5.

Apart from the above elements, crude oils often contain a wide range of trace metals such as V, Ni, Fe, Na, Ca, Cu and U.

The elemental composition already suggests that hydrocarbons are the principal constituents, usually exceeding 75 %. They will therefore be discussed first.

HYDROCARBONS

The hydrocarbons present in crude oils are generally divided into four groups based on their chemical structures (Fig. 1): a. normal alkanes (normal paraffins), b. branched alkanes (branched paraffins), c. cycloalkanes (cycloparaffins or naphthenes), d. aromatics.

Very small concentrations of olefinic hydrocarbons have been reported in some crude oils, but definite confirmation is lacking. For these reasons they will not be discussed here. The hydrocarbons in petroleum cover

a wide range of molecular sizes and boiling points. The number of carbon atoms in the molecule ranges from C₁ to C₆₀ and in some cases compounds up to C₇₈ have been reported (Ludwig, 1965; Denekas et al, 1951), with molecular weights up to about 900.

Until about 20 years ago, determination of the chemical composition of oil was extremely difficult because the analytical techniques were limited. Nevertheless, by 1927 the American Petroleum Institute had started the famous project 6, a detailed investigation of one crude oil, the Ponca City crude, that was chosen as a typical, average crude. It took more than 30 years to identify 169 individual hydrocarbons (Rossini and Mair, 1959), and in 1965 a total of 256 hydrocarbons and 8 non-hydrocarbons had been identified, representing about 60 % of the crude's weight (Mair, 1965).

It turned out that petroleum was much simpler than was expected on the basis of the many theoretically possible compounds. This is clearly demonstrated in Table 1. Only in the lower molecular weight range have most of the possible isomers been found. Nevertheless, petroleum remains extremely complex especially in the higher boiling fractions, where separation becomes increasingly difficult.

Table 1. Alkane isomers possible and identified

Isomers	Carbon atoms in molecule												
	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉	C ₁₀	C ₁₁	C ₁₂	C ₁₃
Possible.....	1	1	1	2	3	5	9	18	35	75	159	355	802
Identified	1	1	1	2	3	5	9	18	30	12	1	1	1

After Smith (1966)

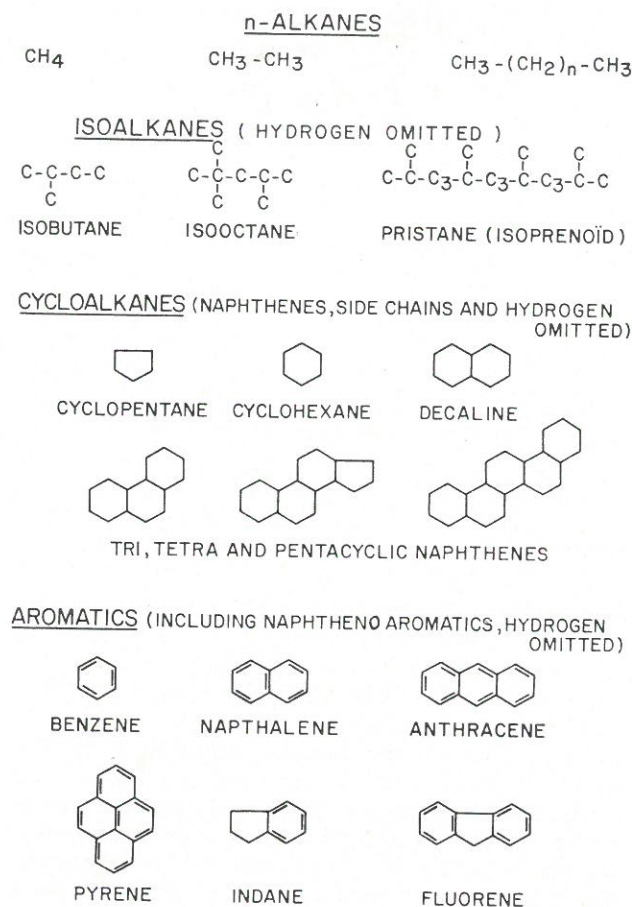


Figure 1. Some basic structures of hydrocarbons in petroleum.

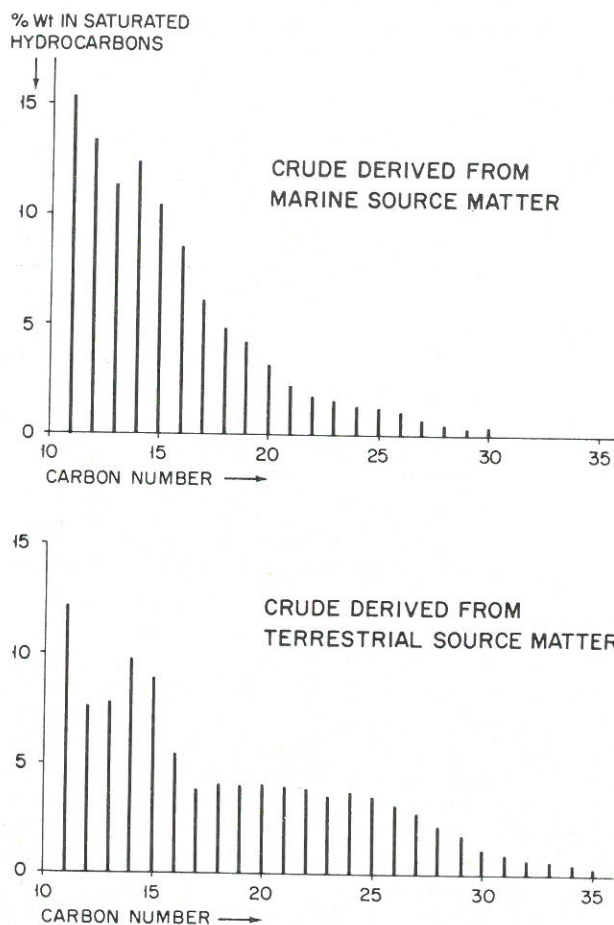
NORMAL ALKANES

n-Alkanes occur in most petroleum as the most abundant series of hydrocarbons usually in the continuous homologous series of CH₄, CH₃-CH₃, CH₃-(CH₂)_n-CH₃. The maximum number of carbon atoms (*n*+2) is usually around 40, although alkanes with carbon numbers > C₆₀ have been reported (Ludwig, 1965; Denekas et al, 1951).

Two typical *n*-alkane distributions are shown in Figure 2.

ISO-ALKANES

Iso-alkanes are present in most oils in relatively large concentrations. Molecules with methyl groups as side chains are most abundant especially those with methyl groups at 2, 3 and 4 positions. Below C₁₀ many isomers have been isolated from Ponca City crude (Mair, 1964 a). Above C₁₃ the most important group of iso-alkanes is the series of isoprenoid hydrocarbons that

Figure 2. *n*-Alkane distributions of two crudes of different origin.

have the isoprene skeleton repeated in their structure (Fig. 1). Various isoprenoid hydrocarbons with more than 13 carbon atoms have been identified in petroleum (Dean and Whitehead, 1961; Mair et al, 1962; Bendoraitis et al, 1963) with pristane (C₁₉) and phytane (C₂₀) as the most abundant. This series of iso-alkanes is now known to be very common in petroleum and sometimes constitutes the predominant hydrocarbons in the C₁₀-C₂₀ range. These iso-alkanes are believed to originate from plant pigments especially from the phytol side chain of chlorophyll (Bendoraitis et al, 1963) and their presence thus supports the biogenic origin of petroleum.

CYCLOALKANES

The cycloalkanes are found in all crudes in quantities ranging from 30-60 % and are present in the fractions from C₅ upwards. The vast majority of cycloalkanes consists of cyclopentane and cyclohexane deri-

vatives. Normally the mono- and bicyclic show the highest concentrations, but in some asphalts 4 and 5 ring naphthenes are predominant. Like the isoprenoids, these polycyclic naphthenes are assumed to be related to specific precursors in animal and plant life (steranes and triterpanes) and therefore considered as evidence for the biogenic origin of petroleum (Hills and Whitehead, 1966; Mair, 1964 b).

AROMATIC HYDROCARBONS

On the definition of aromatic hydrocarbons in petroleum there is no general agreement. It is customary to define aromatics as compounds with one or more aromatic rings in the molecule including those that have both aromatic and naphthenic rings e.g. tetralin. Some investigators put the latter compounds in a separate group, the naphtheno-aromatic hydrocarbons. In this paper the first definition will be used.

The aromatics in petroleum occur in various structures. In light oils the monocyclic compounds are predominant. Rossini and Mair (1960) have identified all possible C_6-C_9 benzene derivatives in several crudes. Bicyclic aromatics are mainly methyl and ethyl naphthalenes and biphenyl, while tricyclic are anthracene, phenanthrene and their simple alkylated forms. Fluorene structures are sometimes also present in significant quantities. Polycyclic aromatics with more than three rings are comprised of mainly pyrene, chrysene, benzanthracene, perylene and benzofluorene structures. In the higher boiling fractions the naphtheno-aromatics increase. The total number of rings in this type of compound may be as high as six. Members of the following series have been identified: indane, tetralin, fluorene and cyclopentanophenanthrene.

NON-HYDROCARBONS

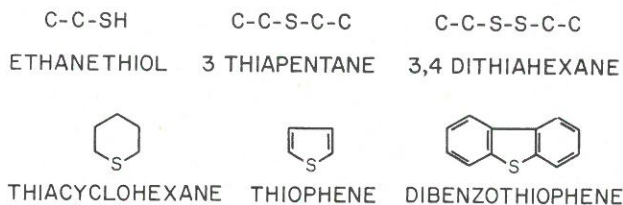
The non-hydrocarbons (Fig. 3) are generally considered to be minor constituents of petroleum but in heavy oils they may sometimes become predominant. For example in the Wilmington crude (California) they account for one third (Ball et al, 1959) and in the Boscan crude (W. Venezuela) for about two thirds of the oil (Bestougeff, 1967). This is well illustrated in Figure 4, where the distribution of the major groups of compounds in a light and a heavy oil is shown.

The following groups of non-hydrocarbon compounds can be distinguished: a) sulphur compounds, b) nitrogen compounds, c) oxygen compounds, d) porphyrins, e) asphaltenes, f) trace metals.

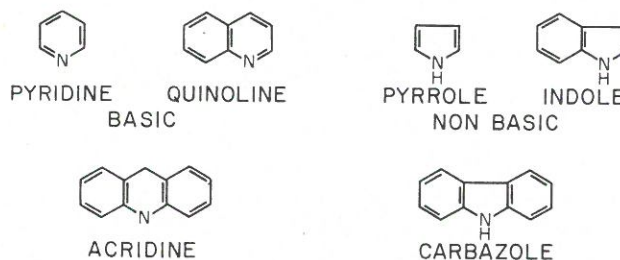
SULPHUR COMPOUNDS

Sulphur compounds form the most important group of non-hydrocarbon constituents with respect both to

SULPHUR COMPOUNDS



NITROGEN COMPOUNDS



OXYGEN COMPOUNDS

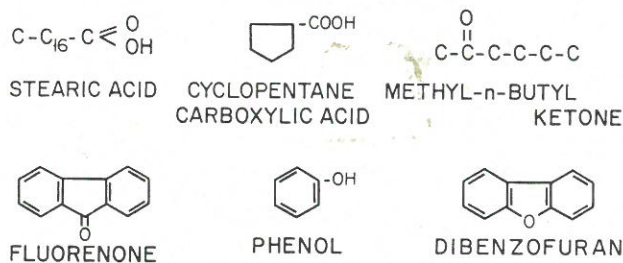


Figure 3. Some basic structures of S,N,O compounds in petroleum.

quantity and to the problems they cause in refineries. Sulphur and its compounds also have a considerable bearing upon the origin of petroleum. The sulphur content of crudes varies widely from almost zero in e.g. the Far East crudes to about 5 % in heavy Western Venezuelan crudes. In extreme cases sulphur contents of almost 15 % have been recorded in asphalt seeps. The general trend is that the sulphur content, especially in one area, increases with the specific gravity of the oils. Most sulphur is present as organically-bound sulphur but sometimes elemental sulphur has been detected in concentrations of more than one percent (Rall et al, 1972; Gransch and Posthuma, 1973). One of the most recent and complete reviews on sulphur compounds in crude oils is USBM report on the API project 48 summarising 20 years of research (Rall et al, 1972).

Crudes contain four main classes of organic sulphur

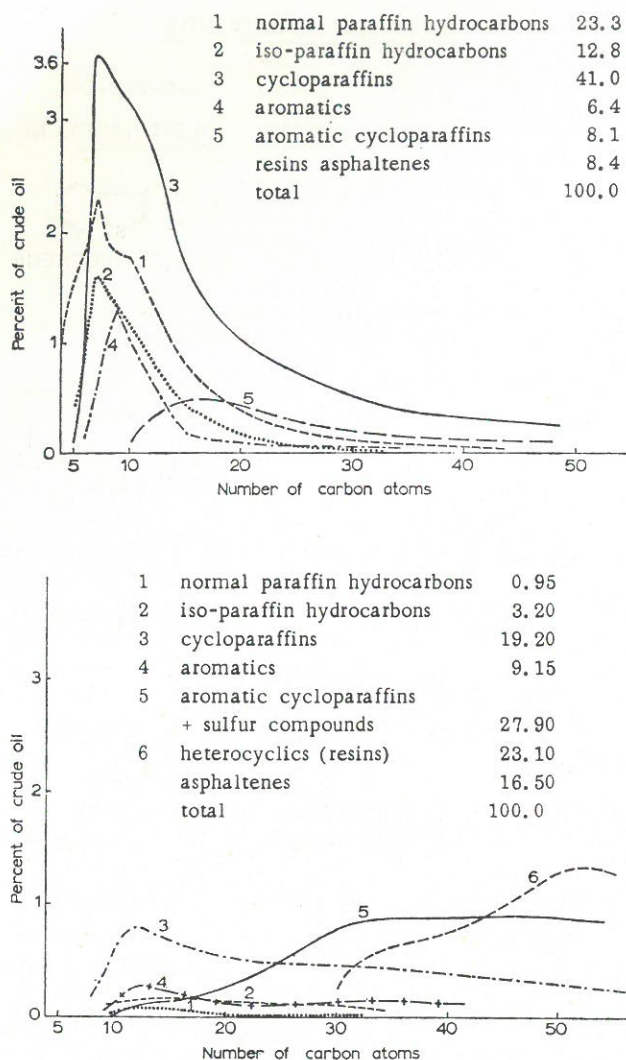


Figure 4. Distribution of the major groups of compounds in a light and a heavy crude oil. (After Bestougeff, 1967).

compounds (Fig. 3): (1) thiols, (2) disulphides, (3) sulphides, (4) thiophenes.

The thiols and disulphides are only present in the low boiling fractions ($< 200^{\circ}\text{C}$) and all possible structures below C_7 have been identified (Smith, 1966). Most sulphur is found in the higher boiling fractions as cyclic sulphides and thiophenes.

Up till now very few molecules containing two sulphur atoms have been identified although mass spectra indicate that they are present (Rall et al, 1972).

The origin of sulphur in petroleum has been the subject of much discussion for many years and for this reason a separate paragraph is devoted to this problem later.

OXYGEN COMPOUNDS

The majority of oxygen compounds in petroleum (Fig. 3) are fatty acids and naphthenic acids. In the carbon number range $\text{C}_1\text{--C}_9$ both straight chain and branched acids have been reported. In the $\text{C}_{14}\text{--C}_{20}$ range the odd-numbered members appear to be absent while isoprenoid acids have been encountered in a Californian crude. The naphthenic acids are by far the most abundant especially in naphthenic crudes. In addition to acids, various phenols have been detected whereas small concentrations of aliphatic ketones, fluorenones and dibenzfurans also occur. In the higher boiling fractions and distillation residues, compounds with two oxygen atoms or oxygen plus nitrogen and/or sulphur also exist (Snyder, 1970).

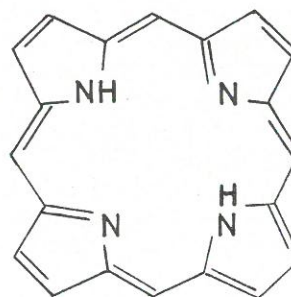
NITROGEN COMPOUNDS

All crude oils contain some nitrogen but the maximum is about 1%. In terms of nitrogen compounds this will probably vary roughly between 0.5 and 15%. Practically all nitrogen compounds are concentrated in the higher boiling fractions and about 90% of them in the distillation residues. They are generally divided into basic and non-basic compounds (Fig. 3). The basic compounds such as pyridines, quinolines, benzoquinolines and acridines have been studied most extensively because they are the easiest to isolate. The non-basic nitrogen compounds are derivatives of pyrroles, indoles, carbazoles and benzcarbazoles.

PORPHYRINS

Although the porphyrins belong to the group of nitrogen compounds they are discussed here separately because they have an important significance in the origin of petroleum. They have therefore received much attention for several years, being first discovered by Treibs (1934).

The detailed chemistry is extremely complex. However, the essential part of the molecules consists of four condensed pyrrole rings of the structure:



in which the pyrrole hydrogen atoms can be replaced by metals. In petroleum the porphyrins occur almost ex-

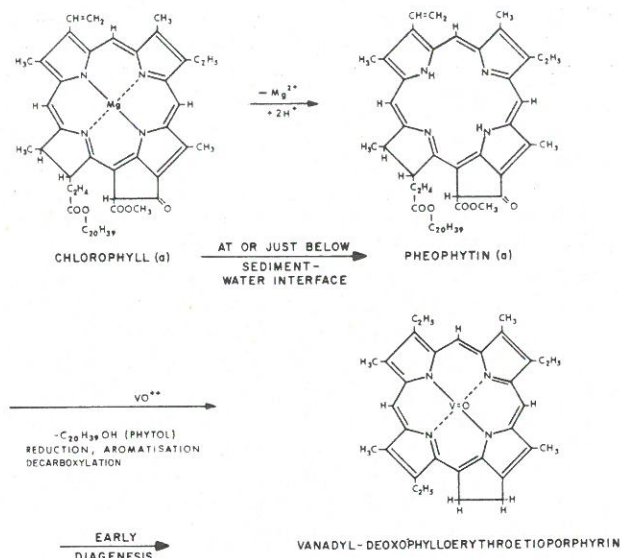


Figure 5. Conversion of chlorophyll into vanadylporphyrin.

clusively as complexes of vanadium (vanadyl) and nickel. The metal porphyrin complexes are the only compounds that can be observed easily from the absorption spectra of crude oils. In high concentrations the red colour betrays their presence.

The porphyrin content of petroleum varies from 1–3500 mg/litre. The highest concentrations are found in sulphur-rich asphaltic oils, while light oils contain practically none (Gransch and Eisma, 1966). It is now generally accepted that porphyrins are derived from chlorophyll molecules and thus provide evidence for the biogenic origin of petroleum. The conversion of chlorophyll into porphyrins is assumed to occur by metal exchange, decarboxylation and hydrogenation as is schematically shown in Figure 5.

ASPHALTENES

Apart from the heteroatomic compounds already mentioned, many oils contain a fraction of high molecular weight material containing nitrogen, sulphur, oxygen and metals that precipitates on addition of low-boiling hydrocarbons e.g. propane or pentane. This fraction, which varies somewhat with the precipitating agent used, is called "asphaltenes" and consists of molecules with an average molecular weight somewhere between 1000 and 10 000, although there is no general agreement on these numbers. The chemical structure has not been fully established, but it is certain that asphaltenes are highly aromatic, partly heterocyclic structures composed of 10–20 fused rings (Fig. 6), with aliphatic and naphthenic side chains, forming stacks of about 4–5 (Yen et al, 1961). The asphaltene content

of crude oils ranges from 0–20 % and in natural asphalts percentages of 30–40 % are not uncommon.

TRACE METALS

The trace metals mentioned in the introduction are all present in the asphaltene fraction of petroleum. Vanadium and nickel are usually the most abundant, sometimes reaching concentrations of thousands of mg/litre. They are not only present in the porphyrins; the total content of these metals is sometimes 5–10 times higher than that complexed in the porphyrins. Due to the small amounts involved the study of the metals in petroleum is hampered by the possibility of contamination.

THE ORIGIN OF PETROLEUM

In a paper on the composition of petroleum, a brief discussion on its origin can hardly be avoided since the composition of a crude strongly depends on its origin. However, the discussion is restricted to two important

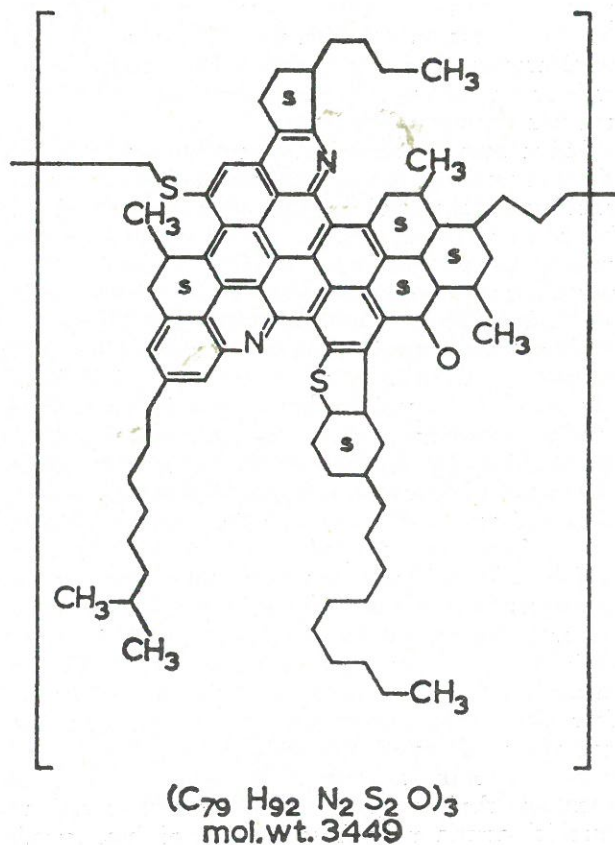


Figure 6. Hypothetical structure for asphaltenes from Venezuelan crude oil. (After Winniford and Bersohn, 1962).

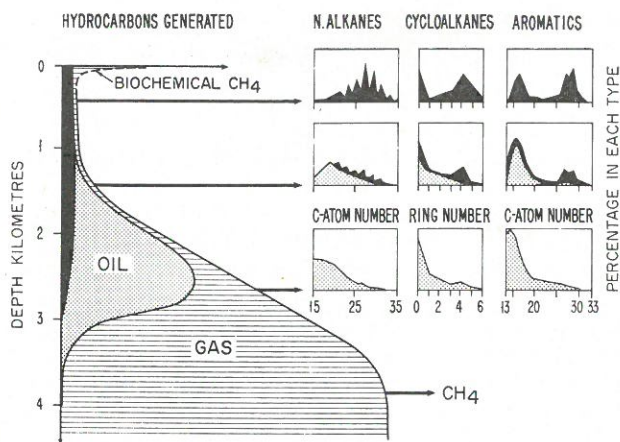


Figure 7. General scheme of hydrocarbon generation. (After Tissot et al, 1974).

aspects, namely the effect of the origin on some general characteristics of crude oils and the origin of sulphur.

It is almost generally accepted that petroleum is of biogenic origin. It contains many compounds which point to such an origin, namely, isoprenoids, porphyrins, carotenes and steranes which have their natural precursors in organic-rich sediments; indeed petroleum in nature is predominantly associated with sedimentary organic matter.

It has been established that petroleum is formed by thermal cracking from organic matter deposited in ancient seas, lakes and lagoons after this material is buried to a sufficient depth. Not all organic matter is suitable for the generation of oil. The nature of the organic matter considered to be the source matter for oil has been discussed recently (Lijmbach, 1975).

Our present concept is that oil source rocks i.e. rocks containing a reasonable amount of hydrogen-rich ($> \sim 5\% \text{ H}$) organic matter are deposited only under special conditions. Normally in aquatic environments an abundant life is present in the upper water layers. Photosynthetic plankton synthesise organic matter from CO_2 and water. In most cases the organic debris resulting from this photosynthetic life is completely oxidised to CO_2 and water again by aerobic bacteria and consequently is almost completely recycled. However, under certain conditions, which include an unusually high photosynthetic activity and stagnant water, an anaerobic situation will develop below the water surface. Only under these conditions will significant concentrations of organic matter be preserved and incorporated into the sediments. This organic matter has been reworked to a large extent by aerobic and anaerobic bacteria and will consist only of these reworkers and the microbially resistant part of the original detritus including pollen, spores, resins and waxes sup-

plied from elsewhere. When this organic matter is buried a sequence of processes will take place resulting in the formation of oil and gas (Fig. 7). In the first stages of burial the organic matter is converted into an insoluble complex polymer (kerogen) by polymerisation and condensation reactions. The initial hydrocarbon content remains low at first but at a certain depth, usually 2000–3000 m dependent on temperature and time, new hydrocarbons are generated by thermal cracking of the kerogen. This is the principle stage of oil generation (Vassoyevich et al, 1969). At still greater depth only gas will be generated both from the kerogen and the oil retained (zone of gas generation). Eventually only a highly carbonised residue will be left behind in the oil source rock.

It seems evident that the composition and the amount of petroleum generated in a source rock depends on the composition of the kerogen. Laboratory heating experiments (Lijmbach, 1975) have provided evidence that the bacterial mass which reworked the organic detritus during deposition seems to be the main constituent of most kerogens. Heating of it would generate a common basis for petroleum with a carbon number distribution as indicated in Figure 8. Contributions of other material to the kerogen would be superimposed on this general distribution. For example, resins would generate C_{15} - and C_{30} -naphthenes and plant waxes would yield n -alkanes in the C_{25} – C_{33} range (Fig. 8, Fig. 2).

Various studies have shown that other constituents of crude oils can be explained as being products of thermal degradation of specific precursors in the kerogen, like the porphyrins and isoprenoid hydrocarbons originating from chlorophyll and related compounds. Discussion of these studies is beyond the scope of this

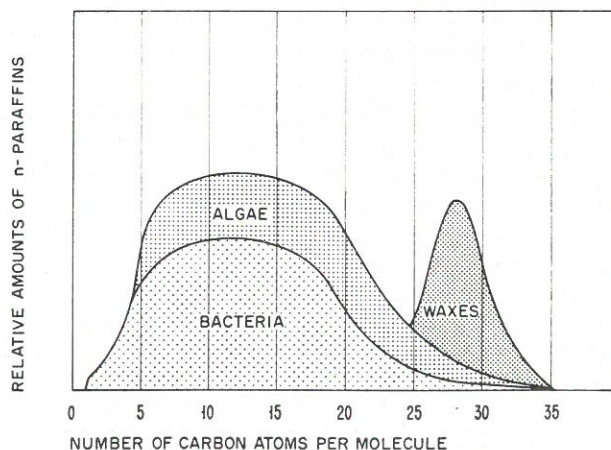


Figure 8. Contribution of the various types of organic matter to the n -alkane distributions of crude oils. (After Lijmbach, 1975).

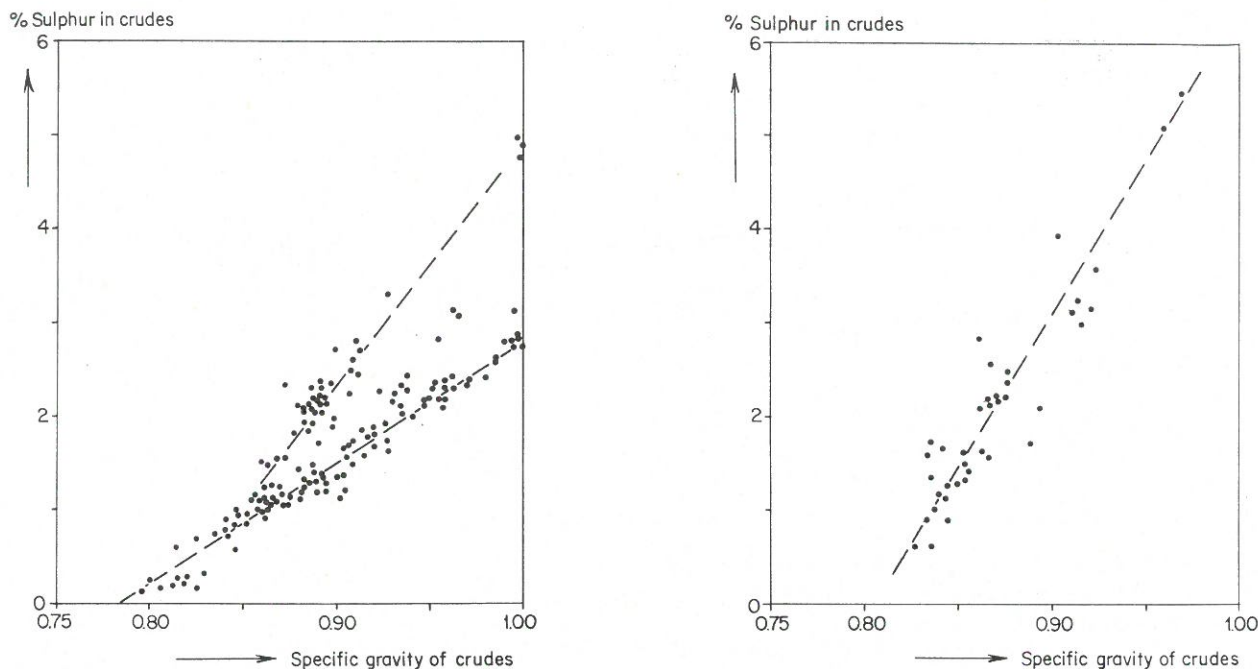


Figure 9. Relationship between sulphur content and specific gravity in high sulphur areas (W Venezuela, Middle East).

paper. Only one aspect, the origin of sulphur, will be discussed in detail, because the presence of sulphur in crude oils has such an important effect on their gravity, chemical composition and economic value.

THE ORIGIN OF SULPHUR IN PETROLEUM

There has never been much doubt that most non-hydrocarbon constituents like nitrogen, oxygen and trace metals originate from the oil source rock. The origin of sulphur, however has caused much controversy in the past. There have been two main theories. The first assumes that crudes are originally poor in sulphur and that most of the sulphur in high-sulphur crudes ($> 0.5\%$ S) was introduced by the action of sulphate reducing bacteria after the oil accumulated in subsurface reservoirs.

The second view is that the sulphur originates mainly from the source rock. Our recent studies (Gransch and Posthuma, 1973) have shown that this latter concept is supported by the experimental data. Analysis of source rocks and oils, particularly in western Venezuela, have revealed that many kerogens contain up to 10% organic-bound sulphur. The kerogens thus provide an excellent source of sulphur. Indeed, it was observed both in the laboratory and in nature that with increasing thermal metamorphism these kerogens first yield a heavy, sulphur-rich crude, rich in asphaltenes and often also in porphyrins. On further heating the

generated hydrocarbon mixture became gradually lighter and contained less sulphur, asphaltenes and porphyrins. This observation explains the occurrence of the whole range of sulphur contents in the crudes encountered in areas with high-sulphur source rocks (Fig. 9).

The formation of kerogen rich in organic sulphur could also be explained. The organic detritus from which kerogen is formed is low in sulphur, but, as already mentioned, anaerobic bacteria rework this detritus during sedimentation. In marine environments, where sulphate is always abundantly present, sulphate reducing bacteria are especially responsible for this anaerobic degradation. During this process the sulphate is reduced to hydrogen sulphide (H_2S). The fate of this H_2S varies with the environment:

(a) If metal ions (e.g. Fe^{++} , Zn^{++} , Cu^{++}) are present (e.g. in clays) it may be trapped as metal sulphides, mostly pyrite, and will thus not be incorporated into the kerogen. As a result the sulphur content of the kerogen will be low and crudes derived from it will be poor in sulphur. This is usually the case if the source rock has been deposited in a marine siliciclastic environment like the Niger delta and the Texas Gulf coast.

(b) If metal ions are absent, the H_2S can be chemically or bacteriologically oxidised to elemental sulphur, as is illustrated in Figure 10.

In recent sediments elemental sulphur is often found. On burial, it will react with the kerogen to form a

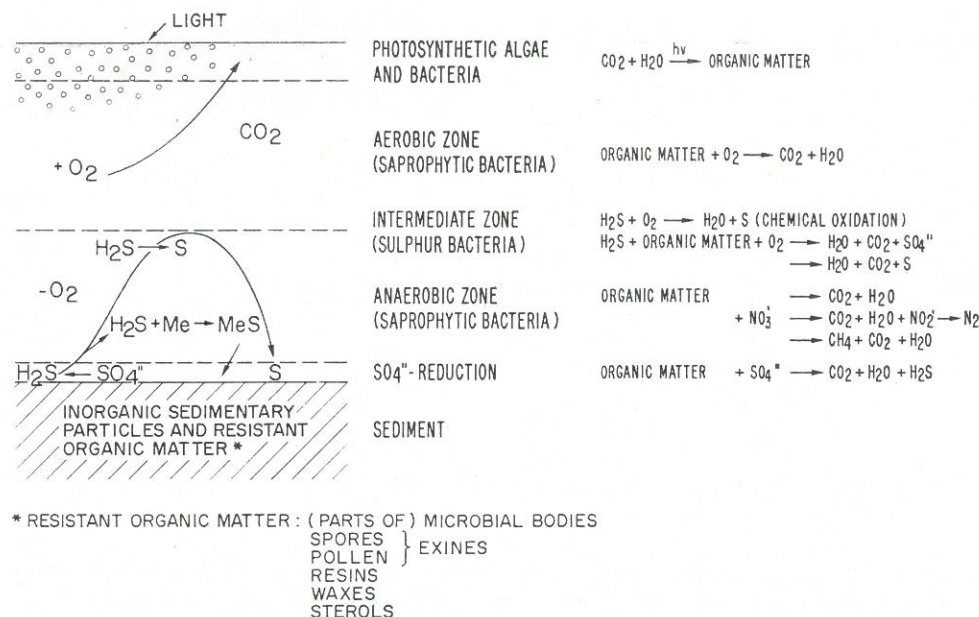


Figure 10. Role of microbes during sedimentation. (After Lijmbach, 1975).

high-sulphur kerogen. On deeper burial this kerogen will crack and yield a heavy asphaltic, sulphur-rich oil. In later stages of organic metamorphism the generated oil becomes increasingly lighter and poorer in sulphur, asphaltenes and porphyrins. Both the incorporation of sulphur in the organic matter and the generation of high- and low-sulphur crudes have been demonstrated in laboratory oil generation experiments (Lijmbach, 1975; Gransch and Posthuma, 1973). Figure 11 summarises our views on the occurrence of high- and low-

sulphur crudes. It explains why in some areas only low-sulphur crudes occur (Brunei, Nigeria), while in others the sulphur content varies widely with the specific gravity of the oil (W. Venezuela).

OTHER FACTORS AFFECTING THE COMPOSITION OF PETROLEUM

In addition to the composition of the kerogen and its thermal history the composition of petroleum can be affected drastically after it has been trapped in the reservoir rock. Firstly, the oil may become lighter and eventually become destroyed by thermal alteration (maturation) which is the result of deeper burial, thus elevated temperatures. This process is, in fact, a pyrolysis and tends to lead to chemical equilibrium. It involves removal of the heteroelements in the form of water, carbon dioxide, hydrogen sulphide etc., with simultaneous formation of increasingly small saturated hydrocarbons on the one hand and increasingly condensed, aromatic structures on the other. Eventually it ends up with methane and graphite only. This process of thermal alteration has been documented very recently (Van der Weide et al, 1975).

Petroleum may also become heavier in subsurface reservoirs. Physical processes, like evaporation of light components and solution in water of the most soluble compounds, result in an increase of specific gravity. The most severe effect, however, is caused by *bacterial transformation or degradation*. The latter process is restricted to relatively shallow reservoirs since it re-

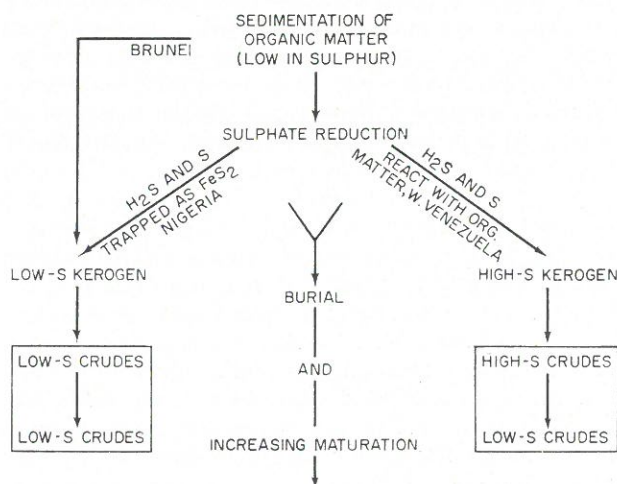


Figure 11. Explanation for the occurrence of high- and low sulphur crudes in nature.

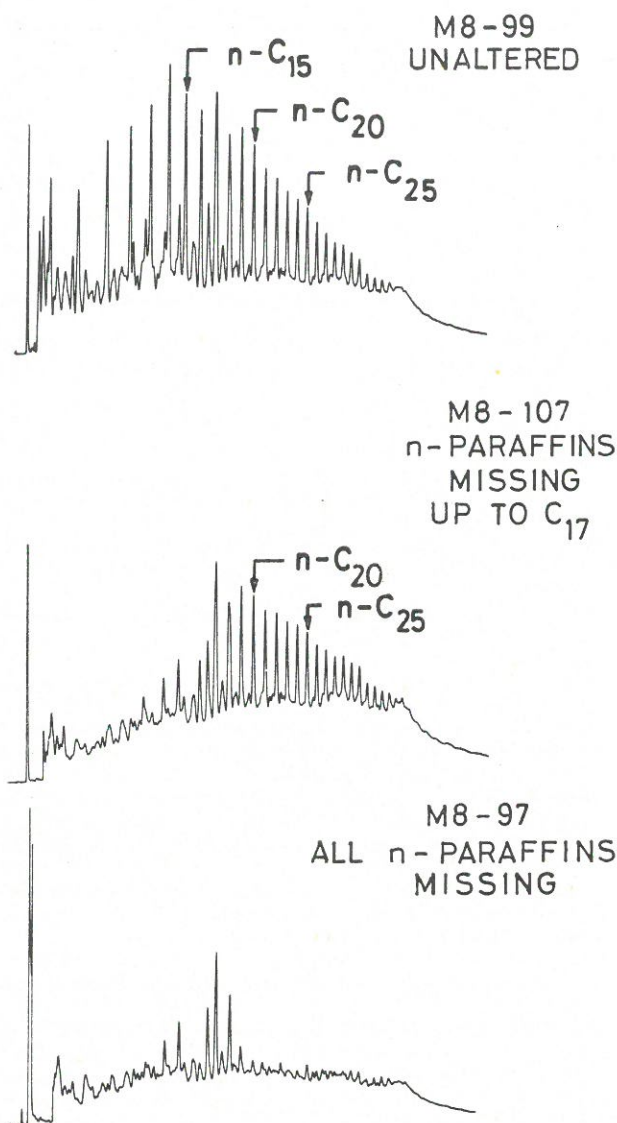


Figure 12. Bacterial degradation of crude oil in the reservoir. (After Winters and Williams, 1969).

quires a moderate temperature — 80°C is about the upper limit in which bacteria can survive — and influx of meteoric water to supply some oxygen and nutrients and to remove the metabolic products of the microorganisms.

The process of biodegradation has probably been encountered by most oil companies in their own fields. The most complete study has recently been published by Winters and Williams (1969) and Bailey et al (1973). Figures 12 and 13 taken from their studies clearly demonstrate how bacteria in laboratory experiments as well as in field samples attack crude oil in a selective

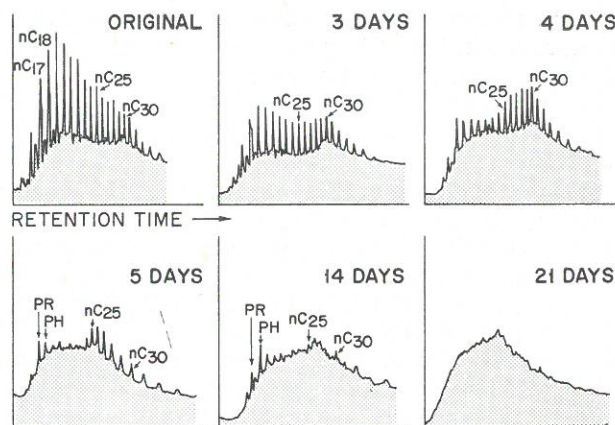


Figure 13. Bacterial degradation of crude oil in the laboratory. (After Bailey et al, 1973).

way by successive removal of *n*-alkane and branched alkanes. Eventually one and two ring naphthenes and aromatics are also attacked. The result is about the same as weathering of oil at the surface (Blumer et al, 1973). A medium-gravity oil may become heavy or even a tar or asphalt.

It has often been suggested that biodegradation can

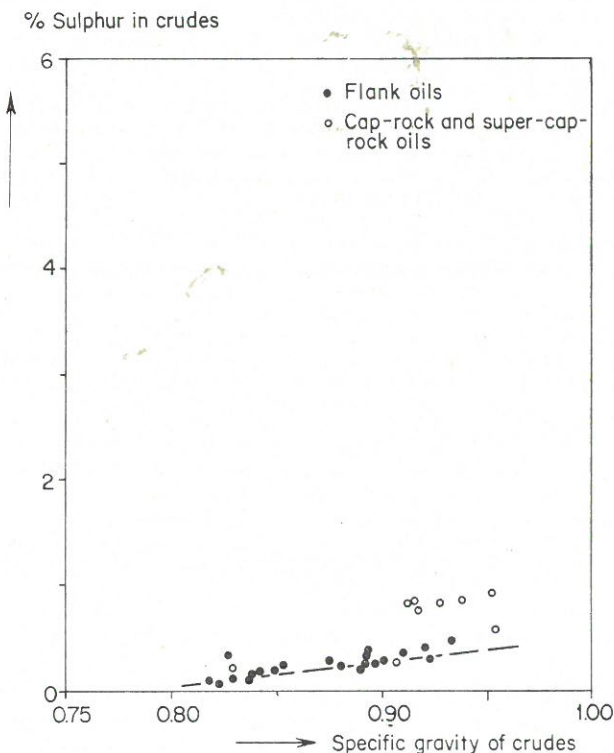


Figure 14. Sulphur in crudes associated with salt domes (Texas and Louisiana Gulf Coast).

change a light low-S crude into a heavy asphaltic sulphur-rich one. From the preceding it will be clear that biodegradation will increase the sulphur and asphaltene content to a limited extent because it removes that part of the oil that contains no asphaltic material and practically no sulphur thus causing a relative enrichment of the latter compounds. In our studies (Gransch and Posthuma, 1973) we have found no indications that sulphate-reducing bacteria introduce much extra sulphur into petroleum.

In the classical example of Gulf Coast cap-rock oils associated with salt domes, where biodegradation was detected and elemental sulphur was present as a result of bacterial sulphate reduction, the oils were found to be only slightly higher in sulphur (Fig. 14) and still extremely poor in asphaltenes, compared with the corresponding (unaltered) flank oils. Thus, although the conditions seemed to be ideal for the introduction of extra sulphur, the H_2S and/or elemental S hardly reacted with the oils and certainly did not lead to the formation of heavy, high-sulphur asphaltic oils as are present in western Venezuela and the Middle East.

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