

CHAPTER 11

The Origin of Petroleum

Framework of limiting conditions. Inorganic origin. Organic origin: nature of organic source material – modern organic matter. Transformation of organic matter into petroleum: bacterial action – heat and pressure – alteration of petroleum.

THEORIES of the origin of petroleum* may be divided into two groups according to their view of the primary source material as organic or as inorganic. Early ideas leaned toward the inorganic sources, whereas the modern theories, with few exceptions, assume that the primary source material was organic. The change was brought about by an increasing number of objections to the inorganic ideas; but, since these objections have not completely eliminated the possibility that inorganic substances—especially hydrogen—played some part in the origin of petroleum, inorganic theories still find occasional favor.

Although agreement on the organic origin of petroleum is nearly complete, there are many differences of opinion about the details of the processes by which it was formed and about the relative importance of the different source materials. Were they primarily marine or terrestrial? How much petroleum was derived from hydrocarbons that were part of living organisms and how much was derived from the transformation of hydrocarbon compounds into petroleum? What was the nature of the energy involved in the transformation? Bacterial action, heat and pressure, radioactive bombardment, and catalytic phenomena have all been suggested as energy sources that may have made conversion possible, and each may have participated either separately or in combination with one or more of the others.

Theories on the accumulation of oil and gas have a direct bearing on origin.

* The reader is especially referred to the thorough analysis by Hollis D. Hedberg, "Geologic Aspects of Origin of Petroleum," Bull. Amer. Assoc. Petrol. Geol., Vol. 48, No. 11 (November 1964), pp. 1755–1803. Includes an extensive bibliography.

Some geologists hold that all petroleum was formed in place, either at or adjacent to the position of the present pools; others hold that petroleum has migrated from areas of origin to trap areas, and that the source area does not necessarily coincide with the accumulation area. Some theories assume that oil was transported along with circulating water, whereas others assume that it migrated independently of water movement. Some geologists believe that the source material was deposited in the shale formations or transformed into petroleum within them, and migrated from there into the reservoir rocks, while others believe that the source material, possibly in the form of colloidal or water-soluble organic matter, was concentrated in the reservoir rocks, or even in the places where the traps are now found, and was there changed to petroleum. Each theory has some evidence and reasoning in its support, and each has some against it.

The theory one adopts—and it must always be a theory, since no one was present when the origin and accumulation took place—has a bearing on the method of exploration one pursues. If one believes, for example, that petroleum originated *in situ*, one looks for areas favorable to origin; if one believes that petroleum has migrated into traps at some distance from the area of origin, the critical question becomes the location of suitable traps and barriers to migration. Belief in a marine environment of origin suggests that the best place to explore is in marine sediments, whereas belief in the possibility of fresh-water sources would encourage exploration in areas underlain by continental and fresh-water sediments. If migration is permissible, however, the question of marine or nonmarine environment of origin is not always decisively significant, for migrating petroleum could concentrate wherever there was a trap within the limits of the barriers to migration.

FRAMEWORK OF LIMITING CONDITIONS

Hydrocarbon compounds* similar to those found in petroleum may be formed in the laboratory from various source materials. Laboratory conditions, however, are quite different from those in oil and gas pools. It is helpful, therefore, to list some of the natural environmental conditions known to prevail in present pools, in order to ensure that any theories or laboratory results proposed will be applied within a framework of conditions that can reasonably be compared to the known field conditions. These limiting conditions have been called a *geologic fence*.³ Some of the limiting factors are summarized as follows:

1. Nearly all petroleum occurs in sediments. These sediments are chiefly of marine origin, and it follows that the contained petroleum is also most likely

* A hydrocarbon compound is a complex hydrocarbon that contains, in addition to hydrogen and carbon, small amounts of other elements, such as sulfur, nitrogen, and oxygen.

marine, or related to marine conditions. Substantial amounts of petroleum are also found in sediments of continental, or nonmarine, origin. This petroleum, therefore, might conceivably have originated within the continental formations; but, since continental deposits are generally oxidized and grade into or are in unconformable contact with marine sediments, the petroleum in them is more likely to have been of marine origin and to have migrated into the nonmarine rocks.

2. Petroleums are extremely complex mixtures of many hydrocarbons occurring in homologous series, and no two petroleums are exactly alike in composition. This variation in composition is probably chiefly due to variations in the primary source material, or it may in part be the result of subsequent environments and of such vicissitudes as migration, catalysis, polymerization, pressure and temperature changes, and metamorphism. Although the components of petroleum unite to form an extremely complex mixture, the elemental chemical analyses of most petroleums are remarkably similar, even of those that vary greatly in physical properties. Most petroleum is chiefly composed of 11–15 percent hydrogen and 82–87 percent carbon by weight.

3. Petroleum is found in rocks from the Precambrian to the Pleistocene, although the occurrences in Precambrian and Pleistocene rocks are rare and anomalous. Organic carbon that is possibly of petroleum or petroleum-like origin, however, has been identified in rocks of Precambrian age.⁴ Some petroleum existed as such in Ordovician and Pennsylvanian time, for certain conglomerates of these two ages contain oil-saturated pebbles embedded in a barren matrix. Inspissated (?) petroleum deposits in the unconformity zone below Pennsylvanian rocks in Oklahoma would appear to be at least as old as Pennsylvanian. Asphaltic sandstone and grahamite in an unconformity zone within the Ordovician in the Lucien field, Oklahoma, appear to have formed in Ordovician time.⁵ These occurrences show that petroleum, once formed, may have been preserved against the forces of destruction and decay over long periods of geologic time.⁶

4. Until the advent of chromatographic and similar tools, no soluble (in organic solvents) liquid petroleum hydrocarbons had been found in the shales and carbonates that make up such a high percentage of the sediments of the world. Insoluble organic matter was found to be almost universal in the sediments, but no soluble petroleum hydrocarbons had been detected. Such soluble petroleum hydrocarbons as well as petroleum have now been found by a number of investigators,⁷ the amounts varying up to 50 or more barrels per acre-foot but commonly less than 10 barrels per acre-foot. Many of the hydrocarbons are also found in living organisms.

5. The temperatures of petroleum reservoirs rarely exceed 225°F (100.7°C), but temperatures as high as 300°F (141°C) have been measured in some of the deeper reservoirs. Minimum temperatures approaching the mean atmospheric temperature occur in some shallow pools. The presence of porphyrins in some petroleums indicates that the temperature of such petro-

origin, some 11,800–14,600 \pm 1,400 years ago, of both the source material and the enclosing sediments.

At Pedernales in eastern Venezuela,¹¹ a 20-foot sand enclosed within the 200-foot Paria clay formation contains an appreciable concentration of hydrocarbons—about four times that of the surrounding clays or the sands opening to the surface. Carbon-14 dating indicates that the entire Paria formation was deposited in less than 10,000 years and that the enclosed sand was deposited in about 5,000 years. The average hydrocarbon concentration in the sand is about 150 ppm; subtracting the average—25 ppm of hydrocarbons for the entire formation—leaves 125 ppm hydrocarbons as having accumulated since the sand was deposited. This is an average of 0.025 ppm per year, which if projected into the future would require only 1,000,000 years to accumulate 500 barrels per acre-foot of oil—a rich field.

INORGANIC ORIGIN

The chief interest of the "inorganic theories" on the origin of petroleum is historical, for most of them have long since been abandoned. It was natural that they should develop, however, in view of what was known about the universe during the eighteenth century.* The chief support for theories of inorganic origin lies in the fact that in the laboratory the hydrocarbons methane, ethane, acetylene, and benzene have repeatedly been made from inorganic sources. There has not been, however, any field evidence that the processes have occurred in nature, while there is an expanding mass of evidence of organic origin.

Theories that uphold the inorganic origin of petroleum have few supporters¹² today for several good reasons. In the first place, optical rotary power is a characteristic of petroleum, and especially of the intermediate boiling fractions (250–300°F). As far as is known, this phenomenon is almost entirely confined to organic matter and is observed only where biological agencies have prevailed. Another serious objection to any inorganic origin is that several homologous series of hydrocarbon compounds, containing great numbers of individual members, are found in all petroleum. All known compounds of this kind are of organic origin and could hardly be formed by inorganic agencies.

The lack of association of petroleum with vulcanism or its products, except in rare and anomalous occurrences, is another reason for doubting that there is any important relation between volcanic action and the origin of petroleum. As has been pointed out by White* and by DeGolyer,¹³ areas where oil or gas is found associated with igneous material, hot springs, or other evidence of vulcanism are underlain by sediments; there is no record of the occurrence of petroleum in volcanic areas where the underlying material is igneous. Most

* Don E. White in a personal communication:

leums has never exceeded 392°F (200°C), for porphyrins are destroyed at slightly lower temperatures. In other words, it suggests that the origin of petroleum is a low-temperature phenomenon.

6. The origin of petroleum is within an anaerobic and reducing environment. The presence of porphyrins in some petroleums means that anaerobic conditions developed early in the life of such petroleums, for chlorophyll derivatives, such as the porphyrins, are easily and rapidly oxidized and decomposed under aerobic conditions. The low oxygen content of petroleums, generally under 2 percent by weight, also indicates that they were formed in a reducing environment.

7. The fluctuations in pressure and temperature within a petroleum reservoir that result from the erosion, deformation, and deposition accompanying uplift, truncation, and burial in many basins are known to have been extensive. Pressure variations on petroleum have ranged from atmospheric pressure up to 8,000 or 10,000 psi. Temperatures also have fluctuated by as much as 250 degrees Fahrenheit. Petroleum, therefore, can undergo considerable change in pressure and temperature without being appreciably changed in physical character; changes in chemical composition have been observed, however, which may be attributed to either the environment of deposition or to depth of burial.*

8. The geologic history of oil pools indicates that in some of them neither lateral nor vertical oil migration of any consequence has occurred, whereas in others there has been extensive lateral and vertical migration. No consistent differences have been observed between oils that are known to have migrated and those that are known to have been formed where they are now found. Any valid theory of the origin of petroleum, therefore, must be independent of migration effects.

9. The time required to form petroleum and concentrate it into pools is probably less than one million years. The highest ratio of oil pool occurrence to volume of sediments occurs in the Pliocene series, which ended about one million (?) years ago.⁹ Late Pliocene sandstones and rocks such as the Plio-Pleistocene rocks in the Quirequire field of eastern Venezuela contain commercial oil. Small oil pools at Baku and in the Turkmen SSR, USSR, have been found in the "Baku stage" and in the "Apsheiron stage" of the Pleistocene. Oil has also been produced from Plio-Pleistocene rocks in the Summerland field of California. Pleistocene oil in pools such as these may have moved in from older rocks, yet could equally well have formed from equivalent marine rocks, and thus could measure the minimum time for forming petroleum and concentrating it into a major oil pool. The time required for hydrocarbons to form, however, may be much less, as shown by the hydrocarbons found in shallow cores (3-103 feet) of Recent sediments in the Gulf of Mexico,¹⁰ where measurable amounts of paraffinic, naphthenic, and aromatic hydrocarbons were found to range between 9 and 11,700 parts per million of dried sediments. The measurement of age by carbon 14 indicates a recent

occurrences of hydrocarbons associated with volcanic rock appear to be better explained as having emanated from associated sediments than as being genetically related to the igneous material.

If petroleum were of cosmic origin, we would expect to find it more uniformly distributed over the earth than it is, and to find it abundant in the older rocks. Petroleum of cosmic origin would be no respecter of the age of the rock, and should be uniformly distributed throughout the geologic column wherever there is permeability. We find, however, that the Precambrian, Cambrian, Triassic, and Pleistocene rocks are relatively low in hydrocarbons, even though they all contain large volumes of porous and permeable rocks.

ORGANIC ORIGIN

Three compelling reasons favor the belief that the chief primary source material of petroleum—the "protopetroleum"—was organic:

1. The vast amounts of organic matter and hydrocarbons now found in the sediments of the earth. Carbon and hydrogen predominate in the remains of organic material, both plant and animal. Furthermore, lesser but still important amounts of carbon and hydrogen and hydrocarbons are continually produced by the life processes of plants and animals. An abundant and widely distributed source of the two essential elements of petroleum—carbon and hydrogen—is therefore provided by organic material.

2. The fact that many crude oils have been found to contain porphyrin pigments,* and the fact that nearly all petroleum contains nitrogen, are more or less direct indication of the animal or vegetable origin, or both, of petroleum, because all organic matter contains both porphyrins and nitrogen.¹⁶ The porphyrins occur in the asphalts, and in the medium-to-heavy fractions when they have not been filtered and still contain asphaltic components. The amounts present vary, but in nearly half of the samples examined, which came from nearly all parts of the world, the porphyrin content ranged from 0.004 to 0.02 mg per 100 grams. In others it ranged from 0.4 to 4.0 mg per gram.

Nitrogen is an essential component of the amino acids [$\text{CH}_2(\text{NH}_2)\text{COOH}$]—that is, of the hydrolyzed protein of all living matter. Our noses remind us of that whenever we smell the ammonia (NH_3) given off by rotting refuse. Trask and Patnode¹⁷ found that the amount of organic nitrogen in sediments varied in weight almost in direct proportion with the organic carbon content. Either the nitrogen or the carbon content may be used to give an approximate measure of the organic matter present in a sediment; the organic matter in the

* Porphyrins are formed from the red coloring matter of blood (hemin) or from the green coloring matter of plants (chlorophyll). The porphyrins in petroleum occur in the form of complex hydrocarbon compounds that oxidize readily. Treibs found the vegetable porphyrins ($\text{C}_{20}\text{H}_{22}\text{N}_4$ and $\text{C}_{20}\text{H}_{20}\text{N}_4\text{COOH}$), derived from chlorophyll, to be far more plentiful than the animal porphyrins ($\text{C}_{20}\text{H}_{22}\text{N}_4$ and $\text{C}_{20}\text{H}_{20}\text{N}_4\text{COOH}$), derived from hemin.

some were formed from the lipid fraction of both plants and animals and have survived through geologic time with little change because of their stability; and that others were generated from nonhydrocarbon material such as fatty acids, aldehydes, and alcohols.

Asphalt. The asphaltic constituents, such as resins, maltenes, and asphaltenes, are the dark, nonhydrocarbon fractions of the organic portion of the sediments and of petroleum and consist primarily of carbon and hydrogen together with oxygen, nitrogen, sulfur, and the metals vanadium and nickel. They are complex high-molecular-weight substances, probably ranging in number from a few hundred into the hundred thousands, and make up from a trace to 50 percent of some crude oils.

The asphalt found in the nonreservoir sediments is similar to the asphaltic fraction of crude oil and of many natural asphalts deposited in seepages of crude oil. Asphalts have been found in the sediments in amounts that range from about 1 to 70 barrels per acre-foot, or slightly more than the hydrocarbons. Asphalts are complex compounds that have not been found in living organisms but which may have been derived from such materials as cellulose, lignin, purines, and pyrimidines. The presence of porphyrins (natural pigments related to chlorophyll and hemoglobin) in crude oil is evidence of its biological origin. Porphyrin mixtures are found in appreciable amounts chiefly in the crude oils of high asphaltic content, which further suggests an early origin for the asphaltic content.²⁷ Porphyrins occur as complicated metal-porphyrin mixtures, which suggests a low-temperature history, and also cause petroleum to cling to oil-wet reservoir rock surfaces.

Kerogen. Most of the organic material (85–95%) found in the nonreservoir rocks consists of kerogen, a solid pyrobitumen that is insoluble in ordinary organic solvents.²⁸ Heat is required to break it down. Its elemental analysis shows that it is chiefly carbon, hydrogen, and oxygen, with lesser amounts of nitrogen and sulfur. Kerogen found in typical marine nonreservoir rocks, is, when dried, a fine amorphous dark-brown to black powder that frequently shows a marked resemblance to coal dust. When the material is heated in test tubes, little or no oily distillate is formed as is formed when oil shales are heated. Apparently kerogen is of different types, even though the elemental analyses are similar. Some are indistinguishable from coal, whereas others, probably with a high asphaltic content, form the oil shales. Except for the variable asphaltic content, kerogen probably is not a source material for petroleum, but might be likened to the carrier material for the petroleum hydrocarbons and the related hydrocarbon compounds.

* *The Nature of Organic Source Material*

Organic matter that contains both soluble and insoluble hydrocarbons that might be considered as a potential source material for petroleum occurs in a

This organic matter is, in general, of three different kinds:

1. Hydrocarbons, similar in composition and in form to the heavier fractions of the crude oil found in the reservoir rocks.
2. Asphalts, similar in composition and in form to the asphaltic constituent of crude oil.
3. Kerogen, an insoluble, pyrobituminous organic matter that makes up the bulk of the organic matter of most nonreservoir sediments.

Hydrocarbons. The hydrocarbons found in the nonreservoir sediments presumably have come directly, either wholly or partly, from the hydrocarbons that are found in living plant and animal matter. They may result, in part, from processes whereby organic matter, or petroleum-like hydrocarbon compounds in the organic matter, were converted through minor changes into petroleum hydrocarbons. This conversion must have occurred either before or during diagenesis of the sediments, for the petroleum content of shales and carbonate rocks is rather universally distributed.

Studies have been made by Erdman²⁶ of many of the common petroleum hydrocarbons that are found in the sediments. He has analyzed the following characteristic fractions that are present both in petroleum and in the sediments in appreciable quantities:

1. The low-molecular-weight aromatic hydrocarbons—benzine, naphthalene, toluene, ethylbenzene, the xylenes, and other derivatives boiling up to 250°C—make up as much as 5 percent of the total hydrocarbon fraction of crude oils and are widely distributed in ancient sediments. They are not found in Recent sediments, however, and hence a chemical mechanism must be provided for their genesis by other than life processes.

Erdman suggests that such compounds as squalene, the carotenes, terpenes, and unsaturated fatty acids may have been precursors of the light aromatic hydrocarbons. All of these are formed in considerable quantities by land and sea plants and animals, and are converted by simple chemical reactions into aromatic hydrocarbons.

2. The light aliphatic hydrocarbons—methane, ethane, propane, the butanes, pentanes, etc.—are a characteristic fraction of crude oils and consist of the members through C_7 , or *n*-heptane, which is the lowest hydrocarbon known to be a constituent of living organisms, hence it is necessary to seek a chemical mechanism for the generation of these hydrocarbons.

Proteins are an important, and probably sufficient, source of the aliphatic hydrocarbons. Known reactions of many of the amino acids that make up the proteins will yield all the aliphatic isomers needed. Many amino acids are found in ancient sediments, but many more are found in Recent sediments, and in greater abundance.

3. The intermediate and heavy aliphatic, naphthenic, and aromatic hydrocarbons are found both in sediments and in crude oil. Erdman believes that

CURRENT THEORY

A recent far-reaching advance in our thinking concerns the discovery that petroleum hydrocarbons and related hydrocarbon compounds occur in many living organisms and are deposited in the sediments with little or no change. Many investigators have participated in these discoveries; a few are listed at the end of the chapter.²⁴

Nearly all shales and carbonates contain disseminated organic matter of three general kinds: soluble liquid hydrocarbons, soluble asphalts, and insoluble kerogen. The quantities range from a fraction of a barrel to more than 50 barrels per acre-foot of soluble hydrocarbons, and this represents the material remaining after the removal of an unknown amount during and after diagenesis. A significant observation by Hunt²⁴ is that with the exception of a few red shales, sandstones, and metamorphosed sediments, the presence of petroleum hydrocarbons is practically universal in the nonreservoir sediments.

In addition to the soluble petroleum hydrocarbons, the organic matter contains numerous insoluble hydrocarbon compounds, asphalts, and complex organic substances, some of which through bacterial action, heat, pressure, or catalytic action, or combinations of these, may be transformed into petroleum hydrocarbons.

These complex insoluble organic substances constitute kerogen—a pyrobitumin. Two types of kerogen are now known, a coaly type and an oily type. The coaly type does not form petroleum but contributes to the cannel coal and lignite deposits. The oily type does form petroleum. These organic substances tend to be oil-wet, and petroleum hydrocarbons may travel far attached to and protected by them.

The same kinds of hydrocarbons are found in both the nonreservoir sediments and in the living organisms. Most living organisms contain hydrocarbons,²⁵ hydrocarbon compounds, fatty acids, terpenoids, and steroids, all of which may have been deposited directly in the shales and carbonate rocks with little or no change. Thus an abundant and direct source is provided for petroleum hydrocarbons found in the sediments of the world. The migration and accumulation into oil and gas pools will be considered in the next chapter.

The organic matter now found in the nonreservoir sediments has the following general composition in percentages by weight as compared with the composition of petroleum:

	ORGANIC MATERIAL	PETROLEUM (CRUDE OIL)
Carbon	52-71	83-87
Hydrogen	5-10	11-15
Oxygen	5-20	Trace to 4
Nitrogen	4-6	Trace to 4
Sulfur		Trace to 4

ancient sediments is, on the average, 1.1 times as abundant as the carbon and 24 times as abundant as the nitrogen. Nitrogen is present in practically all petroleum, chiefly as a constituent of complex hydrocarbon compounds. The continuous chain of occurrence of nitrogen, from living matter through organic matter in sediments to petroleum, therefore seems to offer a reasonable indication of the organic nature of the source material.

3. Optical activity—the power to rotate the plane of polarization of polarized light—is a property of most petroleum, and is not known to occur in oils of inorganic origin or in inorganic substances or minerals with the exception of cinnabar (HgS) and quartz (SiO_2). The power of optical rotation is not uniform throughout the distillation range, but is usually at a maximum in the fractions having intermediate boiling points (from 250° to 300°C). It is believed that the optical activity in most petroleum is due to the presence of cholesterol ($\text{C}_{27}\text{H}_{46}\text{OH}$), which is found in both vegetable and animal matter.¹⁸

4. A wide variety of petroleum hydrocarbons, and even crude oil, have been found included in the organic material that is found in nearly all nonreservoir rocks, such as the shales and carbonates. The same types of hydrocarbons occur in both the fine-grained sediments and in crude oil. The intimate relation of the organic material and the petroleum in the sediments leaves no doubt that organic matter was the original source of the petroleum.

Sir William Logan may have been the first to express the view that petroleum is possibly of organic origin. In 1863 Robb¹⁹ credited him with the view that ". . . petroleum owes its origin, in all probability, to the slow decomposition and bituminization of organic matter . . . deposited with the other materials of which the rocks are composed."

Hackford²⁰ showed in 1922 that the ash content of algae is similar to that of crude oil—both contain iodine, bromine, phosphorus, and ammonium salts. Later he enlarged on this idea²¹ and reached the conclusion that oil and bitumen could be produced by the pyrolysis and hydrolysis of algae at low temperatures.

An even more direct approach to a correlation between petroleum and its source material is contained in the work of Sanders.²² He found a wide variety of micro-objects in crude oils from many pools. The long list of materials he found includes calcified or siliceous skeletal tests or frameworks, petrified wood fragments, foraminiferal tests, minute pyrite globules or concretions, vegetable remains encrusted with silica, small crustaceans, insect scales, barbules, spore coats, algae, fungi, cuticles, resins, and fragments of coal and lignite. Some of this material may well have been entrained in the petroleum from a foreign source as it moved through the rocks. The large variety of organic material, however, strongly suggests a genetic relation between it and the petroleum in which it occurs.

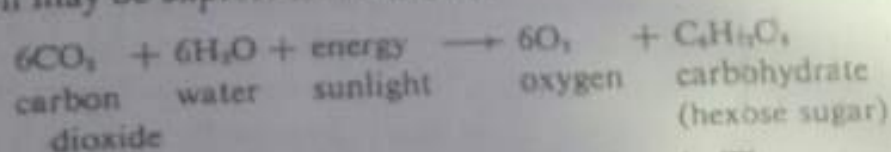
The evidence of petroleum hydrocarbons in modern Gulf of Mexico sediments is an additional proof of organic origin.²³ The age of the oil studied, as determined by carbon, indicates that the oil has not migrated and is not seepage oil. It was most likely formed at such shallow depths and in such late sediments by the decomposition of organic matter deposited along with the sediments.

ing, and burrowing organisms of the sea bottom are known as the benthonic (Greek, *benthos*, deep sea).

The organic cycle of the sea begins with an abundance in sea water of the necessary inorganic elements—carbon, hydrogen, oxygen, phosphorus, nitrogen, iron, and many trace elements, which, together with sunlight, make plant life possible. Many of the plants are of minute or even microscopic size, and these constitute the food material for animals that, although minute, are larger than the plants on which they feed or graze. These tiny animals, in turn, become food for larger animals. The death of the plant and animal organisms, followed by their decomposition and decay, permits a partial return of the elements of which they consist to the sea in the form of various chemical compounds; only a small part of the organic material, in various stages of decomposition, is buried and preserved under the sediments that are being deposited. Decomposition and decay of organisms involves bacterial action, and bacterial action may be the chief agency that converts or aids in the conversion of hydrocarbon compounds into more petroleum-like hydrocarbons. During the organic cycle of both plants and animals, in fact, many, if not all, of them also produce hydrocarbons as a normal part of their existence.³¹

Most of the organic content of the ocean is either dissolved or in a colloidal form in the sea water. The rest is contained in the plant and animal life, chiefly in the microscopic and semimicroscopic organisms, the suspended, floating, or free-swimming plankton found in the water penetrated by sunlight. It is difficult to estimate the rate at which organic matter is produced in the sea because of the many variable factors concerned in the process, but several observations have shown that phytoplankton is produced at a rate as high as several hundred grams of carbon per cubic meter of sea water per year.³² Photosynthesis in the oceans has been estimated to produce 12 million tons (80,000,000 barrels) of hydrocarbon material annually.³³ A minute fraction of this amount, preserved in the sedimentary rocks, would supply all the known petroleum deposits, plus those that we can expect to discover in the future.

Plant Life. Marine plants are able to synthesize complex organic substances by photosynthesis from the inorganic compounds dissolved in the sea water. Photosynthesis is the process whereby the pigments in the plant tissue are able to intercept the radiant energy from the sun, and, in the presence of carbon dioxide, to manufacture carbon compounds from water and carbon dioxide. The equation may be expressed as follows:



Photosynthesis is an endothermic reaction (uses heat). The energy of sunlight, stored in the complex organic product, becomes the source of energy for plant life and indirectly for animal life. The free oxygen released by photosynthesis

is used in the respiration of both the plant and the animal life of the sea. The carbohydrates, in part, are presumably reduced in the direction of hydrocarbons in the reducing, oxygen-free environments into which they fall and in which they are buried.

The depth to which sunlight penetrates the water therefore determines the thickness of the layer of sea water that is favorable for the production of plant life and consequently of the life that feeds upon plant life. This depth varies, depending on the turbidity of the water, but in clear water it is about 250 feet or more. It has been estimated that coastal waters³⁴ produce at least fifty times more plant life than do the open ocean waters, and the coastal water that is richest in organic material is off the mouths of rivers.

Marine algae offer some of the most promising source material for petroleum.³⁵ The blue and green algae are the most common; in addition to utilizing sunlight to form chlorophyll and other, unidentified substances, such as enzymes, they assimilate their mineral constituents through their entire surface from the waters in which they grow. Because of this faculty, the same algal species may vary in chemical composition, depending upon the composition of the water in which it lives. Algae are probably the chief agents of lime secretion and deposition:³⁶ one genus, *Halimeda*, deposits aragonite, and another, *Lithothamnium*, deposits calcite. Both genera are especially common in organic reef deposits.

Diatoms are algae characterized by siliceous shells, or frustules. They have formed great deposits known as diatomaceous earth and are probably the most important group of algae in the organic economy of the sea. Some geologists believe that they provide the source material for much of our oil.³⁷ A significant product of their life process is vegetable oil, droplets of which may be frequently seen within diatom shells.³⁸ It has been estimated that from 5 to 50 percent of the volume of these diatoms consists of oil globules,³⁹ which may be freed from the shell if it should encounter fresh water and break because of the osmotic pressure from within the shell.⁴⁰ In the colonial algae *Elaeophyton*, even the cell walls have been observed to consist largely of oil or oily substances.⁴¹ This oil may be considered the medium in which such organisms store food energy, serving the same purpose as the oils contained in nuts and seeds.

Marine water normally provides an equilibrium between the various organisms that constitute its population. This equilibrium is not stable, but is changing constantly with changes in marine conditions—currents, waves, upwelling, rainfall, and fluctuations in temperature and the supply of nutrients. From time to time, therefore, the conditions will be especially favorable to one organism or type of life, which will then multiply rapidly and thus upset the normal balance. This rapid multiplication of microorganisms is termed *blooming*. It may sometimes be recognized from a discoloration of the water—which is most commonly tinged with blue, red, or green—or from the decomposition of a deposit of organisms washed up on the shore. Along the Copalis

organic compounds that form on the land and are carried into the oceans by the rivers are the humus substances, which include humic acid ($C_{26}H_{10}O_6$), geic acid ($C_{20}H_{12}O_7$), and ulmic acid ($C_{27}H_{11}O_6$). These humus substances are formed by the slow decomposition of the lignins in peat and are found in soils highly charged with decaying vegetation.⁵² Vast quantities of humic acid are forming constantly in swampy regions and, especially in the tropics, are carried into the oceans, either in solution or in colloidal dispersion. Mingling of fresh and salt water might cause the precipitation of the organic material.⁵³ One part of humic acid dissolves in 8,333 parts of water at 6°C and in 625 parts of water at 100°C. Temperature changes alone, therefore, would be sufficient cause for extensive precipitation of some of the organic matter upon reaching the oceans.

Waxes and resins are commonly produced by many kinds of vegetation. They are generally more resistant to decay than other organic residual products, and probably are the source of the benzene-soluble montan waxes that are obtained commercially from lignite coals in both Europe and the United States. A similar wax is also found in some peat deposits. These substances are organic, but because of their close association with the rocks they are generally grouped with the "mineral" waxes, such as ozokerite and the paraffin hydrocarbons. The chemical constituents that have been identified in these waxes include a number of esters, acids, alcohols, ketones, hydrocarbons, and resins.⁵⁴ An analysis (in percent) of five benzene-soluble waxes from Europe and the United States gives the following average composition:⁵⁵

Hydrogen	11.9
Carbon	79.4
Nitrogen	0.1
Sulfur	0.4
Ash	0.2
Oxygen (by difference)	7.8

A possible important source of hydrocarbon is apparently forming at the uppermost surface² of the ground, where it might readily be washed away and into the rivers. McDermott* has had the material occurring in the upper half inch of the soil and at depths of 5-7 feet below the surface analyzed, and finds the following average composition (in percent) of the wax obtained from samples covering the whole of southern Taylor County, Texas:

	UPPER HALF INCH	5-7 FEET BELOW SURFACE
Hydrogen	10.6	11.9
Carbon	71.5	75.2
Oxygen	10.8	12.4
Nitrogen	0.0	0.5
Ash	1.1	0.0
Molecular weight	170	475
Melting point	32-36°C	33-38°C

* Eugene McDermott in a personal communication.

be as likely a source of organic matter as might at first be thought, since the shells may have been concentrated after the living tissues had left them. In the modern seas the naked masses of protoplasm leave the tests to drift around freely, so that a large proportion of the tests preserved in the rocks were probably empty of animal tissue at the time of burial.⁴⁷

Silliman,⁴⁸ in a significant article published in 1846 on the living calcareous corals, stated that the organic content of corals ranged between 4 and 8 percent of the total mass. Silliman also noted that a fatty, wax-like residue, soluble in ether, but insoluble in alcohol, could be produced by dissolving the corals. Later Clarke and Wheeler⁴⁹ verified his observations, finding the percentage of organic matter in the shells of marine organisms to vary between 2 and 10 percent for common invertebrates. Many less-common invertebrate shells contained as much as 40-50 percent organic matter. Bergmann and Lester⁵⁰ investigated these chemically and found that they contained sterols, cetyl alcohol, low-melting hydrocarbons, and small amounts of ketones. The yield of ether-soluble waxes runs from 0.3 to 0.5 percent by weight of the total mass of the coral, or about 10 percent by weight of the organic content of the stony corals. The organic material was found to penetrate deep into the coral structure, some sea fans (*Gorgonaceae*) containing up to 3.0 percent of the total weight of nonsaponifiable material. Reef-builders are thus seen to be vast storehouses of potential source material for petroleum.

Nonmarine Organic Matter

Much organic matter reaches areas of marine sedimentation by way of streams. The organic matter found in modern streams may constitute more than 50 percent by weight of the total solids,⁵¹ as shown in Table 11-1.

Probably the most important potential source materials for the biochemical

TABLE 11-1 Percentage of Organic Matter in Dissolved Solids of River Waters

River	Percentage	River	Percentage
Danube	3.25	Amazon	15.03
James	4.14	Mohawk	15.34
Maumee	4.55	Delaware	16.00
Nile	10.36	Lough Neagh, Ireland	16.40
Hudson	11.42	Xingú	20.63
Rhine	11.93	Tapajos	24.16
Cumberland	12.08	Plata	49.59
Thames	12.10	Negro	53.83
Genesee	12.80	Uruguay	59.90

Source: from Clarke, Bull. 770, U.S. Geol. Surv. (1924), p. 110.

Beach of Washington,⁴² for example, rapid propagation of the diatom *Aulacodiscus* periodically causes great masses of it to accumulate for several days along the tidal flats.

Extensive "oily patches" are formed during the months of August and September along the western coast of Japan because of the swarming of the pelagic diatom *Rhizosolenia*, and the same alga covers the Sea of Azov from September to December, giving it the dark-brown color, smooth surface, and marshy odor of a placid swamp. A different effect of blooming is the occasional development of a toxic substance that causes the death of great numbers of fish, whose bodies sink to the bottom or pile up on shore.⁴³ Twice a year in Whale Bay, on the west coast of Africa, a blooming of plankton secretes a poisonous substance that kills all the fish in the area. The dead organic tissue falls to the bottom and forms a *sapropel** in the anaerobic environment.⁴⁴ A gelatinous agglomeration of diatoms, buoyed up by oxygen bubbles resulting from photosynthesis, forms the *mare sporco* of the Adriatic. The floating masses become large enough to break fishermen's nets by their weight.⁴⁵

We have, then, in marine algae and the modern phenomenon of algal and diatom blooming, a mechanism whereby material with a high carbon and hydrogen content, including petroleum hydrocarbons, may form in large quantities. Whether some form of algae or algal blooming has provided a source material for crude oil is unknown, but they form what is probably the most promising and widespread potential source material now known.

Animal Life. Partly as a result of Engler's distillation of oil from menhaden,[†] and also because of the common association of petroleum with fossiliferous marine sediments, fossils, especially microfossils, have long been considered as evidence of a possible petroleum source material. The association of oil pools with fossiliferous limestone, shale, or sandstone seems, on the face of it, a good reason for believing that at least a portion of the soft parts of the organisms were decomposed and changed into petroleum, leaving the hard skeletons behind as fossils. Support is given to this idea by the fossil casts filled with oil or with petroleum-like liquids⁴⁶ that have been found in many places and by the hydrocarbons that are found in nearly all living organisms. (See also pp. 514 and 516.) The animal population of the modern seas is both enormous and complex, and it alone produces soluble organic matter and hydrocarbons in quantities adequate for all organic source requirements.

The sorting and transporting action of ocean waves and currents may cause large volumes of shells to accumulate far from the areas in which the shell-bearing animals lived. Therefore, a rock that consists largely of shells may not

* From Greek *sapros*, "rotten"; organic debris that consists largely of the remains of recently deposited marine plants and animals and accumulates on the ocean floor.

† A fish found along the Atlantic coast of the United States and used for the making of oil and fertilizer.

The waxes are insoluble in water and appear to be attached to the soil particles. The amounts vary widely at the surface, but average about 300 ppm, whereas they vary little in the deeper samples, where the average is about 75 ppm. McDermott is of the opinion that these hydrocarbon waxes are formed from hydrocarbon gases that migrate from below and become concentrated at the surface of the ground, possibly in part as a function of photosynthesis; an alternative possibility is that they are formed at the upper surface of the ground, where the sunlight can reach the microscopic plants. The changed character and lower concentration of the deeper waxes may be explained as being due to their having been carried downward by surface waters. If the subaerial surfaces of unconformity of the geologic column were all the loci of hydrocarbon formation such as this, there has been a continuous source of organic matter to be carried to the oceans for as long as there have been sunlight and microscopic plant life on the earth.

Decomposed grass and root hairs in the upper soil contain unsaturated hydrocarbons and all of the saturated hydrocarbons into the C_{20} range. The spectrograms from soil samples correspond closely with those of the vegetation, and this suggests that the soil hydrocarbons are at least partly if not wholly due to vegetation, and not to the upward migration of hydrocarbons from buried petroleum accumulations—the basis for geochemical prospecting. It further suggests that the organic matter of the streams that empty into the oceans may contain large amounts of hydrocarbons that require little if any further treatment to become a part of the petroleum hydrocarbons of the sediments.⁵⁶

Cate⁵⁷ suggests that *podzolization* or the downward movement of organic matter, metals, and clay through the weathering profile of soils may involve catalytic reactions that transform some of the organic matter into bituminous substances, including petroleum and coal. Although such a process is complex, it appears to be possible, and certainly should be considered as providing a possible source for some petroleum hydrocarbons and hydrocarbon compounds.

Recycled Petroleum. Petroleum hydrocarbons and related hydrocarbon compounds eroded from the land may conceivably be carried by the rivers to the ocean and redeposited along with recycled sedimentary particles in both reservoir and nonreservoir sediments. Eroded petroleum may come from two sources: (1) the oil disseminated through the nonreservoir shales and carbonates and (2) the oil contained in any fields that have undergone erosion since the beginning of Paleozoic time. Such petroleum is in addition to the hydrocarbons that form at the surface of the ground, probably with the aid of photosynthesis, and are later eroded off. Presumably the more stable, heavier hydrocarbon fractions and the asphaltic fractions eroded from the nonreservoir rocks and from the oil pools would be the most susceptible to preservation and redeposition; this might help explain why the oil in the younger Tertiary rocks is generally heavier (of lower gravity). The oil-wet properties of some clays and of insoluble organic matter may have provided a protective carrier mechanism by which these hydrocarbons were transported from areas of erosion to the oceans. The volume of such petroleum source material is vast beyond comprehension, and it seems reasonable to speculate