INFERENCES ABOUT THE ORIGIN OF OIL AS INDICATED BY THE COMPOSITION OF THE ORGANIC CONSTITUENTS OF SEDIMENTS

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ABSTRACT

Petroleum originates mainly from the organic matter in marine sediments, which is derived chiefly from remains of planktonic organisms in the overlying water. The original organic source material, represented by the plankton, is taken in as food by many other types of organisms in succession, and in this process of utilization it decreases very greatly in quantity before the time it reaches the sea floor and is deposited in the sediments. The quantity of organic material continues to diminish after it is buried in the sediments, but the rate of diminution is small compared with the rate while the organic matter is in the overlying water. The composition of the average plankton is 24 percent of protein, 3 percent of fat, and 73 percent of carbohydrates and other nonnitrogenous compounds. In recently deposited sediments the proportion is protein 40 percent, fat 1 percent, and carbohydrates and other compounds less than 60 percent. In ancient (lithified) sediments the proportion is protein 27 percent, fat 1 percent, and other compounds more than 60 percent.

As the organic matter passes from plankton to lithified sediments it tends to become more complex in composition. This is because the oxygen content decreases progressively with depth in the buried sediments, and in an environment deficient in oxygen complex organic matter becomes progressively less satisfactory as food for living organisms; thus the unutilizable residue becomes more and more complex. The influence of the lack of free oxygen in the environments in which the organic matter lies is reflected in the progressive loss of oxygen in the organic constituents between the time of formation of the plankton and the time of the burial of the organic matter in the sediments. In plankton the oxygen content of the organic constituents is estimated to be 39 percent, in recent sediments 30 percent, and in ancient sediments 23 percent. These are average figures; individual samples may vary considerably.

Estimates of the ultimate composition of the organic matter in different stages of its history afford a means of evaluating the ratio of organic matter to carbon. This ratio is a useful index in calculating the organic content of substances provided the quantity of carbon is known. The average ratio of total organic matter to carbon in plankton is 2.1, in recent sediments 1.8, and in ancient sediments 1.6.

Cellulose, fats, and simple proteins ordinarily seem to be present in sediments in amounts too small to be the principal source of petroleum. Further evidence against fats as a source of oil is the unsaturated character of the fats compared with the saturated character of petroleum; the prevalence of naphthene and other ring compounds in crude oil and their scarcity in fats; and the chemical stability of fatty substances. Petroleum apparently must come mainly from other compounds, such as complex proteins and nonnitrogenous complexes.

The tendency of the organic constituents to come to chemical equilibrium after they have been buried to a depth at which bacterial decomposition is insignificant is regarded as a possible factor in the generation of liquid hydrocarbons. Liquid hydrocarbons after they are formed may dissolve organic substances. The organic constituents of the resulting solution may then react with one another in an effort to reach a point of equilibrium. Repeated solution and subsequent adjustments of this character lead eventually to the formation of petroleum.

INTRODUCTION

To solve the problem of the origin of petroleum it is essential to know something about the composition of the substances from which the oil might be derived. Much information concerning source beds has been gathered in the course of studies supported jointly by the United States Geological Survey and the American Petroleum Institute. The available data suggest certain inferences about the origin of oil, which are presented in this paper for consideration by geologists.

Petroleum is generally believed to be formed from organic substances that have accumulated in sediments. The geologic conditions under which it is found indicate that it is commonly derived from fine-grained marine deposits, though some oil possibly may have originated from continental sediments. The mother materials of petroleum, therefore, being largely confined to marine sediments, must be derived from organic matter present in the overlying water. Most of this organic matter originates in the sea water itself, but some is washed from the land.

The successive changes in the chemical nature of the mother substances of petroleum from the time these substances first get into the water until they accumulate in the underlying sediments give clues as to the processes that may take place after they have been deposited. After sediments have been buried to a depth of a few feet they cannot be collected for study by ordinary coring devices, and the changes that take place in them have to be ascertained largely by inference and by comparison with lithified sediments of different geologic ages which appear to have had a similar origin. Petroleum, apparently, is not generated until the sediments have been buried for some time.[1] Consequently, any method of study that affords evidence of ways in which organic substances in sediments may be altered is an aid in the solution of the problem.

[1] Trask, P. D., and Wu, C. C., Does petroleum form in sediments at time of deposition?: Am. Assoc. Petroleum Geologists Bull., vol. 14, pp. 1451–1463, 1930.

The chemical composition of organic substances in sea water and in the underlying sediments is difficult to ascertain, because of the paucity and inadequacy of available information. The data, therefore, have to be presented in very general form, and care must be taken in drawing conclusions. The inferences presented in this paper may serve mainly to stimulate discussion and to suggest lines of study that may advantageously be pursued further.

DECREASE IN QUANTITY OF SOURCE MATERIAL WITH TIME

DECREASE IN WATER

The main source of organic matter in sediments is the floating plant life—the phytoplankton.[2] The phytoplankton serves as the main supply of food for the animal life of the sea, and much of it is devoured or decomposed before it is buried in the underlying sediments.

When organic matter in any form is taken in as food by another organism, part of it is assimilated into the tissues of the organism, part is excreted as unutilizable residue, and the rest is used by the organism to generate energy. The part that is converted into energy is largely destroyed in the process, leaving waste products, such as carbon dioxide and water.

The quantity of unutilizable residue in food is small, though the proportion varies somewhat with the form of food and the type of animal that eats it. In human beings the quantity of unassimilable residue is about 5 percent of the food consumed,[3] and this figure can be taken as generally indicative of the small proportion of unassimilable organic matter in the food eaten by other organisms, such as marine animals.

The proportion of the food transformed into body tissue also is small. If the mature stage of the animal is long compared with the growing stage, this proportion is particularly small. The plaice, a kind of flounder, may be taken as an example of an organism of this type in the sea. While the plaice is growing, about one-sixth of the food it consumes is transformed into body tissue,[4] but after it reaches maturity it increases very little in weight; therefore, for its life as a whole the quantity of food material transformed into protoplasm is small. If the mature stage of the organism is short compared with the growing stage, the proportion of food converted into protoplasm might be thought to be relatively large. However, bacteria, which may be taken as an example of this type of organism, utilize less than 20 percent of the energy they evolve.[5] Accordingly it may be presumed that less than 20 percent of the food they consume is transformed into protoplasm. Consequently, even in the type of organism that has a relatively long growing period, probably a comparatively small proportion of the food consumed is transformed into protoplasm.

Thus the first time the planktonic organisms serve as food, a relatively large part—under ordinary conditions much more than half—is transformed into energy and is lost as organic matter; a small part is excreted as unassimilable residue; and only the part that goes into the building of protoplasm remains as organic matter more or less similar in nature to the original food material.

The organism that fed upon the plankton in turn serves as food for some other organism, with a similar transformation of organic matter into energy, residue, and a relatively small amount of new protoplasm. This process may be repeated several times. The ultimate result is an immense diminution in volume of the original organic matter, the presence of a moderate amount of unassimilable residue, and the formation of a very small proportion of living organic matter.

The unassimilable residue may still serve as food for certain types of organisms, but, as pointed out by Krogh,[6] being composed of waste products, it is likely to be a relatively poor source of nourishment for most forms of life. As the organisms that feed upon it are subsequently consumed by other organisms, the resulting waste products become progressively less satisfactory as sources of food, until ultimately the residue consists of rather complex substances that are resistant to decomposition. In the later stages of its history, particularly after it has been buried some distance beneath the surface of the deposits, where micro-organisms are the main forms of life present, some of the organic residue may consist of undecomposed cells of bacteria.

The nature and quantity of the ultimate residual material depends to a considerable extent upon the availability of oxygen for the oxidation of the organic substances and the resulting production of energy. In the water and in the upper few inches of the sediments the supply of oxygen is ordinarily adequate to support considerable life. In this zone, therefore, the organic matter decreases greatly in quantity. In fact, in some areas in which the water is well aerated the organic matter may be almost completely destroyed before it reaches the sea bottom, and only very little residual organic material may be deposited.

DECREASE IN SEDIMENTS

The organic matter that accumulates in sediments consists mainly of the resistant residual compounds. After it has been buried a few inches beneath later sediments, it is associated with little or no free oxygen [7]

[2] Trask, P. D., Origin and environment of source sediments of petroleum, pp. 110–172, Houston, Tex., Gulf Publishing Co., 1932.

[3] Sherman, H. C., Chemistry of food and nutrition, p. 101, New York, Macmillan Co., 1918.

[4] Petersen, C. G. J., and Jensen, P. B., Valuation of the sea, I, Animal life of the sea bottom, its food and quantity: Danish Biol. Sta. Rept. 20, p. 66, 1911.

[5] Waksman, S. A., Principles of soil microbiology, p. 420, Baltimore, Williams, Wilkins Co., 1927.

[6] Krogh, A., Dissolved substances as a food of aquatic organisms: Conseil perm. expl. mer Rapports et procès-verb., vol. 75, pp. 7–37, 1931.

[7] ZoBell, C. E., and Anderson, D. Q., Vertical distribution of bacteria in marine sediments: Am. Assoc. Petroleum Geologists Bull., vol. 20, p. 266, 1936.

and hence is unlikely to be altered greatly during its future history. The remarkable decrease in number of bacteria within the upper 8 inches of marine sediments [8] is evidence of the decrease in oxidation of organic matter. Thus, the rate of decrease in quantity of organic matter is much greater during the interval between the time it is formed by the phytoplankton and the time it is buried a few inches beneath the sea floor than in the subsequent stages of its history.

The data on the organic content of recent (unconsolidated) and ancient (lithified) sediments obtained by the writer and his associates in general support this conclusion. The average decrease in organic matter within the upper 12 inches of marine sediments, as indicated by 150 samples of sediments from many types of environment, is 15 percent,[9] and the range of decrease is from less than 1 percent to 45 percent. Twenhofel [10] mentions a lake in Wisconsin in which the organic content of the sediments practically disappears within a few feet of the surface of the deposits, but complete decomposition of the organic matter within a few feet of the surface almost certainly is not a general characteristic of marine sediments. Of many thousand samples of ancient sediments analyzed by the writer and his associates,[11] practically all contain measurable amounts of organic matter, and the average organic content is 1.5 percent of the weight. In recent marine sediments of similar character, represented by about 2,000 analyses from many parts of the world, the average organic content is 2.5 percent.[12] The number of samples is so large and the localities from which they came are so widespread that the data may be considered as indicating the general order of magnitude of the organic content of recent and ancient fine-grained marine clastic sediments. The average loss in organic content during burial is therefore of the order of magnitude of 2.5−1.5, or 1 percent, and the proportionate loss is 1.0÷2.5, or 40 percent. This figure of 40 percent naturally is an approximation, and the loss in individual sediments may differ considerably from it. Nevertheless, the loss of organic matter in buried sediments is relatively small compared with the loss of organic matter between its planktonic source and the form in which it occurs in the upper layers of sediment.

[8] Idem, p. 262. Reuszer, H. W., Marine bacteria and their role in the cycle of life in the sea, III, The distribution of bacteria in the ocean waters and muds about Cape Cod: Biol. Bull., vol. 65, pp. 480–497, 1933.

[9] Trask, P. D., op. cit., p. 206.

[10] Twenhofel, W. H., Sedimentation and stratigraphy from modern points of view: Jour. Paleontology, vol. 8, pp. 456–458, 1934.

[11] Trask, P. D., and Hammar, H. E., Organic content of sediments: Drilling and Production Practice, 1934, pp. 117–130, Am. Petroleum Inst., 1935.

[12] Trask, P. D., Origin and environment of source sediments of petroleum, pp. 249–284, Houston, Tex., Gulf Publishing Co., 1932.

GENERAL COMPOSITION OF ORGANIC MATTER

PLANKTON

The phytoplankton (the part of the plankton consisting of plants) comprises two main groups of organisms—the diatoms, which have siliceous skeletons, and the peridineans or dinoflagellates, which consist entirely of soft parts. Other forms of plant life are present, but these two groups represent the types that are most commonly caught in the nets used in oceanographic investigation. The copepods, small crustaceans that feed on the phytoplankton, are generally considered a part of the plankton.

The composition of these three forms of plankton, as determined by Brandt,[13] is summarized in table 1. The results are presented on an ash-free basis and are given in terms of ether extract, crude protein, and nonnitrogenous constituents. The ether extract is roughly equivalent to the fat content; the crude protein represents the nitrogenous constituents and is 6.25 times the nitrogen content; the nonnitrogenous constituents represent the remainder of the organic matter—that is, the nitrogen-free, nonfatty compounds. The nonnitrogenous compounds correspond principally to the carbohydrates. The term "crude fiber" refers to the nonnitrogenous compounds that are insoluble in weak acid and weak alkali; cellulose is included with the crude fiber.

[13] Brandt, K., Beiträge zur Kenntniss der chemischen Zusammensetzung der Plankton: Wiss. Meeresuntersuchungen, neue Folge, Abt. Kiel, Band 3, pp. 43-90, 1898.

TABLE 1.—*Composition of different types of organic matter on ash-free basis*

	Percent [1]				Ratio		
	Crude protein	Ether extract	Nonnitrogenous compounds	Crude fiber or cellulose	Organic matter to carbon	Carbon to nitrogen	Hydrogen atoms to carbon atoms
Marine plankton:[2]							
Peridineans	14	1. 5	85?	42?	2. 2	12. 3	1. 77
Diatoms	29	8	63	0	2. 0	8. 0	2. 2?
Copepods	[3] 65	8	22	0	2. 0	4. 9	1. 88
Average plankton	24	3	73	14?	2. 1	10. 2	1. 87
Lake plankton:[4]							
Net plankton	53	8	39	5	1. 97	6. 2	------
Nannoplankton	49	5	46	5	1. 98	6. 4	------
Micro-organisms:[5]							
Marine algae	6	3	85	4	------	------	------
Soil fungi	7–50	1–10	37–82	------	2. 05	8–50	1. 94
Soil bacteria	40–75	------	------	------	1. 78	5±	1. 65
Marine invertebrates:[6]							
Crustaceans	75	6	5	0	2. 05	4. 0	1. 70
Pelecypods	72	8	20	0	2. 19	4. 2	1. 67
Gastropods	64	9	25	0	2. 10	4. 9	1. 67
Echinoderms	67	11	18	0	2. 10	4. 6	1. 76
Worms	64	13	19	0	1. 89	5. 1	1. 68
Coelenterates	78	11	7	0	2. 00	4. 2	1. 66
Fishes:[2]							
Herring	60	38	0	0	------	5?	------
Flounder	95	5	0	0	------	4?	------
Marine plants:[7]							
Fresh Zostera	19	------	75	------	2. 18	11. 4	------
Decaying Zostera	6	------	90	------	2. 41	34. 9	------
Decomposed Zostera	8	------	88	------	2. 15	25. 2	------
Land plants:[2]							
Hay	15	4	81	29	------	20±	------
Legumes	22	3	75	36	------	12±	------
Rye straw	4	2	94	54	------	60±	------
Sediments:[8]							
Recent sediments	40	1	47	1	1. 7–2. 0	8–12	1. 7?
Ancient sediments	27	1	63	0	1. 4–1. 8	13–20	1. 7?
Surface soils	34	1	56	12	1. 7–2. 0	9–14	------

[1] Where the items do not add up to 100 percent the figures given represent material recovered during the analysis.
[2] Brandt, K., Beiträge zur Kenntniss der chemischen Zusammensetzung der Plankton: Wiss. Meeresuntersuchungen, neue Folge, Abt. Kiel, Band 3, pp. 55–88, 1898. The figures for the average plankton represent the average composition of the plankton that is caught in nets, not the numerical average of the composition of the three main components of the plankton, except for the figure of 14 percent for crude fiber or cellulose, which is an average for the three main groups of plankton.
[3] Does not include chitin compounds.
[4] Birge, E. A., and Juday, C., The inland lakes of Wisconsin, The plankton, I, Its quantity and chemical composition: Wisconsin Geol. and Nat. History Survey Bull. 64, p. 196, 1922.
[5] Waksman, S. A., Principles of soil microbiology, pp. 377–383, Baltimore, Williams, Wilkins Co., 1927; The role of bacteria in the cycle of the life in the sea: Sci. Monthly, vol. 38, pp. 35–47, 1934.
[6] Delff, C., Beiträge zur Kenntniss der chemischen Zusammensetzung wirbelloser Meerestiere: Wiss. Meeresuntersuchungen, neue Folge, Abt. Kiel, Band 14, pp. 56–71, 1912.
[7] Jensen, P. B., Studies concerning the organic matter of the sea bottom: Danish Biol. Sta. Rept., vol. 22, pp. 36–39, 1915.
[8] Trask, P. D., Origin and environment of source sediments of petroleum, p. 200, Houston, Tex., Gulf Publishing Co., 1932.

The average composition of the plankton is 24 percent of protein, 3 percent of fat, and 73 percent of carbohydrates and similar nitrogen-free substances. The crude fiber is given as 14 percent, but this figure is based on the analysis of a single catch of plankton and can be considered only as indicating that the cellulosic compounds may be present in the basic planktonic source material. In fact, all the figures for the average composition of the plankton are based on few data and represent only a rough approximation.

Crude protein is more plentiful in animal life than in plant life. The copepods contain 65 percent of crude protein, in contrast with 29 percent in the diatoms and 14 percent in the peridineans. The diatoms and copepods each contain 8 percent of fat, the peridineans only 1.5 percent. The peridineans are rich in carbohydrate, and some forms presumably contain appreciable quantities of cellulose.

In order to illustrate the relation of the marine plankton to other forms of life, the composition of several groups of animals and plants is given in table 1. The animal forms are rich in protein and fat. The plant forms are poor in protein, rich in carbohydrate, and, as compared with animals, poor in fat. The proportion of protein, fat, and carbohydrate differs considerably in the different groups of plants and animals. Moreover, some types of organisms differ in composition during different periods of the year. This seems especially true of the plankton.[14]

In the absence of data for the forms of marine plankton that pass through the meshes of the net (the nanoplankton), figures for organisms of this group living in lake water in Wisconsin are included in table 1.[15]

[14] Brandt, K., op. cit., pp. 43–90.

[15] Birge, E. A., and Juday, C., The inland lakes of Wisconsin, The plankton, I, Its quantity and chemical composition: Wisconsin Geol. and Nat. History Survey Bull. 64, p. 196, 1922.

In this lake water the nannoplankton is similar in composition to the net plankton. By analogy it might be assumed that in the sea also the nannoplankton is similar in composition to the net plankton. Thus the average for plankton given in the table may be assumed to indicate roughly the general composition of marine plankton, which may be considered a basic source of petroleum. However, in interpreting the significance of these figures with respect to the origin of oil, one should bear in mind the probability that different types of planktonic substances are not all equally good sources of oil.

ORGANIC MATTER IN SEDIMENTS

The composition of the organic constituents of sediments is more difficult to determine than that of plankton, because of the admixtures of inorganic debris.

The data that have been compiled indicate that recent marine sediments contain 40 percent of crude protein, and ancient sediments 27 percent. The proportion of nitrogenous compounds in the organic constituents of recent sediments, therefore, is less than in most animals and higher than in most plants. Furthermore, the proportion of nitrogenous compounds is less in ancient sediments than recent sediments.

The fat content of the organic substances in sediments, as indicated by the ether extract, is 1 percent, which is considerably less than in plants or animals. Fatty substances, however, may be present in sediments in greater amounts than 1 percent, as they may occur as insoluble soaps [16]—that is, they may be combined with metals, such as calcium, magnesium, or aluminum, and therefore insoluble in ether. One of the most urgent needs at present is a practicable method of ascertaining the amount of such metallic soaps in sediments.

The nonnitrogenous constituents are present in ancient sediments in greater proportion than in recent sediments, and from this it may be inferred that they are relatively more resistant to decomposition than nitrogenous compounds.

The cellulose content of marine sediments is very small. In recent sediments it forms only 1 percent of the total organic content, and in ancient sediments it is practically absent. The small content of cellulose in recent sediments and its disappearance as the sediments become progressively more deeply buried may be explained as due to the readiness with which cellulose is attacked by microorganisms.

Data on the composition of soils are given for comparison in table 1. The crude protein content of soils is 34 percent, as compared with 40 percent for recent sediments. The lower protein content of soils may be due to the fact that the organic constituents of soils are derived to a greater extent from plants, which contain less protein than animals. The fat content of soils is approximately the same as that of sediments. Soils are richer in nonnitrogenous compounds than recent sediments, and they contain much more cellulose. The difference in the source of the organic matter would account for the greater content of carbohydrates and cellulose.

[16] Trask, P. D., Results of distillation and other studies of the organic nature of some modern sediments: Am. Assoc. Petroleum Geologists Bull., vol. 11, p. 1228, 1927. Wells, R. C., and Erickson, E. T., The analysis and composition of the fatty material produced by the decomposition of herring in sea water: Am. Chem. Soc. Jour., vol. 55, pp. 338–341, 1933.

COMPOSITION OF ORGANIC MATTER ON BASIS OF ULTIMATE ANALYSIS

METHODS OF DETERMINING COMPOSITION

The segregation of organic matter into protein, fat, and carbohydrate, though generally satisfactory for living matter, is not so satisfactory for the organic constituents of sediments, which consist mainly of residual products that have resisted decomposition and therefore no longer may properly be called proteins or carbohydrates. The organic constituents of possible source materials of oil may advantageously be examined in terms of the elements of which they are composed, but this procedure, too, is accompanied by difficulties, because in sediments it is impossible to segregate the organic constituents from the inorganic constituents.

In the determination of the organic content of sediments, the total quantity of organic matter must be determined, as well as the proportion of different elements. The principal elements in organic substances are carbon, oxygen, hydrogen, and nitrogen; other elements are present but ordinarily in quantities so small that they can be ignored without serious disadvantage for the purposes of this report. On this basis the organic content can be considered as the sum of the carbon, oxygen, hydrogen, and nitrogen.

Nitrogen in sediments is found almost exclusively in the organic constituents and is readily determined. Carbon can be measured directly if the mineral carbonates are first removed with acid. Hydrogen generally cannot be determined directly, as there is no good means of separating organic from inorganic hydrogen. Oxygen also cannot be determined directly, even in organic matter that contains no admixed mineral debris.

OXYGEN CONTENT

In living organisms the oxygen content is ordinarily taken to be the remainder after all the other elements have been determined. On this basis, the oxygen content in average plankton is 39 percent, in marine invertebrates 34 percent, in marine worms 30 percent, and in bacteria 25 percent. (See table 2.) The oxygen content therefore seems to decrease progressively in the forms of life that feed successively on the original plankton.

TABLE 2.—*Composition of different types of organic matter on basis of ultimate analysis*

[Percent. Based mainly on same sources as table 1]

	Carbon	Nitrogen	Hydrogen	Oxygen
Peridineans	45	3	7	45
Diatoms	50	6	8	36
Copepods	50	10	8	32
Average plankton	48	5	8	39
Soil fungi	49	4	8	41
Soil bacteria	56	11	8	25
Marine invertebrates	48	11	7	34
Worms	53	10	7	30
Recent sediments	52–60	6	7–8	25–35
Ancient sediments	55–71	4	8–10	15–30

In recent marine sediments the organic matter should be essentially the same in composition as in the organisms that can live in the upper layers of these sediments, such as marine invertebrates, and therefore the oxygen content of the organic matter should range chiefly between 25 and 35 percent. The deeper layers of sediment, which are inhabited mainly by bacteria, might be expected to have the minimum content of 25 percent, but the surface layers, which are at or near the point of supply of organic matter from the overlying water, would probably have more nearly the maximum content of 35 percent. The mean of the postulated minimum and maximum percentages—30 percent—seems the most reasonable single figure for the oxygen content of the organic constituents of marine clastic sediments at and shortly after the time of their deposition. However, the quantity almost certainly differs considerably in different sediments.

In ancient sediments the oxygen content of the organic constituents generally should be less than in recent sediments, because of the greater ease with which oxygen, as compared with carbon, can be lost from organic constituents under reducing conditions. Moreover, the oxygen content would probably differ among different sediments because of the different conditions to which the sediments have been subjected during and after lithification.

The smaller content of oxygen in the organic constituents of ancient sediments, as compared with recent sediments, is indicated by the greater amount of chromic acid the ancient sediments can reduce per unit of carbon. In this process of reduction both organic and inorganic constituents are oxidized, but most of the oxygen is used for oxidizing the organic substances.[17]

The quantity of oxygen required to oxidize the sediments varies with the carbon content. The more oxygen consumed, the less is the state of oxidation (or the greater is the state of reduction) of the sediment. The ratio of the carbon content of the sediment to the quantity of chromic acid of standard strength that a given amount of the sediment will reduce may be used as a measure of the state of oxidation (or reduction) of the sediment. A satisfactory form to use is the ratio of the percentage of organic carbon in the organic constituents of the sediment to the number of cubic centimeters of 0.4 normal chromic acid that can be reduced by 100 milligrams of sediment. The greater this ratio, the less is the oxygen required for oxidation of the sediment and the greater the oxygen content of the organic constituents. The ratio is therefore a direct index of the oxygen content of the organic constituents and hence is called the "oxidation factor." The oxidation factor, however, cannot be used as an exact means of determining the oxygen content of the organic matter, because of the uncertainty as to the amount of oxygen consumed by the oxidation of the inorganic constituents of the sediments.

The oxidation factor for ancient sediments ranges mainly between 0.75 and 1.20 and the average is approximately 1.00. For recent sediments, according to data supplied by Waksman,[18] the factor is 1.20. The higher oxidation factor for recent sediments indicates that their organic constituents contain more oxygen than those of ancient sediments.

The oxygen content of the organic matter can be calculated from the oxidation factor if data are available to show the proportion of organic matter oxidized and the proportion of oxygen used for oxidation of the inorganic constituents. In the absence of accurate data on the magnitude of these two variables it does not seem practicable in this paper to attempt more than a rough calculation. The oxygen content of the organic constituents of recent sediments as estimated from a comparison with living organisms ranges between 25 and 35 percent. The oxygen content of ancient sediments is materially less and, as indicated by the oxidation factor, may be 15 to 30 percent, or an average of about 23 percent.

When these figures for the oxygen content are substituted in the equation for calculating the oxygen content from the oxidation factor, certain figures for the proportion of organic matter oxidized and the proportion of oxygen required for oxidation of inorganic constituents have to be assumed in order to make the equation balance. As the assumed figures are reasonable and in accord with known data, these estimates of the oxygen content of ancient sediments, though questionable, are presumably of the proper order of magnitude.

In a significant proportion of ancient sediments the oxidation factor is less than 0.85, which indicates that the oxygen content of their organic constituents is considerably below the average, perhaps as low as 15 percent. The hypothesis should be considered that such reduced sediments may be more favorable source beds than sediments of average reduction. The re-

[17] Trask, P. D., and Hammar, H. E., Degrees of reduction and volatility as indices of source beds: Drilling and Production Practice, 1935, pp. 250–266, Am. Petroleum Inst., 1936.

[18] Waksman, S. A., personal communication.

search project on source beds now being carried on by the United States Geological Survey and the American Petroleum Institute includes an intensive study of the relation of the oxidation factor to the occurrence of oil, to see if this factor can be used as an index of source beds.[19]

CONTENT OF CARBON, HYDROGEN, AND NITROGEN

If the amount of oxygen in the organic constituents is known the percentages of the other major constituents—carbon, hydrogen, and nitrogen—can be calculated readily.

In the average plankton the ratio of hydrogen atoms to carbon atoms is about 1.9. (See table 1.) In marine invertebrates the ratio ranges from 1.66 to 1.76 and the average is 1.7. As the marine invertebrates as a class feed on the plankton, it would appear that the planktonic organic matter loses hydrogen with respect to carbon in being transformed into the protoplasm of the animals that feed upon it. In soil bacteria, which may be considered analogous to marine bacteria, the ratio of hydrogen atoms to carbon atoms is 1.65. Bacteria feed upon the organic matter at a later stage than invertebrates, and the composition of the bacteria is similar to that of the organic substances upon which they feed.[20] It therefore seems probable that in the organic constituents of recent sediments the ratio of hydrogen atoms to carbon atoms should be of the same order of magnitude as in bacteria and bottom-living organisms—namely, about 1.7—though the ratio presumably varies among different sediments. The hydrogen content, accordingly, can be estimated by multiplying the carbon content by the factor 1.7. In the absence of evidence to the contrary the same ratio can be used tentatively for ancient sediments. As carbon is 12 times as heavy as hydrogen, the relative weight of the hydrogen is $1.7 \div 12$ or 0.14 times the weight of the carbon.

In recent sediments the ratio of the weight of carbon to nitrogen is about 9;[21] accordingly, the weight of the nitrogen is 0.11 times the weight of the carbon. In ancient sediments the carbon-nitrogen ratio seems to range mainly between 13 and 20 and to average about 17;[22] the weight of the nitrogen is therefore 0.06 times the weight of the carbon.

Thus, the combined weight of the carbon, hydrogen, and nitrogen in recent sediments is $1.0+0.14+0.11=1.25$ times the weight of the carbon, and in ancient sediments it is $1.00+0.14+0.06=1.20$ times the weight of the carbon. In recent sediments the weight of the oxygen is estimated to be 30 percent of the total weight of the organic matter; the weight of the carbon, therefore, is $(100-30) \div 1.25=56$ percent; hydrogen, being 0.14 times the carbon, is 8 percent; and nitrogen, being 0.11 times the carbon, is 6 percent. (See table 3.) In average ancient sediments oxygen is assumed to be 23 percent of the total weight of the organic matter, whence carbon is 64 percent, hydrogen 9 percent, and nitrogen 4 percent. In reduced ancient sediments, where the oxygen may be as low as 15 percent, carbon is 71 percent, hydrogen 10 percent, and nitrogen 4 percent.

[19] Trask, P. D., and Hammar, H. E., op. cit., pp. 250–266.

[20] Waksman, S. A., Principles of soil microbiology, pp. 377–383, Baltimore, Williams, Wilkins Co., 1927.

[21] Trask, P. D., Origin and environment of source sediments of petroleum, p. 21, Houston, Tex., Gulf Publishing Co., 1932.

[22] Trask, P. D., and Hammar, H. E., Organic content of sediments: Drilling and Production Practice, 1934, p. 118, Am. Petroleum Inst., 1935. Also data in a paper to be published in Drilling and Petroleum Practice, 1936.

TABLE 3.—*Ratio of organic matter to carbon in different types of organic matter in sediments*

	Percent by weight				Ratio of organic matter to carbon
	Carbon	Hydrogen	Oxygen	Nitrogen	
Plankton	48	8	39	5	2.1
Recent sediments	56	8	30	6	1.8
Ancient sediments	64	9	23	4	1.6
Reduced ancient sediments	71	10	15	4	1.4

CHANGES IN COMPOSITION WITH RESPECT TO TIME

As the total quantity of organic matter represented by the original planktonic source decreases in the course of time, the relative proportions of its constituents change. The oxygen content of the organic constituents decreases from 39 percent in plankton to 15 percent in reduced ancient sediments. Carbon increases from 48 to 71 percent. Hydrogen increases from 8 to 10 percent. Nitrogen is 5 percent in plankton, 6 percent in recent sediments, and 4 percent in ancient sediments. These quantities of carbon, hydrogen, oxygen, and nitrogen refer to the average percentage by weight of the particular type of organic matter, not to the proportions of the original quantity of organic matter in the plankton.

Table 3 shows the relative changes in the carbon, hydrogen, oxygen, and nitrogen as the organic matter diminishes. The main change is the progressive loss of oxygen with respect to the other constituents. As the proportion of oxygen decreases, the proportions of carbon and hydrogen necessarily increase. The increase in nitrogen from 5 percent in plankton to 6 percent in recent sediments is mainly a mathematical consequence of the decrease in oxygen and implies no real increase in nitrogen; but the decrease to 4 percent in the ancient sediments indicates a relative loss of nitrogen during burial of the sediments.

The changes in the nature of the organic matter during the course of time may be illustrated more clearly if the composition is expressed in terms of atomic ratios rather than as percentages by weight. The percentages given in table 3 have been recalculated as atomic ratios and reduced to a common denominator in table 4. Throughout this series the carbon content has been arbitrarily taken as 18. According to this calculation hydrogen decreases from 34 in average plankton to 31 in recent and ancient sediments. Oxygen decreases from 11 in plankton to 7 in recent sediments and to 3 in reduced ancient sediments. Nitrogen decreases from about 2 in plankton to 1 in ancient sediments. Thus the organic matter as it changes from plankton to organic constituents of ancient sediments loses most of its oxygen and a considerable part of its nitrogen. It must be borne in mind, however, that the figures for the atomic ratios are based on general averages and that the ratios may vary considerably among individual sediments.

TABLE 4.—*Atomic ratios of constituents of different types of organic matter in sediments*

	Carbon	Hydrogen	Oxygen	Nitrogen
Plankton	18	34	11	2
Recent sediments	18	31	7	2
Ancient sediments	18	31	5	1
Reduced ancient sediments	18	31	3	1

RATIO OF ORGANIC MATTER TO CARBON IN SEDIMENTS

The determination of the total quantity of organic matter in sediments is an essential step in the study of source beds. The common procedure for estimating the organic content is to determine the carbon content and multiply it by a factor which is the reciprocal of the proportion of carbon to total organic matter. This factor naturally differs for different types of sediments and for different types of organic matter. It has been calculated for each of the four groups of organic matter considered in this report. For plankton it is 2.1, for recent sediments 1.8, for ancient sediments 1.6, and for reduced ancient sediments 1.4. (See table 3.)

In previous work [23] the writer has assumed a ratio of 1.7 for recent sediments, which is the same that soil chemists have used for many years for soils. Recently Alexander and Byers [24] have questioned the propriety of a single ratio of 1.7 and have pointed out that the ratio varies considerably among different soils. They have suggested that 1.93 is probably the most satisfactory single factor. Waksman [25] has proposed the factor 1.92 for recent marine sediments, and Potonié and Reunert [26] present data that indicate the factor 1.83 for certain recent lacustrine sediments in Germany.

[23] Trask, P. D., Origin and environment of source sediments of petroleum, p. 18, Houston, Tex., Gulf Publishing Co., 1932.

[24] Alexander, L. T., and Byers, H. G., A critical laboratory review of methods of determining organic matter and carbonates in soil: U. S. Dept. Agr. Tech. Bull. 317, pp. 1–24, 1932.

[25] Waksman, S. A., The role of bacteria in the cycle of life in the sea: Sci. Monthly, vol. 38, pp. 35–49, 1934.

[26] Potonié, R., and Reunert, D., Geologisch-chemische Untersuchungen von Sapropelen des Unterücker und Sakrower Sees: Schriften aus dem Gebiet der Brennstoff-geologie, Heft 10, pp. 149–169, 1935.

Organic constituents of recent sediments, being always submerged in water, should usually be more reduced than those of soils, which are not always completely saturated with water. The ratio of organic matter to carbon in recent sediments, therefore, would as a rule probably be less than in soils. Consequently, a ratio of 1.8 presumably would be better than 1.9.

In the absence of data to the contrary the writer in previous work [27] assumed that the ratio in ancient sediments was 1.5. According to the data given in table 3, the ratio 1.6 would be better for general use for ancient sediments and 1.4 for reduced ancient sediments.

The writer presents these ratios of organic matter to carbon content very tentatively. In order to estimate the organic content of sediments it is necessary to use some kind of a ratio of this type. At present, the ratio of organic matter to carbon seems the most practicable, and according to available data the figures given here seem the most satisfactory.

INTERPRETATION OF DATA

POSSIBLE SOURCE MATERIALS

General character and relative quantity of organic material.—The foregoing attempt to discuss quantitatively the changes in the organic constituents of sediments during the course of their history seems to indicate rather clearly that only a very small proportion of the original organic matter generated by the plankton actually accumulates in sediments, and that organic constituents buried a few inches in the muds on the sea bottom do not thereafter decrease greatly in quantity.

The organic constituents in sediments consist chiefly of complex resistant compounds, which with respect to their original planktonic source are chemically reduced in that they contain comparatively little oxygen. The relatively elementary substances such as sugars, celluloses, fats, and simple proteins, of which the original plankton is mainly composed, are decomposed or altered to a considerable extent during the process of deposition and probably occur in sediments in quantities so small that they are not likely to be major sources of petroleum.

In most oil fields the proportion of the organic matter that is converted into petroleum is difficult to ascertain. In the Santa Fe Springs field of California the proportion is probably about 4 percent, though it may be as low as 2 percent or as high as 15 percent.[28] In other fields the amount transformed into oil may be less, but as the sediments in the Santa Fe Springs field

[27] Trask, P. D., Results of the American Petroleum Institute research project on origin and environment of source beds of petroleum: Am. Petroleum Inst. Production Bull. 211, pp. 19–31, 1933.

[28] Trask, P. D., Proportion of organic matter converted into petroleum in Santa Fe Springs field, Calif.: Am. Assoc. Petroleum Geologists Bull., vol. 20, pp. 245–257, 1936.

are mainly Pliocene and hence relatively young, the figures given are presumably minimum figures. Any constituent present in an amount less than 1 or 2 percent of the organic matter, therefore, in all probability cannot be a major source of petroleum.

Cellulose.—The three main constituents of the original planktonic protoplasm are carbohydrates, fats, and proteins, but by the time the derived organic materials are deposited in the sediments their nature has changed considerably. Cellulose, though perhaps constituting 14 percent of the original plankton, ordinarily is found in amounts of 1 percent or less in recent marine sediments.[29] Many sediments contain no measurable trace of cellulose, and the maximum observed was in a shallow lagoon deposit, where it was 5 percent of the organic constituents. In recent marine sediments the cellulose decreases in quantity from the surface downward, and in ancient sediments it is usually not present at all.[30]

Because of the small quantity of cellulose found in sediments, therefore, it does not seem probable that petroleum is derived mainly from the cellulosic constituents of the sediments, as advocated by Berl.[31] However, as the original planktonic source material may contain as much as 14 percent of cellulose, it is possible that some of the mother substances of petroleum in sediments may be derived from cellulose.

Other carbohydrates.—Other carbohydrates, such as hemicelluloses, starches, and sugars, are present in recent sediments in as small quantities as celluloses, and hence in all likelihood they are not major sources of oil. The organic constituents present in the sediments, however, may be derived to a considerable extent from carbohydrates of these types in the original planktonic protoplasm. The pentoses, because of their similarity to ring compounds, such as naphthenes, have been postulated as possible mother substances of petroleum,[32] but they also seem to be present in sediments in quantities too small to be a main source of oil.

Proteins.—Proteins can be considered as possible source material, as nitrogenous compounds form about 40 percent of the organic constituents in recent sediments and 27 percent in ancient sediments.[33] These nitrogenous compounds are derived largely from proteins in the basic planktonic organic matter, but the proteins in the sediments consist mainly of complex resistant compounds that apparently differ considerably from the proteins in the original plankton. Petroleum contains appreciable quantities of combined nitrogen, though the proportion ordinarily is less than in the organic constituents of the sediments from which the oil seems to be derived.

Simple proteins are present in recent marine sediments in quantities so small that they probably should not be considered as major sources of oil. The average quantity of simple water-soluble proteins in the upper layers of recent marine sediments is about 3 percent of the organic matter.[33] This protein content in part may represent the protoplasm of micro-organisms living in the sediment and therefore may be destroyed or considerably modified after death of the organisms. Simple proteins tend to decompose rather readily in sediments and in the overlying water.[34] Therefore, if petroleum is derived from proteins, it presumably comes from the more resistant, complex nitrogenous compounds.

Fats.—Fatty substances have been regarded by many writers [35] as the main source of petroleum, but this hypothesis may not be correct. The chief reasons for believing that oil is derived from fatty substances are the low oxygen content of fatty materials and their similarity in composition to paraffin hydrocarbons. However, fats are chain compounds; all petroleums contain an appreciable proportion of ring compounds, and many petroleums contain more ring compounds (naphthenic, polycyclic, and benzenoid) than chain compounds (paraffenic).[36] Fatty materials are either saturated or unsaturated; petroleum is composed almost entirely of saturated substances.[37] The iodine number of the fatty substances found in marine animals and plankton ranges chiefly between 110 and 120;[38] in most crude oils the iodine number is less than 20, and in some it is as low as 2.[39] As the iodine number is an index of the degree of unsaturation of fatty and oily substances, the fatty materials that eventually are deposited in sediments evidently are much more unsaturated than the compounds ordinarily present in crude oil.

Consequently, if petroleum is derived mainly from fats, some special process such as polymerization has to be invoked to account for the formation of the ring compounds and the almost complete absence of unsaturated compounds. If polymerization or some other process has to be assumed, why limit the source to fatty materials? Other organic substances, in all probability, could serve as well as fats.

[29] Trask, P. D., Origin and environment of source sediments of petroleum, p. 302, Houston, Tex., Gulf Publishing Co., 1932.

[30] Idem, pp. 200–218.

[31] Berl, E., Origin of asphalt, oil, natural gas, and bituminous coal: Science, new ser., vol. 80, pp. 227–228, 1934.

[32] Brooks, B. T., The chemical evidence for the low-temperature history of petroleum: Inst. Petroleum Technologists Jour., vol. 20, pp. 177–205, 1934.

[33] Trask, P. D., op. cit., p. 200.

[34] Hecht, F., Der Verbleib der organischen Substanz der Tiere bei meerische Einbettung: Senckenbergiana, Band 15, pp. 165–249, 1933. Jensen, P. B., Studies concerning the organic matter of the sea bottom: Danish Biol. Sta. Rept. 22, pp. 1–39, 1915.

[35] Notably Engler, C., and Höfer, H., Das Erdöl, Band 2, pp. 59–146, 1909.

[36] Gruse, W. A., Petroleum and its products, pp. 4, 36, New York, McGraw-Hill Co., 1928.

[37] Sakhanov, A., and Wirabianz, R., Die chemische Zusammensetzung der Erdöle der U. S. S. R.: Petroleum, Band 25, pp. 867–892, 1929.

[38] Rosenfeld, G., Studien über das Fett der Meeresorganismen: Wiss. Meeresuntersuchungen, neue Folge, Abt. Helgoland, Band 5, pp. 57–84, 1904.

[39] Sakhanov, A. and Wirabianz, R., op. cit., pp. 877–882. Gruse, W. A., op. cit., pp. 27–32. Gurwitsch, L., The scientific principles of petroleum technology, translated and revised by H. Moore, pp. 28–33, London, Chapman & Hall, Ltd., 1926.

Another argument against the derivation of oil from fatty substances is the chemical stability of such substances.[40] Large quantities of fatty and waxy materials (which contain fatty acid radicals) are present in oil shales of continental origin, yet oil shales of this type are associated with very few oil fields.

Furthermore, fats—that is, fatty materials soluble in carbon tetrachloride—form less than 1 percent of the organic content of recent marine sediments[41] and therefore apparently are present in quantities too small to be a major source of oil. Other fatty materials, such as metallic soap or waxes, may be present in sediments in larger amounts than fats.[42] Fatty materials tend to ionize in water, and in the presence of an excess of metallic ions they are precipitated as soaps. No data are yet available on the quantity of metallic soaps in sediments. Metallic soaps may possibly be present in sufficient amounts to account for the oil, but if they exist in such quantities the problem still remains as to how they can be transformed into naphthenic and other ring compounds.

Other substances.—Cellulose, carbohydrates, simple proteins, and fats, which form the major part of the organic constitutents of the planktonic source material, are so much altered in the course of deposition that they form not more than 5 percent of the organic constituents of sediments and therefore are present in quantities probably too small to be main sources of petroleum. The oil evidently must come from the remaining 95 percent of the organic matter—the indigestible residues that probably consist mainly of complex compounds and are relatively deficient in oxygen. Petroleum in several areas in the United States is associated with sediments whose organic constituents are comparatively low in oxygen.[43]

ORIGIN OF OIL

The complex residual substances that constitute the main part of the organic matter in sediments may contain loosely attached radicals of chain or ring structure. Under favorable conditions, perhaps aided by polymerization or methylation,[44] these loosely attached radicals may become separated from their parent substances and form liquid hydrocarbons. One of the conditions that might favor such a process is the tendency of the organic constituents of sediments to come to chemical equilibrium after the sediments have been buried beyond the limit of effective microbial action. Individual organic substances found in sediments may be relatively stable in a free state but not stable when pressed in close contact with other organic substances in a sediment. If they are unstable with respect to adjoining organic materials they will tend to reach a stable state, and liquid hydrocarbons may possibly be formed as a result of the readjustments that take place as the organic constituents endeavor to come into equilibrium. As the residual organic substances consist mainly of solids and are largely insoluble in water, the chemical changes caused in this manner would take place very slowly as compared with changes resulting from the activities of organisms.

While the organic constituents are in the overlying water or in the upper layers of sediments, alterations caused by living things greatly predominate over changes caused by purely physical and chemical agencies. In such environments the organic substances have less physical contact with one another and are, therefore, less susceptible to purely chemical (nonbiologic) changes than when in the deeper layers of sediment, where they are firmly pressed together. Consequently, they would have relatively little time to come into chemical equilibrium with one another before they would be attacked by some living organism.

As the sediments become buried deeper and deeper, the activity of living organisms becomes progressively less, and ultimately a depth is reached where the changes in the organic matter resulting from the activity of organisms becomes relatively insignificant.[45] The sediments thenceforth are dominated by purely physical and chemical agencies, and the organic constituents proceed toward effecting a state of equilibrium. A state of complete equilibrium, however, might never be attained because of the effect of changes in temperature and pressure to which the sediments may be subjected during the course of time.

As soon as liquid hydrocarbons were generated, they would form an oily phase insoluble in water—the ancestral petroleum. Certain organic constituents, such as some of the pigments, waxes, and fatty acids that hitherto had existed in the solid state, would be soluble in this oily liquid. Organic substances that lay near the place where the oil was first formed might be dissolved before the ancestral petroleum migrated. Other substances that lay in the path of the migrating oil might be dissolved later. The optically active constituents of petroleum might to some extent be due to such a process. The similarity between certain organic pigments in ancient and modern sediments[46] suggests that some substances, after being dissolved by the

[40] Brooks, B. T., The chemical evidence for the low-temperature history of petroleum: Inst. Petroleum Technologists Jour. vol. 20, p. 185, 1934.

[41] Trask, P. D., Origin and environment of source sediments of petroleum, p. 200, Houston, Tex., Gulf Publishing Co. 1932.

[42] Trask, P. D., Results of distillation and other studies of the organic nature of some modern sediments: Am. Assoc. Petroleum Geologists Bull., vol. 11, p. 1228, 1927. Wells, R. C., and Erickson, E. T., The analysis and composition of the fatty material produced by the decomposition of herring in sea water: Am. Chem. Soc. Jour. vol. 55, p. 338–341, 1933.

[43] Trask, P. D., and Keyte, W. R., Degree of reduction of sediments in the east Texas basin as an index of source beds: Oil Weekly, vol. 81, no. 10, pp. 60–70, May 18, 1936.

[44] Pratt, W. E., Hydrogenation and the origin of oil: Problems of Petroleum Geology, pp. 235–245, Tulsa, Okla., Am. Assoc. Petroleum Geologists, 1934.

[45] White, David, Geology and occurrence of petroleum in the United States: Petroleum investigation, pt. 2 (73d Cong., H. R., Comm. on Interstate and Foreign Commerce, Hearings on H. Res. 441), p. 901, 1934.

[46] Dhéré, C., and Hradil, G., Fluoreszenzspektrographische Untersuchungen an Oelschiefer: Schweizer. min.-pet. Mitt., Band 14. pp. 279–295, 1934

ancestral petroleum, might persist in a relatively unchanged condition for a long time.

As soon as any materials were dissolved, the equilibrium relations of the constituents of the ancestral petroleum would be altered, and these constituents would tend to readjust themselves in an effort to come to a stable condition. As the oil migrated and dissolved new constituents, its composition would be subject to continued change. Even after it reached the reservoir, it seems evident that it would slowly alter until a final stable condition was reached. Such a concept is in accordance with the progressive paraffination of crude oils advocated by Barton.[47] Nevertheless, an ultimate state of complete equilibrium may never be attained. If the conditions of heat and pressure should change while the ancestral petroleum was in the process of developing into crude oil, new conditions of equilibrium might be set up, and consequent readjustments in composition would ensue.

This discussion of the origin of oil by physicochemical readjustment of the organic constituents of sediments is incomplete in that it does not consider what particular types of organic substances are likely to be transformed into oil, but it seems inadvisable to speculate further in the study of possible source material until more detailed information is available on the chemical nature of the organic constituents of sediments. The most favorable mother substances of petroleum are presumably compounds deficient in oxygen. Additional data on the chemical composition of possible source materials of petroleum are urgently needed.

[47] Barton, D. C., Natural history of Gulf coast crude oil: Problems of Petroleum Geology, pp. 109-155, Tulsa, Okla., Am. Assoc. Petroleum Geologists, 1934.