The Occurrence of Hydrocarbons in Recent Sediments from the Gulf of Mexico

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THE ORIGIN OF PETROLEUM has been a widely debated subject for many years. It has been rather generally accepted that organic matter deposited in marine or brackish water sediments served as the source material for eventual petroleum formation. Conceptions of the process from this point have, however, been many and varied. The most prevalent viewpoint, perhaps, has held that burial of the original complex organic matter by several thousands of feet of overburden and a lapse of several millions of years were necessary conditions for its conversion into hydrocarbons (*1*).

More recently a school of thought has developed which believes that oil formation may begin soon after deposition of the organic matter in the sediments (*2*), but the presence of liquid hydrocarbons in Recent marine sediments has never been definitely demonstrated (*3*). Probably the most extensive study ever carried out on Recent sediments was that of Parker D. Trask and his associates under A.P.I. Project 4. They collected samples from almost every kind of environment and with a worldwide distribution. In summarizing his monumental work in this field, Trask has written,

> No liquid hydrocarbons were found, and if any were present they must have occurred in quantities less than . . . 1 part per 100,000 in the marine samples. The sediments investigated represent the richest deposits in the writer's collection of 2,000 samples from all parts of the world; consequently, the absence of petroleum in them indicates that in all probability petroleum does not form in sediments at the time of deposition (*4*).

Several years ago a project dealing with the nature of the organic matter in recent marine sediments was initiated in the Standard Oil Co. (New Jersey). It was aimed at learning something about the types of organic compounds present in the sediments and, if possible, at determining whether a noticeable change in the nature of the organic matter could be observed with increasing age or depth of burial. One of the surprising results of this study has been the discovery of liquid hydrocarbons in Recent sediments from the Gulf of Mexico. Aliphatic and aromatic hydrocarbons have been identified in ten Recent marine sediment samples from four different locations in Texas and Louisiana, in which specimens representing near-shore and off-shore locations (Table 1), and oxidizing and reducing environments, were included. Depths of these sediments ranged from a few inches up to a hundred feet below the water floor, and they were of a mucky or silty nature.

The general procedure involved the following steps: The sediment samples were frozen in dry ice at the collecting site and were maintained in this condition during transit to the laboratories. The material was then dried at 50° C in an oven evacuated to 2 mm Hg and ground in a micropulverizer to an average particle diameter of 2–3 μ. Extraction at refluxing temperatures by a mixture comprising 70 vol % benzene, 15 vol % acetone, and 15 vol % methanol followed. In spite of careful distillation of the solvents prior to use, minute residues were obtained upon evaporation to dryness. In no case did the blank amount to more than 1.6 wt % of the extracted organic matter. After removal of the solvent with a stream of nitrogen, the extracted organic matter was

TABLE 1

RECENT SEDIMENT SAMPLES

Location	Description
7 miles off Grande Isle, La. Long. 90° 01′ W Lat. 29° 08′ N	A core of sediments taken from the floor of the Gulf of Mexico downward to a depth of 106′. Water depth—41.2′. Gray silty clay, occasionally interbedded with gray, fine-grained silty sand.
17 miles off Corpus Christi, Texas Long. 97° 43′ W Lat. 27° 50′ N to 27° 55′ N	A series of samples scooped off the Gulf floor.
Laguna Madre Flats, Texas Sample I Long. 97° 31′ W Lat. 26° 59′ N	Black, organic algal muck. Typical of material that collects in low places in the Laguna Madre flats surface and associated with a strong concentration of hydrogen sulfide. Wind-blown lagoon water remains in these low places for long periods of time after adjacent flats become dry. Sample representative of the uppermost 12 in. of the flats surface.
Sample II Long. 97° 31′ W Lat. 26° 58′ 30″ N	Thinly laminated black and gray algal clay from area which is sometimes dry and sometimes flooded. Uppermost 12 in. of the flats surface.

separated by chromatography over freshly activated, powdered alumina (Harshaw, Al-0101-P). Successive fractions were eluted with *n*-heptane, benzene, pyridine, acetone, and methanol. The heptane cut was designated as the paraffin-naphthene fraction, the benzene cut as the aromatic fraction, and the last three were combined to give an oxygenated or asphaltic fraction.

The concentration of extractable organic matter in many sediments is quite low. In the samples studied, it has ranged from 30 to 450 parts per 100,000 of dried sediments. The quantity of free hydrocarbons has varied from 2 to 19 parts per 100,000.

In Table 2 are found data for several representative samples. In all cases hydrocarbons were isolated, and furthermore, in the case of the Grande Isle core from Louisiana, the amount of hydrocarbons increases and the quantity of complex organic matter decreases with increasing depth of burial below the floor of the Gulf. Since the amount of extractable organic matter is constant for these three sections, the data certainly indicate a change in the nature of the organic matter in the direction of petroleum. It is interesting to note that the Laguna Madre sample (from Texas), in a reducing environment, contains 3.9 times as much free hydrocarbons as the specimen from an oxidizing environment. The former, incidentally, also contains 3.9 times as much sulfur as the latter.

Although the relationship between the hydrocarbon and sulfur contents of the two samples may be fortuitous, it fosters a bit of conjecture. Strains of autotrophic sulfur bacteria are known, of course, which utilize carbonates as a carbon source, oxidize hydrogen sulfide, and deposit free sulfur inside or outside their cells. The sediment sample with low hydrocarbon and sulfur contained 6 times as much carbonate as the hydrocarbon- and sulfur-rich sample. Since the sediments are from the same lagoon and are only a few thousand feet apart, the original organic and carbonate contents were probably quite similar. This combination of circumstances suggests, then, that there may be a direct relationship between sulfur and hydrocarbon production, at least in the case of a particular group of bacteria. Recent work by ZoBell and his co-workers (*5*), disclosing the production of hydrocarbons by autotrophic, sulfate-reducing bacteria cultivated in an inorganic medium in the laboratory, lends credence to this hypothesis.

Proof that the paraffin-naphthene and aromatic fractions are actually hydrocarbons has been furnished by elemental analysis, infrared absorption spectra, and their behavior on the alumina during the chromatographic separation.

If one were to extrapolate the data obtained on a 106-foot core of sediments taken from the floor of the Gulf of Mexico 7 miles off Grande Isle (186 parts hydrocarbons + asphaltics per million parts of dried sediment), a cubic mile of these sediments would contain 4,500,000 barrels of a paraffin-naphthene, aromatic, and asphaltic mixture resembling crude oil. In smaller units, this would be 7000 barrels per acre for a column one mile deep. Since the concentration of hydrocarbons increased with depth in this core, the estimate is probably conservative.

With the presence of liquid hydrocarbons in Recent sediment samples established, the question resolved itself into, "What is the origin of these hydrocarbons?" They could be present (1) by contamination during either the collection or the analysis of the sediments, (2) by migration or diffusion from greater depths, or (3) by deposition or genesis in the sediments themselves. Great care has been exercised during the whole program to prevent contamination, so it is felt with certainty that this possibility can be discounted. It would be difficult to rule out the possibility of migration or diffusion from greater depths

TABLE 2

EXTRACTION OF ORGANIC MATTER FROM RECENT SEDIMENTS

Sample description	Grams organic matter extracted /100 g dried sediment	Chromatographic analyses of extracted organic matter			
		% Paraffin-naphthene	% Aromatic	% Asphaltic	% Remaining on alumina
The following sections are from a core of Recent sediments taken about 7 miles off Grande Isle, La. The numbers indicate feet below the floor of the Gulf of Mexico					
3–4	0.031	6.0	1.5	14.0	78.5
18–22	.032	17.9	2.5	12.1	67.5
102–103	.031	25.0	5.7	10.6	58.7
Laguna Madre Flats, Texas (0–12″ below surface)					
Reducing environment	.185	9.2	1.0	5.1	84.7*
Oxidizing environment	.450	1.1	< 0.5	26.8	72.1*
Sediment free of extractable organic matter	0.0005†				

* Includes free sulfur present in aromatic cut.
† Solvent blank.

were it not now possible to settle the question by means of carbon 14 age determinations.

Ages of 11,800–14,600 ± 1400 years were obtained for the hydrocarbons extracted from several sections of the Grande Isle core of Recent sediments. A composite carbonate sample from the entire core proved to be 12,300 ± 1200 years old, and the nonextractable organic matter, which comprises a major portion of the original organic content, had an average age of 9,200 ± 1000 years. This slightly younger age can be readily explained by the somewhat larger amounts of nonextractable organic matter present in the shallower sections of the core.

For control purposes, a sample of shale was extracted, and the resulting extract was separated by chromatography, using the same technique as was applied to the Recent sediment samples. The hydrocarbons thus obtained were "dead" by carbon 14 analysis, as might be expected, giving a net count, in cpm/g carbon, of 0.03 ± 0.08. In a similar manner, samples of cetane, produced by the hydrogenation of sperm oil, were analyzed before and after going through the same sequence of analytical steps. Net counts of 3.18 ± 0.10 and 3.10 ± 0.06 were recorded, which check the value of 3.14 ± 0.07 obtained for modern wood under the same conditions. All age determinations were carried out by J. Laurence Kulp, of the Lamont Geological Observatory of Columbia University.

The data demonstrate that the analytical procedure used on the Recent sediment samples does nothing to make the hydrocarbons appear either younger or older than they should. Hence it may be concluded that diffusion did not occur to any appreciable extent, and that the isolated hydrocarbons were either deposited with, or generated in, the sediments themselves.

It is interesting to speculate as to the source of these hydrocarbons. Shimkin *et al.* (*6*) have established the presence of polynuclear aromatic compounds in extracts from barnacles. ZoBell and coworkers (*5, 7*) found paraffins and naphthenes in extracts from laboratory cultures of marine bacteria. In our laboratories, hydrocarbons have been detected in concentrations of 45–58 ppm dry weight in oysters and bluefish. Until much more work is done to clarify the picture, it seems plausible to suggest that the petroleumlike mixture being formed in the present era is a composite of the hydrocarbon remains of many forms of marine life. It is a logical extension of this hypothesis to state that crude oils of varying composition might result from changes in the relative contributions of different forms of marine life.

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Dangers Confronting American Science

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The Status of Science

The changed status of science. During the past ten years science in the United States, through a series of outstanding developments, has won for itself a public acceptance and support that it has never known before. The main achievements have been the technological ones that contributed so notably toward winning the war, as well as the sequence of revolutionary medical discoveries in the fields of antibiotics and hormones. It seems natural that enthusiastic public and governmental support of science should have arisen from results as palpable as these. Nevertheless, many scientists believe that the form this support has taken is fundamentally unsound, that a dangerous situation has developed, and that analysis and remedial measures are urgently needed. Indeed, it was fairly apparent at the outset (and was pointed out by many at the close of the war) that science was not being supported for its own sake, nor for what it *could* do, but, in far too narrow and specific a way, only for those things that it had so spectacularly *done.* The resulting cumulative damage to science has now reached conspicuous dimensions, and it is the purpose of this article to outline and examine this situation.

Classically, science has had two distinct but harmonious goals: the discovery of the secrets of nature for humanitarian purposes—that is, for improving the

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[1] The present report is the work of no single author: It represents the result of extended discussion by officers and many members of the Amercan Association of Scientific Workers over the past two years. Officers for 1951–52 were T. Rosebury, president, and a panel of vice presidents: S. S. Cohen, I. Fankuchen, W. F. Hewitt, R. Hodes, K. F. Mather, W. H. Pearlman, L. Pauling, E. L. Smith, and C. J. Witton. Melba Phillips was 1951–52 secretary.