HYDROCARBONS IN TERRESTRIAL SAMPLES
AND THE ORGUEIL METEORITE

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Abstract. Meteorites contain extraterrestrial carbonaceous materials. The Alais, Orgueil, Tonk, and Ivuna meteorites resemble in their carbon, free sulfur, and non-metamorphosed mineral contents, densities, and general appearances certain organic-rich terrestrial sediments. Structural and isotopic determinations of carbon compounds in the Orgueil chondrite indicate that these compounds are primarily indigenous. Physically and chemically the benzene extractable carbonaceous materials from the Orgueil and certain near-surface terrestrial sediments are similar. Mass spectrometric type analyses of the alkanes from an Orgueil fragment, terrestrial sediments and organisms are statistically indistinguishable at the 95 per cent confidence level. Theoretical considerations and experimental data are presented, and these permit an assessment of the potential and reliability of hydrocarbons as biological indicators. Based on the production and preservation or organic substances in terrestrial environments, alkanes in the Alais, Orgueil, Tonk, and Ivuna (Type I) carbonaceous chondrites could retain the best evidence of organisms that may have lived on a parent body of meteorites.

1. Introduction

The first analyses of carbon compounds from meteorites were reported by BERZELIUS (1834). He was less convinced than was his former student, WOHLER (1858, 1859ab, 1860), that meteorites contained biologically derived materials. WOHLER felt that the "ozocerite-like" substance in the Kaba chondrite was "undoubtedly of organic origin". But WOHLER's feelings were not shared by most nineteenth century researchers. A detailed review of the work and opinions of these investigators has been written by COHEN (1894).

Between 1894 and 1950, interest in the carbon compounds in meteorites was negligible (MASON, 1963a). The inability of classical analytical methods to provide definitive data on the compositions of complex mixtures of carbon compounds, and the prevalent belief that the carbonaceous substances in meteorites were of abiotic origin probably contributed to this disinterest. In the 1950's, only three articles reporting analyses of carbon compounds from meteorites were published.

MUELLER (1953) determined the elemental analyses of extracts from the Cold Bokkeveld chondrite. After he had picked out the free sulfur by hand, he found the composition of the extract to be: C — 19.84%, H — 6.64%, S — 7.18%, Cl — 4.8%, ash — 18.33%, and undetermined (0, etc.) — 40. 02%. Benzene solution of the extract did not show detectable optical activity.

BOATO (1954) determined the abundances of stable carbon, as, δC^{13}, and of stable

hydrogen, as δH^2, isotopes in 14 meteorites. He observed, "It is interesting to note that CRAIG (1953) found a $15^0/_{00}$ depletion in C^{13} to result from the process by which organic materials of marine plants and animals is concentrated to form petroleum and the carbonaceous materials in black shales. The carbonaceous materials in the meteorites are, of course, not derived from living sources, but it is noteworthy that the range of variation in C^{13} in meteorites is of the order of the depletion observed in a terrestrial process involving loss of volatile carbon compounds." BOATO found that δH^2 values of the bound waters in meteorites were several times greater than any δH^2 found for terrestrial waters.

Infrared and ultraviolet spectra of extracts from the Murray and Orgueil meteorites were studied by CALVIN and VAUGHAN (1960). They found absorption bands that could be attributed to a variety of carbon compounds. Certain absorptions were suggestive of cytosine, a nucleic acid "building block". CALVIN noted that the heterocyclic bases, carbonyl compounds, and hydrocarbons in meteorites could be biological precursors that had evolved in primordial environments.

Interest in and the controversy about the origin of carbonaceous substances in meteorites were enhanced by the analyses of NAGY, MEINSCHEIN, and HENNESSY (1961). They compared a mass spectrum of a distillate fraction from the Orgueil chondrite with mass spectra of hydrocarbons obtained from butter and terrestrial sediments. They reported, "Based on preliminary studies, the compositions of the hydrocarbons in the Orgueil meteorite provides evidence for biogenic activity." Since 1961, numerous analyses of the carbonaceous materials in various chondrites have supplied substantial information on the compositions of these materials. These analyses, obtained using the most modern instruments and techniques, have not resolved the heated debate on the biological origin of the carbon compounds in meteorites. However, recently gathered data have greatly reduced the number of important issues in this debate.

ANDERS (1961, 1962) listed criticisms of the preliminary findings of NAGY, MEINSCHEIN, and HENNESSY (1961). DEGENS and BAJOR (1962) presented experimental data in support of one of ANDERS' criticisms. Their analyses of amino acids in meteorites suggested that terrestrial organisms could have been the principal source of the carbon compounds in the Murray and Bruderheim chondrites, but subsequent analyses reported by BRIGGS (1963), MEINSCHEIN, NAGY, and HENNESSY (1963), MEINSCHEIN (1963), NAGY, FREDRIKSSON, UREY, CLAUS, ANDERSON, and PERSEY (1963), and KAPLAN, DEGENS, and REUTER (1963) strongly indicate that most amino acids, hydrocarbons, and some other carbonaceous materials in certain meteorites are indigenous. An excellent compilation of many of these analytical results has been prepared by BRIGGS and MAMIKUNIAN (1963). The latter authors conclude, ". . . it seems clear that a great majority of meteorite organic matter is indigenous and was brought to Earth within meteorites." This conclusion is shared by MASON (1963b), who states, "The quantities of the hydrocarbons in the meteorites indicate that there can be no reasonable doubt that they were present when it entered the earth's atmosphere and are not the result of terrestrial contamination. They are truly extraterrestrial in origin." Thus, it would appear that only one major issue concerning the hydrocarbons in meteorites

remains unresolved. That issue is: Are the indigenous hydrocarbons in certain carbonaceous chondrites partly of biological or totally of abiotic origin?

2. Discussion

There are limitations to the accuracy with which biological remnants can be identified. An absolute proof of the former existence of either terrestrial or extraterrestrial life cannot be accomplished because a quantitative definition of the living state has not been made. Organisms vary in size, function, and composition. Furthermore, biological remnants are commonly altered in diverse ways by abiotic processes in sediments. These alterations, as noted by VALLENTYNE (1962), produce carbonaceous materials in sediments that differ markedly in bulk composition from plant and animal matter. Notwithstanding, ancient sediments supply strong evidence that organisms lived on earth long before man evolved. This evidence constitutes the only physical references for the detection of biological remnants of organisms that may have lived in other biospheres. Therefore, it is important to consider the characteristics which permit empirical identifications of terrestrial organisms and biological products.

A. CHARACTERISTICS OF PLANTS, ANIMALS, AND SEDIMENTAL ORGANIC MATTER

Living things are extremely complex. Their complexities and the variations in different kinds of organisms make it difficult to devise a single method or a few criteria for distinguishing animate from inanimate things. Most criteria for the recognition of the living state or biological remnants are more qualitative than quantitative. Whether a plant has yellow, green, or red leaves is of little consequence. Trees may live and bear leaves that vary markedly in sizes, shapes, and colors, but generally these leaves resemble one another grossly in certain structural aspects. There are also gross resemblances between different kinds of life and biological remnants.

Organisms are highly ordered arrays of molecular or cellular components. All living cells share certain functional parts. Living may place such great demands on the spatial, chemical, and electrical compatibility of its constituent parts that biological molecules may be much the same in life everywhere. Certainly, terrestrial organisms in temperate, tropical, and arctic regions share the same compounds. It is apparently this sharing of molecular components and cellular structures that produces an order which make it possible to identify new kinds of living things.

But, natural laws require that work be expended to maintain highly ordered systems. Plants and animals live only as long as biological compounds function in concert to acquire and direct energy to the maintenance and reproduction of living cells. This concerted effort makes biological processes far more efficient and selective than abiotic ones. Plants can convert several per cent of the solar energy they receive into complex molecules. Surprisingly, more than 40 per cent of living matter on earth is constructed by weight from a single 6 carbon sugar, glucose. SAGAN (1961) reported that abiotic reactions convert approximately 10^{-6} of the incident energy into carbon

compounds, and these conversions do not yield as selective a group of precisely structured molecules as do organisms.

Because living things are efficient fabricators and can seek energy, they dominate both the production and utilization of carbonaceous substances in biopsheres. A gross equilibrium is maintained on earth between the carbon in plants and animals and the CO_2 and carbonates of the earth's atmosphere and hydrosphere. Nearly all of the 10^{17} grams of organic matter photosynthesized each year in terrestrial environments is respired as CO_2 and H_2O (VALLENTYNE, 1962). Nevertheless, as sedimental carbonaceous materials attest, this equilibrium is not exact, and it is in the sediments that are rich in these materials that the most legible records of prehistoric life are found.

Since non-metamorphosed sediments containing detectable quantities of abiotic carbonaceous materials are apparently unknown, the mere presence of dark humic- or coal-like substances in deposits with low temperature histories is commonly accepted as evidence of former terrestrial life. But, the similarities between organic-rich sediments on earth and the Alais, Orgueil, Ivuna, and Tonk (Type I) carbonaceous chondrites is not solely restricted to the carbon contents of these samples. Some of the established resemblances between the Orgueil meteorite and certain organic-rich terrestrial sediments are that they contain:

1. Several per cent of combustible carbonaceous materials and several parts per thousand of benzene extractable carbon compounds;

2. Sedimentary minerals;

3 Mineral aggregates which suggest that the samples were deposited in carbon- or organic-rich, reducing, aqueous environments;

4. Free sulfur enriched in S^{34} relative to sulfur isolated from basic terrestrial rocks or the "primordial" sulfur in meteorites;

5. Friable, darkly colored associations of carbonaceous and mineral substances.

The densities of the Type 1 carbonaceous chondrites and organic-rich terrestrial sediments commonly fall in the 2.2 to 2.5 range. The greatest resemblances between terrestrial and meteoritic samples appear to exist between Type 1 carbonaceous chondrites and the organic-rich, near-surface sediments which retain the most legible records of ancient organisms on earth. These chondrites and sediments comprise less than 1 part in a thousand of the mass of known meteorites and of the earth, respectively.

Possibly, our limited sampling of earth may provide a more substantial basis for the interpretation of the analyses of the carbonaceous substances in Type 1 carbonaceous chondrites than in other meteorites. A consideration of the records of ancient terrestrial life may suggest reliable ways of determining the origin of the carbon compounds in these chondrites.

B. LEGIBILITY OF BIOLOGICAL RECORDS

Inasmuch as nature does not favor the preservation of highly-ordered systems, only biological remnants which are stable enough to resist erosion can retain the order which distinguishes animate from inanimate things. Legible records of ancient life and civilizations persist chiefly in a minor portion of the components and artifacts of

former life. More than 90 per cent of the carbonaceous materials found in terrestrial sediments appear as lignites, coal, or kerogens and related substances which do not chemically or physically resemble components of living things. Although it is generally accepted that the solid carbonaceous materials in sediments are principally of biological origin, it is not possible to establish direct structural relationships between most of these materials and biological molecules.

Observations of life and its remnants clearly indicate that the fossils and some hydrocarbons in sediments can be directly related either to organisms or biological molecules. Studies of fossils have permitted the establishment of evolutionary pathways by which many living species apparently reached their present states of being. The use of hydrocarbons may provide a means of studying the biochemical evolution of life. These fossils and alkanes comprise less than 10 per cent of sedimental organic matter.

Certain alkanes are the most stable compounds that have been found in plants and animals. Recent investigations by SMITH (1952, 1954), HUNT (1953), STEVENS, BRAY, and EVANS (1956), HUNT and JAMIESON (1956), MEINSCHEIN (1957a, 1959, 1961ab) and many others have shown that alkanes are distributed throughout essentially all sediments on earth. The stability and ubiquity of these compounds suggest that they may be the best preserved and most widely distributed remnants of former life. Furthermore, the large number of carbon atoms which many alkanes contain in their non-hydrolyzable and analyzable molecular units make it possible for these molecules to display great order.

While the chemical and biochemical stabilities, biological and sedimental distributions, and structural unit sizes indicate that hydrocarbons may potentially provide the most legible records of ancient life, it is important to determine as firmly as possible the origins of various sedimental hydrocarbons. This determination will permit an assessment of the reliability and potential of different hydrocarbons as biological indicators.

C. ORIGINS OF HYDROCARBONS IN TERRESTRIAL SEDIMENTS

Scientists have been intensely interested in how petroleum was made. Because crude oils are unique as regards their hydrocarbon content, most origin studies have sought primarily to learn how these hydrocarbons were formed. A wealth of information has been gathered on the origins and compositions of sedimental hydrocarbons. On an experimental as well as a theoretical basis, the use of hydrocarbons as biological indicators may be strongly defended.

ENGLER et al. (1893, 1897abc) made the first significant contribution to an understanding of how terrestrial hydrocarbons are formed. He destructively distilled biological lipids (fats, oils, and waxes which can be extracted from animals and plants with solvents such as ethyl alcohol and benzene) and obtained hydrocarbons with the same physical properties and elemental compositions as petroleum fractions. His theory that plant and animal acids and alcohols are important sources of hydrocarbons still receives substantial support from scientists today. Distributions of n-paraffins in crude oils and other considerations have been presented by BRAY and

EVANS (1961), ERDMAN (1961), COOPER and BRAY (1963), and MARTIN, WINTERS, and WILLIAMS (1963) as evidence that plant and animal fatty acids are a major source of the n-paraffins in terrestrial sediments. BENDORAITIS, BROWN, and HEPNER (1962, 1963) have proposed that farnesol and phytol, plant alcohols, are the probable precursors of nor-farnesane and farnesane (MAIR, KROUSKOP and MAYER, 1962) and of pristane (DEAN and WHITEHEAD, 1961; BENDORAITIS, BROWN, and HEPNER, 1962) and phytane (DEAN and WHITEHEAD, 1961) which have been identified in crude oils.

WHITMORE (1943) first suggested that plant hydrocarbons rather than lipids could be a source of petroleum. He wrote, "The literature contains ample evidence that plants of many kinds produce small, but significant quantities of hydrocarbons of the paraffin series. We have examined quantities of kelp and of fresh-water algae, and from them have isolated hydrocarbons. The kelp, in particular, produced hydrocarbons which boiled over a wide range. As individual hydrocarbons have a narrow boiling range, it is apparent that this marine plant produces a variety of hydrocarbons. It is of interest to note that the estimated production of organic carbon from kelp and other organisms in the sea would allow for the formation of something like 10 000 000 tons or about 60 000 000 bbl. of hydrocarbon material per year."

OAKWOOD (1953), who succeeded WHITMORE after the latter's death, reported at the conclusion of API Research Project 43, "The theory has been proposed that petroleum arose directly among the components of the organisms furnishing the organic matter. The virtue of this theory lies in its complete congruity with the geological history of sediments. The fault of the theory is that the compositions of vegetable hydrocarbons is not known now to be capable of accounting for the molecules of petroleum. Nevertheless, it is maintained that the factual evidence in favor is, at the very least, better than that offered for other theories."

ZOBELL (1953), who also was associated with API Research Project 43, observed of bacterial hydrocarbons production, "Although the amount of such hydrocarbons is small, if they are more resistant to decomposition than the rest of the bacterial cell substance, hydrocarbons may gradually accumulate as the organic material is used over and over again by bacteria."

The tremendous ten year effort conducted at six large academic and research institutions under API Research Project 43 supplied no evidence that radiological, chemical, and catabolic conversions of carbon compounds were important processes in the formation of alkanes. Partly to the contrary, HEALD (1953) noted, "Inasmuch as the most abundant product of radioactive bombardment is hydrogen, and inasmuch as the bombardment of methane consistently produced some unsaturated liquid hydrocarbons, none of which substances has been found in the petroleum fields of the world – despite the certainty that sediments, gases, and liquids are constantly undergoing radioactive bombardment in the earth – the research on the radioactive bombardment of organic materials not only failed to disclose how petroleum may originate, but it failed to answer additional perplexing problems which were created or emphasized by the work itself."

Utilization of information that organisms made hydrocarbons was temporarily

hampered by the apparent lack of hydrocarbons in most sediments. Because classical techniques did not usually detect hydrocarbons in sediments, a consensus, stated by Cox (1946), was reached that biological hydrocarbons were destroyed in near-surface sediments by bacterial action. This belief directed attention away from plant and animal hydrocarbons as petroleum source materials.

SMITH (1952, 1954) isolated a number of hydrocarbon fractions from segments of a core obtained by drilling vertically 103 feet into sediments in the Gulf of Mexico. Analyses of these hydrocarbons effectively corrected the misconception about the bacterial destruction of all biological alkanes. SMITH found that the sedimental hydrocarbons had the same C^{14} ages as the sediments from which they were isolated. Furthermore, these hydrocarbons had low optical activities similar in direction and magnitude to hydrocarbons from kelp and crude oils.

Although the biological acids and alcohols proposed by ENGLER or the biological hydrocarbons suggested by WHITMORE are most generally believed to be the major sources of terrestrial hydrocarbons, limited scientific support has been given the inorganic and cosmic, or abiotic, origins of hydrocarbons. ANDERS (1961, 1962) and WILSON (1963) indicate that terrestrial-type hydrocarbons could have been made cosmically or inorganically. ROBERTSON (1963) suggested a dual, biotic plus abiotic, origin of petroleum hydrocarbons. Since most hypotheses of the abiotic formation of hydrocarbons do not postulate synthetic processes that permit testing many of these hypotheses can neither be proved nor disproved. But as ZOBELL (1963) states, "The inorganic theories fail to account for the almost overwhelming evidence that like coal, oil formed from organic remains of plants and animals at temperatures probably less than 150°C and at pressures no more than 1000 psi." While inorganic reactions occur and nature does not exclude abiotic products, it seems likely that living things are the major source of hydrocarbons which resemble the hydrocarbons in living things. The C^{14} ages of Recent sediment hydrocarbons, the similarities in the optical activities, molecular weight distributions, structures, and elemental compositions of biological, sedimental, and petroleum alkanes, which have been presented above or will be discussed subsequently, seemingly establish that either biological hydrocarbons or their close structural relatives, biological acids and alcohols, are the predominant sources of the hydrocarbons containing more than 10 carbon atoms ($> C_{10}$) in terrestrial sediments.

Since the hydrocarbons containing less than 10 carbon atoms per molecule may display less order and are more subject to physical redistributions than are $> C_{10}$ hydrocarbons, the potential of light hydrocarbons as biological indicators is both less and more difficult to establish than is the potential of the $> C_{10}$ hydrocarbons. For this reason, discussion hereafter in this review will apply only to hydrocarbons containing more than 10 carbons per molecule.

D. EXPERIMENTAL DATA AFFORDING EVIDENCE OF THE ORIGINS OF DIFFERENT SEDIMENTAL
    HYDROCARBONS

Either biosynthetic hydrocarbons or hydrocarbons which retain structural features of

plant and animal acids and alcohols could serve as biological indicators. But, abiotic reactions that transform acids and alcohols or alter biological into sedimental hydrocarbons could partially destroy the order that apparently distinguishes biotic from abiotic hydrocarbons. Thus, the most reliable indicator of former biological activity may be retained by unaltered remnants of life. The following detailed discussion of the origins of terrestrial hydrocarbons will indicate why alkanes may provide the best means of determining the origins of some carbonaceous constituents in the Orgueil meteorite.

MEINSCHEIN (1957, 1959, 1960, 1961ab, 1963) and MEINSCHEIN and KENNY (1957) presented evidence, gathered by modern analytical techniques, of structural similarities and of some distributional differences between functional (acidic and alcoholic) and hydrocarbon constitutents of biological and sedimental lipids. MEINSCHEIN (1959, 1961b) cited the low concentrations of aromatics in living things and the abundances, structures, and distributions of aromatics in sediments as evidence that aromatic hydrocarbons were formed mainly from biological steroids and isoprenoids (terpenoids). The outstanding analyses of MAIR and MARTINEZ-PICO (1962), MAIR and BARNEWALL (1963), and MAIR and MAYER (1963) have identified over twenty large aromatic compounds in crude oil. They have established that most of these aromatic hydrocarbons are structurally related to steroids and terpenoids in living things.

Whereas agreement apparently exists on the primary origin of sedimental aromatics, disagreements still persist on the origins of alkanes in ancient sediments. MEINSCHEIN (1960) reported, "The fact that the distribution of naturally occurring C_{17} to C_{33} saturated hydrocarbons differ in consistent but chemically unexplainable ways from structurally similar hydrocarbons made by the hydrogenation of the plant and animal acids and alcohols ... clearly indicates that chemical transformations of the remains of living things in sediments are not an important source of the high molecular weight saturated hydrocarbons in petroleum." The preceding opinion is not supported by BRAY and EVANS (1961), COOPER and BRAY (1963), MARTIN, WINTER, and WILLIAMS (1963), BENDORAITIS, BROWN and HEPNER (1962, 1963), ERDMAN (1961), BREGER (1959), and others. Although alkanes in Recent sediments are frequently assumed to be of direct biological origin, many investigators believe that biological acids and/or alcohols are the principal precursors of ancient sedimental alkanes.

Some of the disagreement on the role of biological acids and alcohols in the formation of alkanes may be traced to the use of crude oil alkane distributions for defining the origins of hydrocarbons. A consideration of how chemical and physical processes in sediments may affect biological remnants could suggest other means of appraising the origins of sedimental alkanes.

Biological alkanes display isotopic, structural, and distributional order. Plant and animal remnants in sediments are altered in varying degrees by chemical and physical processes that occur over long periods of time. Chemical reactions change the isotopic and structural compositions which in turn change the distributions of biological materials. Physical processes can alter the isotopic compositions of light hydrocarbons significantly, but these processes probably will detectably change only the distributions

of $> C_{10}$ alkanes. Because either physical or chemical changes may alter alkane distributions, structural and isotopic rather than distributional analyses could permit the best evaluation of the effects of abiotic reactions on the compositions of sedimental alkanes.

Structural analogies between biological and sedimental alkanes have been discussed above. Pristane and phytane are present in crude oils, as has been noted, and in a number of organisms (MOLD, STEVENS, MEANS, and RUTH, 1963; SORENSEN and MEHLUM, 1948). Pristane and phytane compose in excess of 0.5 weight per cent of some crude oils, and similar concentration of these compounds are found in certains biological lipids. n-Paraffins are commonly the most abundant alkanes in crude oils and biological alkanes. These identified common constituents probably comprised in excess of 30 per cent of the sedimental and biological $> C_{10}$ saturated hydrocarbons. Structural similarities reported by MEINSCHEIN (1959, 1960, 1961b) and recently by CIERESKO, ATTAWAY, and KOONS (1963) indicate that additional identifications of alkanes in organisms and crude oils could further extend the structural agreement between constituents of these alkane fractions. So, structural analyses, as yet, do not show that chemical changes have exerted a strong control on the compositions of $> C_{10}$ alkanes in sediments. A similar interpretation may be made of isotopic analyses.

Isotopic data obtained by SILVERMAN and EPSTEIN (1958), PARK and EPSTEIN (1960), SILVERMAN (1960, 1961), ECKELMAN (1961), and KLEIN (1957), and studies of isotope effects on reaction rates and products by YANKWICK and IKEDA (1959), MELANDER (1960), BEVINGTON (1961), and BATES and BEVINGTON (1963) have established that:

1. The range and sizes of δC^{13} values of sedimental alkanes and of biological lipids are comparable;

2. Biological lipids have on the average δC^{13} values which are approximately $3^0/_{00}$ lower than those for total plant and animal matter;

3. C^{14} contents of the acids, alcohols, and hydrocarbons in lipid fractions which were made biosynthetically from C^{14} labelled acetates are identical;

4. Hydrocarbons or compounds formed by partial removal of carboxyl, hydroxyl, or alkyl carbon atoms from acids, alcohols or other hydrocarbons will have higher C^{13} contents than the single carbon fragments or the reactants;

5. Aromatic compounds in crude oils have higher C^{13} contents than do alkanes of the same carbon numbers;

6. In a single crude oil, the δC^{13} values of alkanes decrease less rapidly with increasing carbon number in the C_{10} to C_{25} range than do the δC^{13} values of aromatic hydrocarbons;

7. The δC^{13} contents of crude oils decrease slightly as the geologic ages of the oils increase;

8. Within most crude oils, the differences between the δC^{13} contents of C_{25} and C_{10} alkanes is less than $1^0/_{00}$.

By referring to the observations above, it may be deduced from 1, 2, 3, 4, and 5 that alkanes could be direct and aromatics could be derived products of the bio-

synthesis of lipids. Observations 4, 6, and 7 indicate that aromatics have lower stabilities than alkanes in sedimentary environments. These lower stabilities would lead to decreases in the aromatic and increases in the alkane contents of oils of old geologic ages. Such a change in compositions could partially explain, in conjunction with observation 6, the decrease in the δC^{13} contents of crude oils of greater geologic age. Observations 4, 7, and 8 indicate that the cracking of carbon to carbon bonds in alkane molecules is not appreciable over long periods of geologic time.

Neither structural nor isotopic data apparently indicate that abiotic chemical reactions play an important role either in the formation or alteration of alkanes in most terrestrial sediments. Similar optical properties of sedimental and biological alkanes (WHITMORE, 1945 and SMITH, 1954) suggest, also, that sedimental alkanes are chemically stable biological products. But, additional positive evidence of how physical rather than chemical processes have exerted the principal controls on the distributions of biological alkanes in ancient sediments may increase the recognition of alkanes as reliable biological indicators.

Petroleum occurrence suggests that physical rather than chemical processes may play the dominant role in its formation. Crude oils are seldom found in or near metamorphosed rocks. There is no evidence that high temperatures, which enhance chemical reaction rates, have favored petroleum formation. The largest oil accumulations are usually associated with highly porous sediments. In these sediments, crude oils are trapped above water and below impervious rocks. BAKER (1959, 1961) and MEINSCHEIN (1959, 1961a) proposed that crude oils are selective accumulations of sedimental organic materials. Ground waters forced from organic rich sediments by compaction may pass into porous strata and release some hydrocarbons and other petroleum constituents. The released and washed materials then could form crude oils. Since ground waters are poor solvents for $> C_{10}$ alkanes, this proposal may explain why only a minor fraction of a per cent of sedimental alkanes are found in crude oil deposits (HUNT, 1961).

While the distributions of alkanes in petroleum could be affected greatly by processes that occur during their solution, migration, release, and emplacement by ground waters, the distributions of alkanes in the bulk of sediments may not have been appreciably altered by the removal of the small proportion of alkanes which were transported to crude oil reservoirs. Diffusion, also, may change alkane distributions in sediments. Over long periods of time hydrocarbons could diffuse from sediments of low- to sediments of high-organic contents, but transfers of this type would be slower and restricted to shorter intervals of distance than would the transfers resulting from the irreversible flows of ground waters that may produce crude oils. Thus, if crude oils and certain organic rich deposits which may have acquired most of their hydrocarbons from solutes in ground waters are excluded, many of alkanes in ancient sediments still may resemble distributionally the alkanes in living things. An experimental demonstration of this resemblance would attest to the biological origin and the stabilities of these alkanes.

As suggested above, living things probably are the principal obstacle to the escape

TABLE 1

Percentages of the benzene extracts of cow manure, bat guano, and terrestrial soils that are eluted successively by equal volumes of *n*-heptane (*n*-C₇), carbon tetrachloride (CCl₄), benzene (C₆H₆), and methanol (CH₃OH) from a silica gel chromatographic column. Percentages given for terrestrial soils are averages of the number of analyses shown in parentheses to the right of the sample designations. Standard deviations for the soil analyses are presented to the right of these analyses as σ values.

	Per Cent of Extracts Eluted by			
Sample	*n*-C₇	CCl₄	C₆H₆	CH₃OH
Cow Manure	5.5	3.3	14.0	63.3
Bat Guano	5.0	1.1	11.4	60.0
Soils (49)	5.5 ($\sigma = 2.9$)	4.8 ($\sigma = 4.1$)	6.5 ($\sigma = 2.1$)	64.0 ($\sigma = 7.8$)

of carbon compounds from the carbon cycle. Compounds most capable of escaping biological assimilation could become concentrated in the elimination products of living things and sediments. Table 1 presents a silica gel chromatographic analysis of benzene extracts of cow manure, bat guano, and terrestrial sediments. It is assumed that, since cows and bats consume chiefly plants and insects, respectively, these elimination products contain separate composites made up principally of plant and insect or animal alkanes. The data in Table 1 show that alkane concentrations (*n*-heptane eluate percentages) in the extracts of the elimination products and sediments are comparable.

Gas chromatograms (GLC) of biological, sedimental, abiotic (Fischer-Tropsch) alkanes are shown in Figures 1 through 4. These chromatograms were obtained using
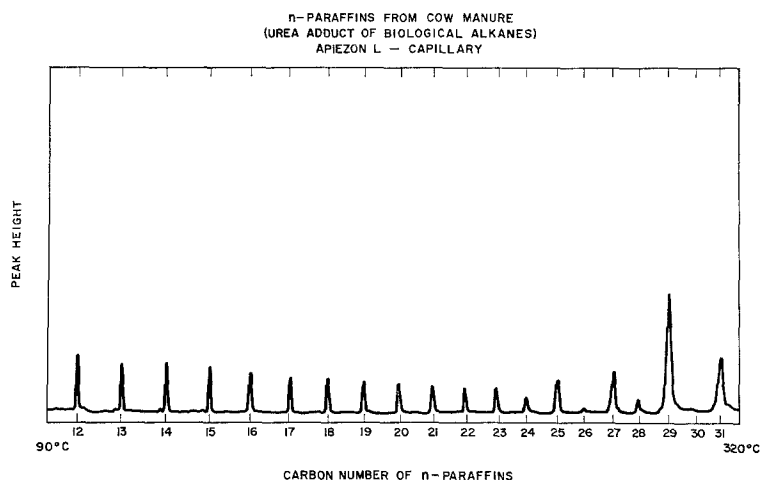

n—PARAFFINS FROM COW MANURE
(UREA ADDUCT OF BIOLOGICAL ALKANES)
APIEZON L — CAPILLARY

Fig. 1. Capillary column chromatogram of urea-adducted fraction (mainly *n*-paraffins) of alkanes from cow manure.

a temperature programmed, Apiezon "L" coated, 0.01 inch capillary column 100 feet in length. The column temperature was raised 4°C per minute from 70° to 300°C. Figure 1 presents a chromatogram of an urea adducted fraction of alkanes from cow manure. This fraction consists primarily of *n*-paraffins and its chromatogram serves as a reference for identification of *n*-paraffin peaks in Figures 2 through 4. Figure 2 is a chromatogram of alkanes from bat guano. Figure 3 presents a chromatogram of alkanes from a 40 to 60 million year old Eocene sediment.

Noteworthy in Figures 1, 2 and 3 are the markedly greater abundances of odd than of even carbon number n-paraffins in 23 to 31 carbon number range. In Figures 2 and 3, the concentrations of even carbon number paraffins in the 12 to 20 carbon
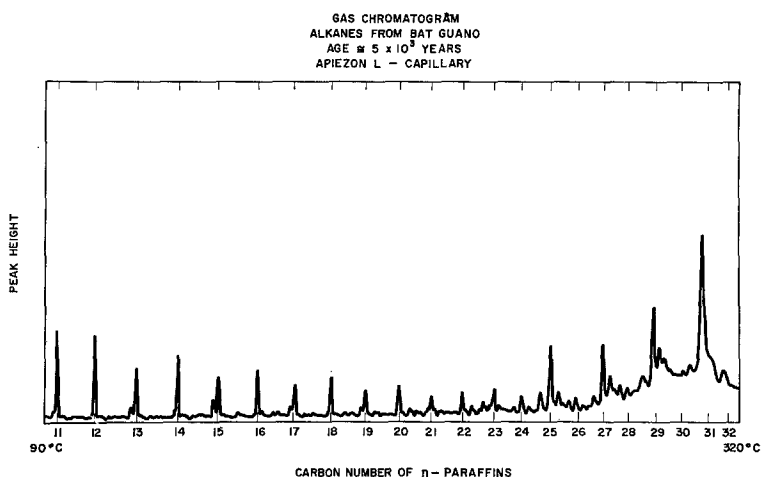

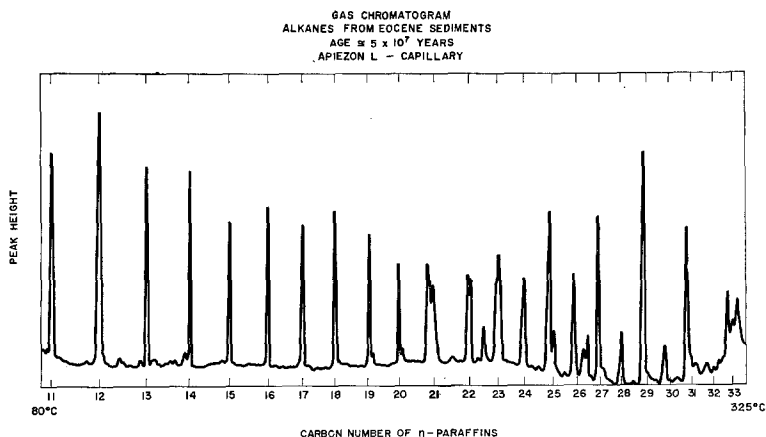Fig. 2. Capillary columns chromatogram of alkanes from bat guano.

Fig. 3. Capillary column chromatogram of alkanes from Eocene (3×10^7 to 6×10^7 years old) sediments.

number range slightly exceed those of their odd carbon number homologs. Data in Figures 2 and 3 indicate as do isotopic and structural analyses that biological alkanes can retain order for geologic periods of time in some sedimentary environments.

A gas chromatogram of alkanes made by Fischer-Tropsch (abiotic) process is shown in Figure 4. It is not presumed that the Fischer-Tropsch alkanes are typical of all abiotic alkanes, but these alkanes probably provide the best synthetic substitutes for petroleum, and SHARKEY, SHULTZ, and FRIEDEL (1962) have suggested the alkane distributions in this abiotic product may resemble those in crude oils.

GAS CHROMATOGRAM
FISHER−TROPSCH (ABIOTIC) ALKANES
APIEZON L − CAPILLARY
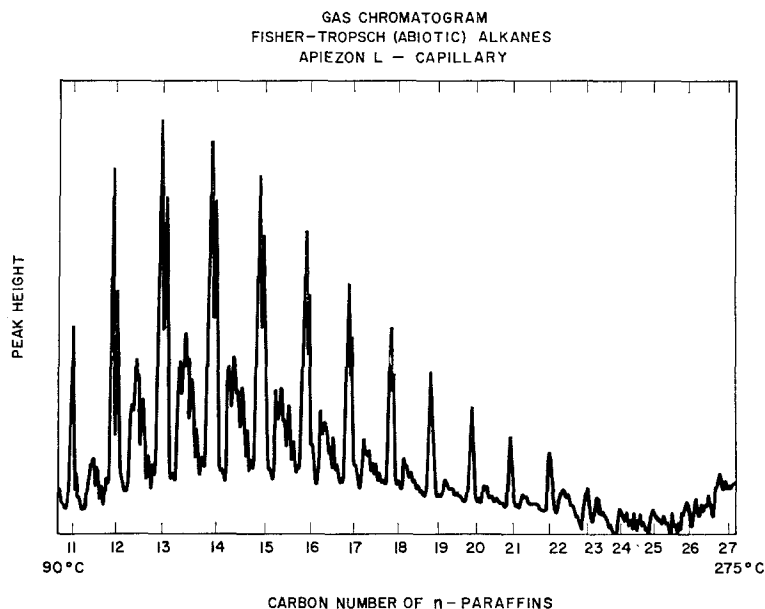
Fig. 4.   Capillary column chromatogram of alkanes from Fischer-Tropsch (abiotic) product.

Changes in the concentrations of the Fischer-Tropsch alkanes in Figure 4 follow a simple pattern. Their concentrations increase at low carbon number because some of the volatile alkanes were distilled away when this sample was recovered by evaporating the solvents used in isolating the alkanes from other compounds in the Fischer-Tropsch product. The systematic decrease in the $> C_{13}$ alkanes show that the yields of alkanes decrease with carbon number in this abiotic fraction as UNDERWOOD (1940) and SHARKEY, SCHULTZ, and FRIEDEL (1962) have noted.

Figure 5 shows the chromatogram of a benzene extract of the Orgueil meteorite. This chromatogram, was furnished by D. J. HENNESSY of Fordham University. The extract contains free sulfur as well as carbon compounds containing elements other than carbon and hydrogen. In addition, this chromatogram was obtained on a packed analytical rather than a capillary column. Although a direct comparison between the data in Figure 5 and Figures 1–4 is not possible, most of the large peaks in Figure 5

are probably hydrocarbon peaks, and these peaks do not vary systematically as do the peaks in Figure 4. In the future, it would be desirable to obtain a gas chromatogram of alkanes from a Type I carbonaceous chrondite which could permit a direct comparison of their distributions with those of alkanes from terrestrial sediments.

GAS CHROMATOGRAM
BENZENE EXTRACT OF ORGUEIL METEORITE
APIEZON L — ANALYTICAL COLUMN

DATA SUPPLIED BY
PROF. D. J. HENNESSY
OF FORDHAM UNIVERSITY

PEAK HEIGHT

TEMP °C
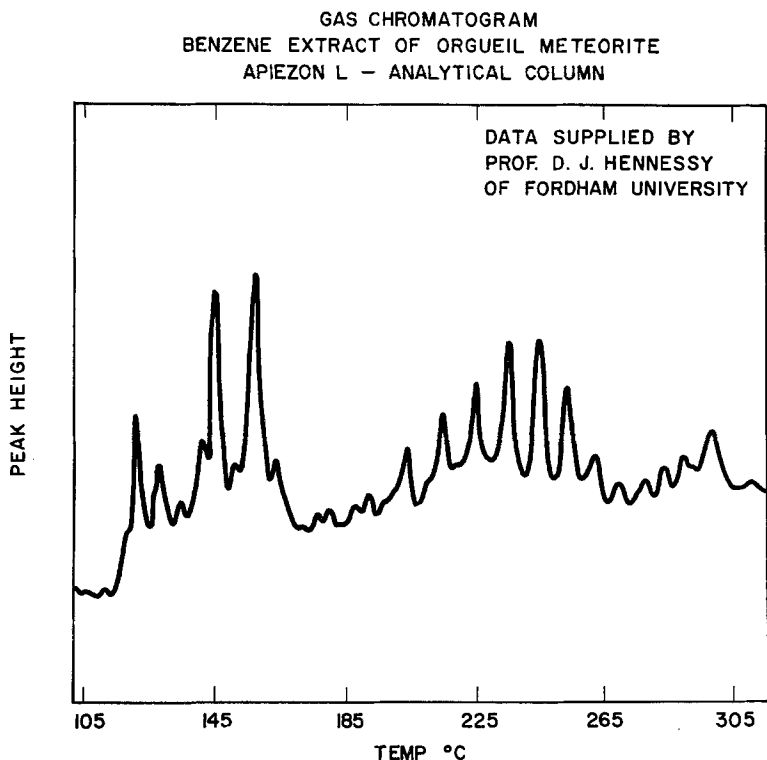
Fig. 5. Analytical column chromatogram of total benzene extract of the Orgueil meteorite.

E. BENZENE EXTRACTS OF THE ORGUEIL METEORITE AND TERRESTRIAL SEDIMENTS

Chromatographic, infrared, and ultraviolet spectroscopic, and mass spectrometric analyses have been obtained of the benzene soluble fractions of living things, terrestrial sediments, crude oils, Fischer-Tropsch products, and the Orgueil meteorite. As noted previously, most constituents of biological and sedimental lipids are not similar, but it is generally assumed that biological precursors have exerted controls on the compositions of most of the benzene extractable materials in terrestrial sediments.

In subsequent discussions, the analyses of the benzene soluble carbon compounds of terrestrial sediments, a Fischer-Tropsch (abiotic) product, and the Orgueil meteorite will be compared. Following these general comparisons, the analyses of the $> C_{10}$ alkanes which are the principal common constituents of biological, sedimental, and

Fig. 6. Infrared absorption spectra of the benzene extractable fractions of the Orgueil meteorite, terrestrial sediments, crude oil, and Fischer-Tropsch (abiotic) product. Carbon disulfide was used as spectral solvent.

meteoritic lipids will be reviewed. Instruments and procedures employed in obtaining these analyses have been described by MEINSCHEIN, NAGY, and HENNESSY (1963).

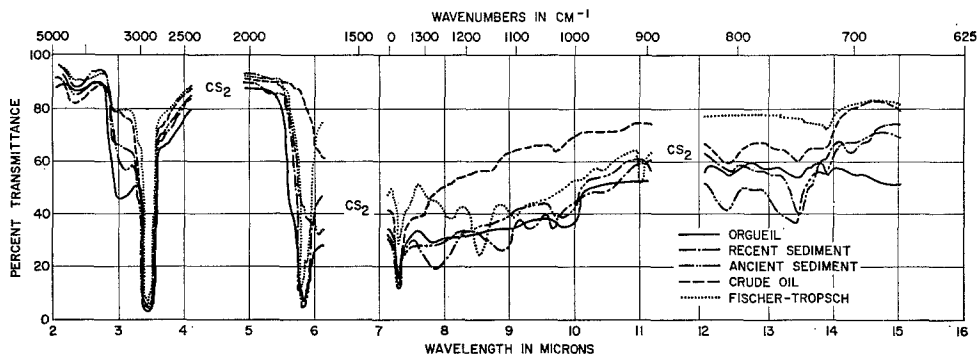Infrared spectra of a crude oil, Fischer-Tropsch product, and the benzene extracts of terrestrial sediments and the Orgueil meteorite are shown in Figure 6. The spectra in Figure 6 differ in certain aspects. Differences can be observed between individual organisms or extracts of various biologically derived substances. But, those absorption bands that are most frequently observed in the benzene extractable fractions of

TABLE 2

Percentage of the benzene extracts of the Orgueil meteorite and various terrestrial samples that are eluted successively by equal volumes of n-heptane (n-C$_7$), carbon tetrachloride (CCl$_4$), benzene (C$_6$H$_6$), and methanol (CH$_3$OH) from a silica gel chromatographic column. Percentages given for terrestrial samples are averages of the number of analyses shown in parentheses to the right of the sample designations. Standard deviations for the analyses of the benzene extracts of terrestrial sediments are presented to the right of these analyses as σ values.

| | Per Cent of Extracts Eluted by | | | |
Sample	n-C$_7$	CCl$_4$	C$_6$H$_6$	CH$_3$OH
Meteorite:				
Orgueil	10.0	5.4	3.2	63.1
Sediments:				
Recent Marine (12)*	6.0 (σ = 5.9)	8.0 (σ = 5.0)	5.0 (σ = 5.5)	63.0 (σ = 8.7)
Soils (49)	5.5 (σ = 2.9)	4.8 (σ = 4.1)	6.5 (σ = 2.1)	64.0 (σ = 7.8)
Ancient (32)*	30.5 (σ = 21.6)	10.3 (σ = 6.8)	23.7 (σ = 7.8)	30.2 (σ = 16.6)
Crude Oils (103)	41.5	10.8	26.6	7.4

* These analyses were corrected for elemental sulfur. The Orgueil extract, also, contained elemental sulfur which was removed prior to the chromatographic analyses.

terrestrial sediments appear, also, in the Orgueil extract. While the carbon to hydrogen (2 775–3 000 and 1 330–1 430 cm^{-1}) bands are too common in carbon compounds to be significant, the absorptions near 3 300 (OH or NH); 1 030 815, and 745 (aromatics), and 1 730 (ester carbonyl) cm^{-1} are found in the infrared spectra of the extracts of many Recent sediments. These absorptions in the Orgueil extract indicate that it is composed of a complex mixture of compounds functionally similar to those in some Recent terrestrial sediments.

Weight per cents of the benzene soluble fractions of terrestrial samples and the Orgueil meteorite which are eluted from silica gel by adding constant volumes of n-heptane, carbon tetrachloride, benzene, and methanol in sequence are given in

Fig. 7.   Infrared absorption spectra of the silica gel chromatographic fractions of the benzene extracts of the Orgueil meteorite. Carbon disulfide was used as spectral solvent.

Table 2. Numbers in parentheses beside the sample designations in Tables 2 and 6 indicate the number of samples averaged to obtain the values noted. Standard deviations (σ) for the terrestrial samples show the variations between samples of a kind reported in these tables. The analyses in Table 2 suggest that the Orgueil, soil, and Recent marine sediment extracts contain similar proportions of the different compound types which were eluted by the four eluants.

Infrared and ultraviolet spectra in Figures 7 and 8 provide information about the types of compounds found in the four silica gel eluates of the Orgueil extract. Spectra in Figure 7 show that the meteorite compounds are structurally or functionally similar to compounds in extracts from terrestrial sediments. Further confirmation of this similarity is provided by the ultraviolet spectra of the eluates of the Orgueil extract in Figure 8. From data in Figures 7 and 8 and mass spectrometric analyses which will be presented subsequently, it can be deduced that the n-heptane, carbon tetrachloride, and benzene eluates of the Orgueil extract are composed mainly of alkanes and aromatic hydrocarbons as are these eluates of most Recent marine sediments. The n-heptane eluate consists predominantly of alkanes; whereas the benzene eluate

contains chiefly aromatic hydrocarbons. Methanol eluates of the sediment and mete-
orite extracts contain alcohols or amino compounds and esters, but the specific
nature of most compounds in these fractions have not been determined.

Ultraviolet and mass data in Figure 8 and Table 3, respectively, and the ultra-
violet spectra in Figure 9 are of appreciable interest. These data show that the aro-
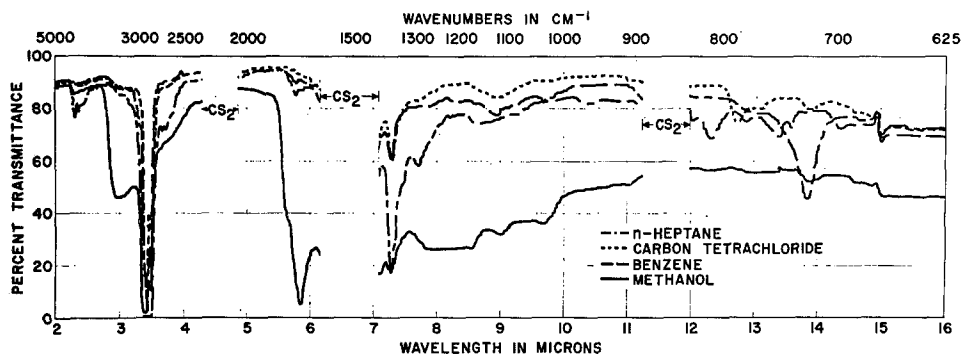matics from the Orgueil are the same types of aromatics found in many Recent
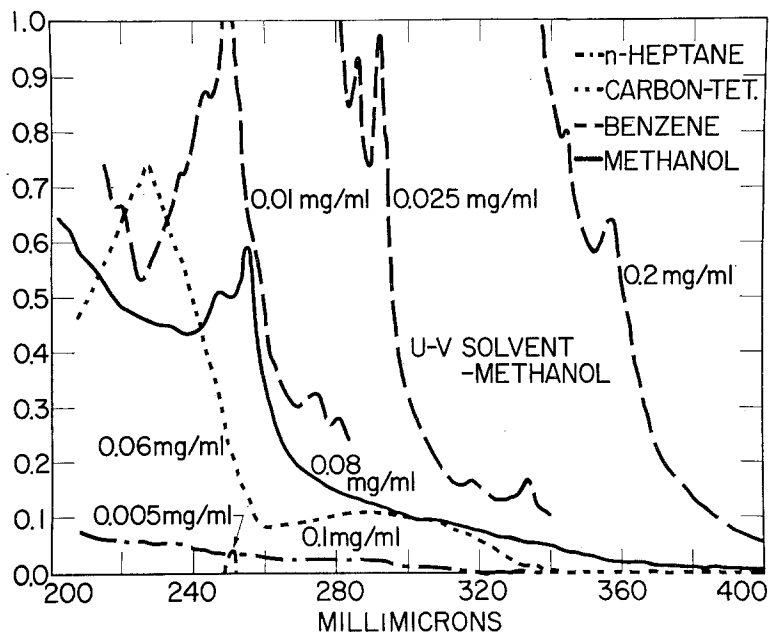
Fig. 8. Ultraviolet absorption spectra of the silica gel chromatographic fractions of the benzene
extracts of the Orgueil meteorite. Iso-octane was used as spectral solvent.

marine sediments. Phenanthrene and alkyl and cycloalkyl phenanthrenes are the most
abundant constituents of the Orgueil aromatic fraction, but chrysene, pyrene and
their alkyl and cycloalkyl derivatives, also, are present in this fraction. MEINSCHEIN
(1959) and BLUMER (1961) have identified phenanthrene, chrysene, and pyrene in
terrestrial sediments. Discussions of the origins and the reasons for the differences
in distributions of aromatics in Recent and ancient sediments have been suggested by
MEINSCHEIN (1959, 1961ab).

None of the terrestrial samples available for this investigation contained aromatic
fractions as simple as the Orgueil aromatics. Alumina chromatograph (MEINSCHEIN,
1959) was used to simplify the terrestrial aromatics. Ultraviolet spectra in Figure 9
were obtained on equivalent alumina fractions of the terrestrial samples. These
fractions had the same adsorption properties as do the phenanthrenes, chrysenes,
and pyrenes which were the major constituents of the Orgueil aromatics. As shown

in Figure 9, the aromatics isolated from the Recent marine sediment aromatic fraction has an ultraviolet spectrum markedly similar to that of the Orgueil aromatics.

The simplicity, composition, and concentration of the aromatic hydrocarbons in this Orgueil fragment effectively eliminates the possibility that this fraction is a terrestrial contaminant (MEINSCHEIN, 1963). Although a relatively small proportion of Recent marine sediments may contain aromatic fractions as simple as the Orgueil meteorite, the average concentrations of carbonaceous materials, alkanes, and aromatic hydrocarbons in terrestrial sediments are a fraction of the concentrations of
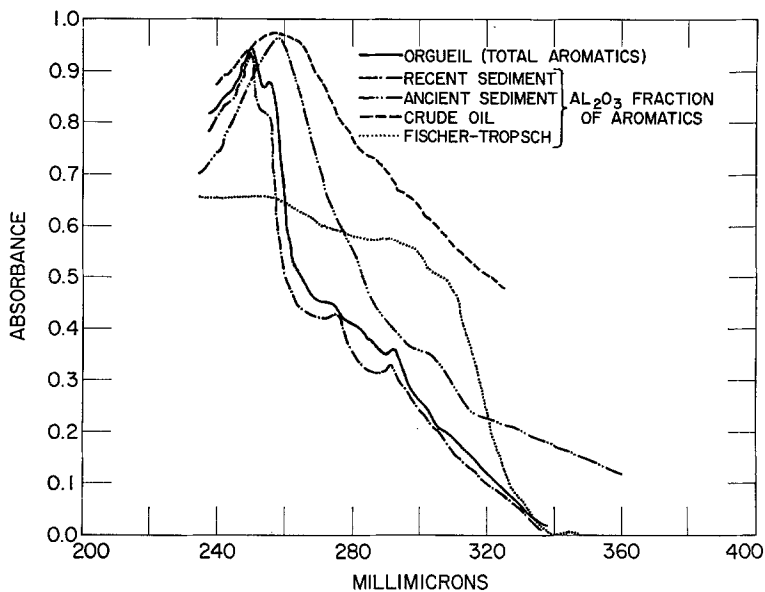
Fig. 9.   Ultraviolet absorption spectra of aromatic fractions from the Orgueil meteorite and terrestrial samples. Iso-octane was used as spectral solvent.

these substances in the Orgueil meteorite. It is highly unlikely that this Orgueil fragment could have contacted and acquired from marine sediments the types and quantities of aromatics it contained.

Data in Table 3, also, show that the simple mixture of aromatic hydrocarbon extracted from the Orgueil stone contain complex molecules. Positions of the values in Table 3 show the carbon numbers, C#'s, and hydrogen contents (as determined from the general hydrocarbon formula Cn H_{2n}+ "x"), "x"'s, of saturated hydrocarbons having masses equal to the aromatic ions. These masses may be calculated by multiplying the C#'s by 14 and adding the "x" values to the preceding product. Since most aromatic hydrocabons in the Orgueil fraction have "x" values which are 14 less than indicated by the column headings in Table 3, the actual carbon numbers

TABLE 3

MASS SPECTRUM OF THE BENZENE ELUATE FROM SILICA GEL OF THE 1-ORGUEIL-6 HOUR EXTRACT. AROMATIC HYDROCARBON FRACTION

Mass spectrum of aromatic hydrocarbon fraction of the benzene extract of the Orgueil meteorite. Numbers ranging from — 11 on the left to +2 on the right at the tops of columns are "x" values. The carbon numbers, C $\neq$'s or n's, are listed in columns, one to the left and one to the right of the "x" columns. The positions and sizes of values in Table indicate the masses and relative abundances of the ions. This spectrum was obtained using a 12 electron volt ionizing potential, and most of the ions are "parent ions". A "parent ion" is an ion formed when a molecule loses a single electron, thus the masses of most ions in this spectrum correspond to the molecular weights of aromatic hydrocarbons from the Orgueil meteorite. Masses of the ions can be determined from C $\neq$'s and "x" values using the general hydrocarbon formula $C_nH_{2+\text{``x''}}$. The mass of an ion equals 14 times its C $\neq$ plus "x". The largest value in the Table appears at C $\neq$ = 13 and "x" = — 4. It has a mass of 182-4 = 178, which is the molecular weight of phenanthrene.

Total Ionization = 3748.80

Normalized Isotope Corrected Peak Heights (300 000)

C≠s	—11	—10	—9	—8	—7	—6	—5	—4 0.	—3 3.	—2 —0.	—1 —0.	0 —0.	+1 —0.	+2 —0.	
4	—0.	0.	0.	0.	—0.	—0.	—0.	—0.	—0.	—0.	—0.	—0.	—0.	—0.	4
5	—0.	0.	—0.	—0.	—0.	—0.	—0.	—0.	56.	1493.	1254.	0.	0.	0.	5
6	0.	0.	0.	33.	0.	0.	628.	1375.	1565.	1150.	1017.	0.	0.	0.	6
7	0.	0.	0.	86.	0.	329.	672.	1204.	2602.	2412.	503.	0.	0.	0.	7
8	0.	0.	0.	0.	0.	11.	136.	364.	504.	2171.	982.	121.	0.	0.	8
9	0.	0.	0.	0.	391.	0.	0.	538.	563.	558.	1598.	0.	452.	0.	9
10	0.	0.	0.	1105.	815.	200.	589.	150.	196.	0.	620.	0.	463.	0.	10
11	0.	6.	0.	379.	90.	123.	120.	0.	300.	3141.	551.	447.	477.	315.	11
12	0.	0.	0.	137.	358.	8.	52.	0.	1180.	12303.	890.	1918.	1150.	526.	12
13	0.	215.	185.	0.	62.	0.	0.	38880.	706.	9265.	379.	871.	83.	515.	13
14	0.	0.	0.	0.	0.	0.	815.	2653.	36.	2021.	461.	442.	221.	336.	14
15	0.	51.	134.	1074.	917.	130.	1062.	438.	0.	295.	7.	211.	341.	0.	15
16	0.	0.	182.	428.	0.	308.	243.	969.	121.	0.	0.	0.	0.	0.	16
17	0.	1128.	0.	416.	0.	308.	560.	1546.	0.	141.	271.	83.	0.	0.	17
18	0.	244.	0.	129.	0.	446.	614.	4647.	0.	0.	0.	2460.	284.	593.	18
19	89.	506.	0.	970.	16.	673.	0.	494.	0.	0.	0.	599.	96.	664.	19
20	0.	256.	0.	378.	0.	0.	0.	1074.	0.	133.	0.	313.	157.	895.	20
21	0.	167.	0.	226.	0.	702.	0.	320.	0.	686.	0.	555.	18.	1799.	21
22	0.	496.	0.	954.	0.	651.	0.	639.	953.	1487.	0.	954.	707.	4257.	22
23	0.	585.	0.	403.	0.	1376.	0.	947.	1498.	8527.	0.	1308.	341.	5767.	23
24	0.	239.	0.	1275.	0.	2294.	29.	3413.	101.	14557.	167.	2635.	187.	6071.	24
25	0.	533.	0.	4600.	0.	2176.	0.	6957.	44.	6348.	0.	3832.	0.	5896.	25
26	0.	758.	0.	2588.	0.	1820.	98.	5077.	22.	4726.	0.	3537.	0.	6088.	26
27	0.	3057.	0.	1957.	0.	1185.	0.	2664.	0.	1676.	0.	3262.	0.	1772.	27
28	0.	1077.	0.	525.	0.	710.	0.	722.	0.	722.	0.	1628.	0.	1788.	28
29	0.	847.	0.	1036.	0.	1069.	0.	49.	0.	—0.	—0.	—0.	—0.	—0.	29

HUMBLE AROMATICS TYPE ANALYSIS IN PERCENT

Alkyl Benzenes	5.11
Naphthalenes	16.156
Acenaphthenes	17.75
Acenaphthylenes	11.10
Phenanthrenes	20.95
Diacenaphthylenes	4.01
Pyrenes	1.43
Chrysenes	0.55
Acepyrenes	1.09
Benzpyrene and other Organic Compounds	21.45
Total	100.00

of the ions are usually 1 greater than the values listed. These errors in carbon numbers of aromatic ions make it possible to standardize the form in which computers prepare mass spectral data (MEINSCHEIN, NAGY, and HENNESSY, 1963). Thus, the positions and sizes of the values in Table 3 show the masses and indicate the relative abundances of the Orgueil aromatic hydrocarbons, but the true carbon numbers of these aromatics must be determined from knowledge of their masses and structures.

As stated above, the ultraviolet spectra in Figure 8 show that the aromatic hydrocarbons from the Orgueil meteorite are composed primarily in order of decreasing abundances of phenanthrenes, chrysenes, and pyrenes. The large values in the even "x" columns in the 23 to 28 carbon number range of Table 3 are chiefly "parent" ions of alkyl and cycloalkyl substituted phenanthrenes, chrysenes, and pyrenes containing from 24 to 29 carbon atoms per molecule. In the 19 to 23 (actually 20 to 24) carbon number range, all values listed in Table 3 are relatively small as are most values in the 9, 10, and 11 carbon number range.

If it is assumed that isoprenoids or terpenoids and steroids were the principal sources of the Orgueil aromatics, as they are indicated to be of aromatics in terrestrial sediments, the high and low concentrations of aromatics in various carbon number ranges shown by data in Table 3 may be explained.

Most isoprenoids and steroids in organisms on earth contain 10, 15, 20, or 27 to 30 carbon atoms per molecule. When terpenoid or steroid ring systems are converted into aromatic ring systems, one or more methyl or some other alkyl group or groups usually must be eliminated from the terpenoids or steroids. This elimination is necessitated by the tetravalence of carbon. Aromatic ring carbons can have at most only one substituent methyl or alkyl group, but many isoprenoids and all steroids contain di- or poly-substituted ring carbons. Consequentially, aromatics formed from steroids or isoprenoids will contain fewer carbon atoms than their biologically produced precursors. Data in Table 3 show that the maxima in concentrations of aromatic hydrocarbons appear at carbon numbers slightly below while the minima in aromatic concentrations appear at carbon numbers equal or slightly greater than those of the most abundant isoprenoids and steroids in terrestrial organisms.

Mass spectra of the alkane fraction and of a concentrate of the polycyclic and n-paraffin constituents of this fraction from the Orgueil meteorite are tabulated in Tables 4 and 5, respectively. Data in Table 4 have been discussed previously by MEINSCHEIN, NAGY, and HENNESSY (1963). An independent review of the preceding publication by competent and experienced organic geochemists was presented by UREY (1962). These reviewers concurred that the organic materials identified in the Orgueil meteorite are comparable to biogenic and sedimentary organic materials on earth. Data in Table 4, as noted by MEINSCHEIN, NAGY, and HENNESSY (1963), show that the alkanes from the Orgueil meteorite have molecular weight distributions and structural features resembling those of alkanes from terrestrial sediments. These resemblances will be noted in the discussion of data in Table 5 which are being presented for the first time.

A polycyclic alkane and n-paraffin concentrate of the Orgueil alkanes was obtained

TABLE 4

MASS SPECTRUM OF THE N-HEPTANE ELUATE FROM SILICA GEL OF THE 1-ORGUEIL-6 HOUR EXTRACT.
SATURATED HYDROCARBON FRACTION

Mass spectrum of alkanes from the benzene extract of the Orgueil meteorite. Numbers ranging from — 11 on the left to + 2 on the right at the tops of columns are "x" values. The carbon numbers, C#'s or n's, are listed in columns, one to the left and one to the right of the "x" columns. The positions and sizes of values in Table indicate the masses and relative abundances of "parent" and "fragment" ions. Alkanes do not yield "parent ion" spectra (as do aromatic hydrocarbons) at low ionization potentials. This spectrum was obtained using 70 electron volt ionizing potential. Masses of ions can be determined by multiplying the C#'s by 14 and adding "x". The ion in the "x" = — 6 column at C# = 27 has a mass of 378-6 = 372, which is the molecular weight of cholestane.

Total Ionization = 58022.28

Normalized Isotope Corrected Peak Heights (300 000)

	— 11	— 10	— 9	— 8	— 7	— 6	— 5	— 4	— 3	— 2	— 1	0	+ 1	+ 2	
								0.	0.	— 0.	— 0.	— 0.	— 0.	— 0.	3
4	— 0.	0.	0.	0.	— 0.	— 0.	— 0.	— 0.	— 0.	— 0.	— 0.	— 0.	— 0.	— 0.	4
5	— 0.	0.	— 0.	— 0.	— 0.	— 0.	— 0.	— 0.	9389.	3350.	19430.	5997.	16219.	74.	5
6	175.	265.	223.	221.	2025.	573.	3593.	1234.	10154.	4045.	13601.	2908.	10411.	67.	6
7	263.	86.	285.	229.	5338.	2511.	3087.	1175.	9135.	3219.	11029.	2118.	2317.	70.	7
8	110.	112.	267.	290.	1885.	436.	2621.	1208.	5861.	1812.	6230.	1651.	1639.	47.	8
9	479.	183.	603.	258.	1418.	405.	1880.	854.	3944.	1173.	3360.	1079.	1338.	376.	9
10	440.	175.	617.	245.	872.	361.	1706.	707.	2465.	734.	1418.	813.	1192.	176.	10
11	354.	161.	566.	171.	687.	312.	1682.	572.	1768.	642.	921.	713.	985.	131.	11
12	270.	137.	433.	141.	581.	266.	1354.	462.	1409.	479.	698.	650.	867.	114.	12
13	208.	101.	286.	142.	544.	280.	1178.	482.	1112.	433.	555.	580.	751.	106.	13
14	234.	74.	263.	127.	585.	263.	1166.	373.	982.	410.	461.	511.	668.	59.	14
15	172.	139.	252.	265.	1099.	335.	962.	252.	626.	324.	344.	422.	585.	29.	15
16	120.	64.	233.	116.	574.	293.	594.	296.	515.	284.	296.	385.	519.	44.	16
17	96.	62.	248.	105.	429.	215.	472.	220.	429.	254.	248.	350.	532.	10.	17
18	106.	59.	222.	87.	344.	176.	427.	178.	394.	215.	237.	318.	478.	67.	18
19	192.	49.	252.	88.	382.	158.	386.	156.	360.	208.	194.	319.	459.	44.	19
20	108.	60.	168.	73.	262.	114.	318.	152.	303.	196.	195.	265.	436.	39.	20
21	180.	53.	122.	72.	292.	83.	312.	124.	312.	185.	215.	294.	477.	60.	21
22	173.	41.	174.	63.	262.	103.	286.	121.	265.	203.	209.	292.	385.	200.	22
23	118.	44.	163.	79.	273.	133.	255.	176.	219.	262.	193.	312.	294.	274.	23
24	78.	56.	155.	84.	229.	218.	201.	221.	164.	287.	101.	260.	177.	189.	24
25	85.	81.	142.	126.	170.	210.	171.	211.	108.	265.	59.	214.	132.	129.	25
26	65.	82.	121.	140.	180.	188.	107.	192.	72.	171.	69.	152.	85.	96.	26
27	49.	150.	85.	167.	114.	261.	80.	169.	36.	114.	44.	88.	57.	59.	27
28	29.	69.	73.	106.	59.	129.	32.	80.	33.	77.	81.	67.	45.	42.	28
29	24.	66.	32.	98.	37.	105.	8.	57.	0.	73.	0.	477.	25.	157.	29
30	0.	31.	13.	38.	5.	0.	1.	0.	— 0.	— 0.	— 0.	— 0.	— 0.	— 0.	30

HUMBLE PARAFFIN-NAPHTHENE TYPE ANALYSIS IN PERCENT

Paraffins	17.57
Non-Condensed Naphthenes	28.86
2-Ring Naphthenes	17.16
3-Ring Naphthenes	11.83
4-Ring Naphthenes	11.25
5-Ring Naphthenes	6.41
6-Ring Naphthenes	6.91
Total	100.00

TABLE 5

Mass spectrum of alumina chromatographic fraction of the alkanes from the Orgueil meteorite. This fraction is a concentrate of the constituents of the alkane fraction which were most strongly retained on an alumina column. These constituents include polycyclic alkanes and the high molecular weight n-paraffins plus, perhaps, some fatty acids (see x = — 10). This spectrum was obtained using 70 electron volt ionizing potential, and the ions are both "fragment" and "parent" ions. Mass of ion at $C\# = 27$ in "x" = — 10 column is 378-10 = 368 which is the molecular weight of a C_{24} fatty acid.

Total Ionization = 37832.00

Normalized Isotope Corrected Peak Heights (300 000)

	−11	−10	−9	−8	−7	−6	−5	−4	−3	−2	−1	0	+1	+2	
								0.	0.	−0.	−0.	−0.	−0.	−0.	3
4	−0.	0.	0.	0.	−0.	−0.	−0.	−0.	−0.	−0.	−0.	−0.	−0.	−0.	4
5	−0.	0.	−0.	−0.	−0.	−0.	−0.	−0.	3822.	2367.	9975.	7866.	21913.	411.	5
6	1940.	579.	419.	1454.	2418.	354.	1558.	777.	4870.	3435.	9136.	3938.	13899.	309.	6
7	1039.	166.	175.	121.	1806.	456.	1689.	939.	4697.	2505.	7168.	3751.	4233.	532.	7
8	1113.	298.	256.	2570.	1923.	496.	1464.	765.	3179.	1484.	4417.	4265.	3650.	255.	8
9	710.	230.	632.	309.	1235.	558.	1470.	763.	2193.	960.	2202.	1266.	2171.	578.	9
10	6617.	98.	746.	702.	2258.	382.	1508.	521.	1433.	615.	970.	1007.	1778.	423.	10
11	807.	225.	816.	447.	1875.	380.	11883.	100.	978.	575.	676.	881.	1481.	265.	11
12	623.	288.	575.	492.	509.	285.	917.	328.	940.	459.	1240.	886.	1299.	231.	12
13	474.	184.	429.	167.	432.	214.	766.	356.	671.	328.	446.	844.	1103.	157.	13
14	831.	124.	384.	161.	415.	180.	856.	349.	586.	365.	404.	583.	983.	134.	14
15	404.	201.	318.	309.	397.	224.	759.	283.	855.	234.	330.	512.	862.	230.	15
16	386.	87.	288.	82.	417.	210.	401.	164.	306.	221.	376.	461.	745.	114.	16
17	159.	190.	311.	145.	364.	143.	284.	142.	254.	330.	211.	367.	759.	80.	17
18	757.	125.	278.	100.	292.	162.	382.	119.	215.	192.	164.	312.	648.	86.	18
19	295.	293.	273.	134.	703.	111.	239.	129.	3171.	0.	166.	278.	532.	103.	19
20	157.	113.	193.	105.	202.	143.	178.	108.	194.	152.	255.	249.	517.	101.	20
21	139.	107.	170.	108.	184.	160.	156.	102.	170.	172.	114.	230.	403.	288.	21
22	152.	90.	124.	126.	180.	127.	162.	99.	153.	166.	106.	231.	273.	426.	22
23	70.	112.	111.	127.	162.	137.	118.	116.	125.	139.	103.	175.	213.	423.	23
24	91.	97.	113.	141.	141.	179.	90.	112.	109.	133.	87.	194.	238.	318.	24
25	65.	105.	86.	170.	76.	147.	83.	98.	96.	128.	95.	143.	162.	290.	25
26	143.	74.	83.	107.	92.	96.	56.	122.	65.	103.	102.	125.	181.	204.	26
27	60.	457.	43.	205.	54.	165.	58.	54.	91.	89.	80.	99.	93.	94.	27
28	54.	82.	91.	95.	69.	108.	50.	74.	77.	83.	81.	121.	109.	87.	28
29	47.	115.	32.	127.	29.	127.	28.	103.	52.	65.	39.	103.	36.	126.	29
30	44.	98.	68.	115.	116.	74.	56.	40.	54.	59.	41.	86.	64.	69.	30

by alumina chromatography (MEINSCHEIN, 1959). On alumina, the meteorite alkanes had adsorptive properties similar to those of alkanes from terrestrial sediments. Many of the "features" that have been cited previously as evidence of the biologic origin of some terrestrial alkanes (MEINSCHEIN, 1957ab, 1959, 1960, 1961ab; MEINSCHEIN, NAGY, and HENNESSY, 1963) are more apparent in Table 5 than in Table 4. Before reviewing certain of these "features", it should be noted that some terrestrial contaminants are present in the polycyclic and n-paraffin concentrate. Large peaks at $C\# = 19$ and "x" = — 3, $C\# = 11$ and "x" = — 5, $C\# = 10$ and "x" = — 7, — 11, and at $C\# = 8$ and "x" = — 8 are caused by phthlates. Phthlate esters are widely used as plasticizers in plastic tubing, in diffusion pump oils, and in melting point baths. It is extremely difficult to keep traces of phthalates from contaminating

the microquantities of organic extracts processed in organic geochemical laboratories, but the presence of these esters are easily detected because of the large peaks they yield at $C\# = 11$ and "x" $= -5$ in the mass spectrometer. The concentration of phthalates in the alkanes from the Orgueil meteorite, as indicated by data in Table 5, probably does not exceed 1 or 2 per cent.

Noteworthy in Table 5 are a number of values which are larger than values that appear above them in their respective "x" columns. These anomalously large peaks indicate the masses of alkanes or of the stable ring or common ion fragments of alkanes (MEINSCHEIN, NAGY, and HENNESSY, 1963) that are most abundant in the ions of the alkanes from the Orgueil meteorites. Many anomolous peaks appear in Table 5 at positions where anomolous peaks are commonly observed in the mass spectra of alkanes from terrestrial sediments. Some of the peaks are found in:

1. The "x" $= -6$ colums at $C\#$'s $= 16, 24, 27, 28$, and 29;
2. The "x" $= -7$ column at $C\#$'s $= 16, 19, 26$, and 28;
3. The "x" $= -5$ column at $C\# = 14$ (11 is ignored because of phthlate contamination);
4. The "x" $= -8$ and -10 columns at $C\#$'s $= 27, 29$, and 30;
5. The "x" $= +2$ column at $C\# = 29$;
6. The "x" $= 0$ column at $C\#$'s $= 28$ and 29.

The common presences of peaks in these positions in the mass spectra of biologic and sedimental alkanes and in the mass spectra of alkanes produced by the hydrogenolyses of plant and animal wax esters were a major basis for the theories stated by MEINSCHEIN (1957, 1959, 1960, 1961ab) on the origins and compositions of naturally occurring alkanes.

Other "features" may be noted in Table 5 which do not indicate a random production of the compounds from the Orgueil meteorite. Among these "features" are the alternately high and low values that appear generally in the $C\#$ 15 to $C\#$ 30 range in the "x" $= -10$ column. Biological fatty acids, alipahtic alcohols, and n-paraffins (see Figures 1, 2, and 3) frequently contain higher concentrations of either even or odd carbon numbered homologs. The high and low values in the "x" $= -10$ column of Table 5 indicate such a concentrational variation in homologous constituents of the Orgueil alkane fraction. These peaks, however, may be fatty acid "parent ions". Since fatty acids have high sensitivities in the mass spectrometer, the latter "features" may be caused by traces of terrestrial contaminants.

Mass spectral type analyses for alkanes from the Orgueil meteorite and from sedimental, biological, and Fischer-Tropsch (abiotic) samples are given in Table 6. Neither these alkane type analyses nor the aromatic type analyses presented in Table 3 accurately record the compositions of the fractions analyzed. Mass spectrometric type analyses (LUMPKIN, 1956) are determined by means of matrices determined from reference compounds. These reference compounds, in most cases, have been abiotically synthesized, and they almost certainly do not closely replicate the structures of the biological derived compounds in sediments. Notwithstanding, type analyses are precise, and they provide a basis of comparing hydrocarbon mixtures which are composed

TABLE 6

Mass spectrometric type analyses of the saturated hydrocarbons (n-C$_7$ eluates from silica gel columns) from the Orgueil meteorite, crude oils, living things, and Recent and ancient terrestrial sediments. Percentages given for terrestrial samples are averages of the number of samples shown in parentheses to the right of the sample designations. Standard deviations in the percents of different types of hydrocarbons in the various terrestrial samples are presented to the right of percentage values.

				Per Cents of Saturated Mydrocarbon Types			
				Cycloalkanes			
Sample	*Paraffins*	*1-Ring*	*2-Ring*	*3-Ring*	*4-Ring*	*5-Ring*	*6-Ring*
Meteorite:	σ	σ	σ	σ	σ	σ	σ
Orgueil	17.6	28.9	17.2	11.8	11.3	6.4	6.8
Living							
Things (11)	24.9 (6.2)	27.5 (2.8)	14.8 (1.4)	11.1 (2.5)	10.0 (2.1)	5.8 (2.6)	5.9 (2.6)
Sediments:							
Recent							
Marine (12)	21.6 (6.2)	23.6 (2.5)	17.3 (2.4)	16.7 (1.1)	11.6 (1.5)	5.9 (1.0)	3.3 (0.6)
Ancient (19)	20.6 (6.0)	22.2 (3.6)	18.5 (2.9)	14.7 (3.2)	11.8 (3.2)	6.2 (1.2)	6.1 (2.7)
Crude							
Oils (5)	26.1	28.5	20.2	13.0	7.6	3.5	2.8

of compounds whose structures have not been completely determined. In Table 6, type analyses of the alkanes from the Orgueil meteorite fall within the ranges of values found for biological and sedimental alkanes, whereas the saturated hydro-carbons from the Fischer-Tropsch (abiotic) sample contain higher concentrations of monocycloalkanes (or perhaps olefins) and much lower concentrations of polycyclo-alkanes than do other terrestrial alkanes.

Separately and collectively the distributions of the aromatic and saturated hydro-carbons, as indicated by the data in Figures 8 and Tables 3, 4, and 5 are of interest. Alkane fractions in the Orgueil meteorite and in many Recent marine sediments are much more complex (contain more different compounds) than are the aromatic fractions in these samples. It seems highly improbable that such a variety of alkanes (see Table 4) could be converted abiotically into so few aromatic compounds (see Table 3) which are concentrated in discrete carbon number ranges. The aromatics in the Orgueil meteorite were not apparently derived from the alkanes in this meteorite. Theories discussed above to explain the origins and compositions of alkane and aromatic hydrocarbons in terrestrial sediments seemingly provide an equally satis-factory explanation of the separate and composite compositions of the alkanes and aromatic hydrocarbons in the Orgueil meteorite.

3. Conclusions

Abiotic processes which produce complex mixtures of homologous hydrocarbons

commonly make these compounds, as in the case of the Fischer-Tropsch process, in concentrations that can be calculated by relatively simple mathematical equations (SHARKEY, SCHULTZ, and FRIEDEL, 1962). Non-equilibria or many different abiotic reactions may be developed that could form mixtures of aromatics, alkanes, and carbonaceous non-hydrocarbons in the relative amounts and of the structural types found in the Orgueil meteorite and terrestrial sediments. But, recognition of the possibility of this development does not discredit the proposal that the compositions and distributions of the Orgueil hydrocarbons constitute evidence of former extra-terrestrial life.

While an ambiguity could arise if the preceding possibility is demonstrated, it would still be necessary to evaluate whether these abiotic reactions or biological precursors were the most likely sources of some or all of the various hydrocarbons and carbonaceous non-hydrocarbons in the Orgueil meteorite. Experimental data have been presented to establish that:

1. The aromatics in the Orgueil resembles those in some Recent marine sediments;
2. The alkanes in the Orgueil resemble biological and sedimental alkanes.

Additional analyses may assist in resolving the controversy on the origin of some carbonaceous compounds in the Type 1 carbonaceous chondrites. Because of the possible scientific importance of these results and the limited quantities of these invaluable meteorites, such analyses should be obtained by the most experienced and competent analysts in the best equipped laboratories.

For reasons stated above, alkanes probably provide the strongest evidence of biological activity. If the alkanes in Type 1 carbonaceous chondrites are products of former life, they would most likely:

1. Rotate polarized light as do the alkanes in terrestrial sediments;
2. Yield chromatograms on capillary (GLC) columns which do not follow patterns that can be simply explained.

Comparisons of these optical and chromatographic measurements on alkanes from the meteorites and from terrestrial samples could augment the comparisons which have been made. Isotopic determinations, as shown by BRIGGS (1963), could be used to indicate the extraterrestrial origin of the alkanes from meteorites that are used for the optical and chromatographic measurements.

References

ANDERS, E.: 1961, *Lunar Colloquium II,* North American Aviation, Downey, Calif., No. 4, 54.
ANDERS, E.: 1962, *Ann. N.Y. Acad. Sci.* **93**, 651.
BATES, T. H. and BEVINGTON, J. C.: 1963, *Nature* **197**, 1294.
BENDORAITIS, J. G., BROWN, B. L., and HEPNER, R. S.: 1962, *Anal. Chem.* **34**, 49.
BENDORAITIS, J. G., BROWN, B. L., and HEPNER, R. S.: 1963, Sixth World Petroleum Congress, Frankfurt, Germany, June 9–26, Abstr. Sect. **5**, 158.
BERZELIUS, J. J.: 1834, *Ann. Phys. Chem.* **33**, 113.
BEVINGTON, J. C.: 1961, *Radical Polymerization,* Academic Press, London, p. 41.
BLUMER, M.: 1961, *Science* **134**, 474.
BOATO, G.: 1954, *Geochim. Cosmochim. Acta* **6**, 209.

BRAY, E. E. and EVANS, E. D.: 1961, *Geochim. Cosmochim. Acta* **22**, 2.

BREGER, I. A.: 1959, *Preprints General Petroleum Symposium,* Fordham University Chemistry Department, New York, p. 79.

BRIGGS, M. H.: 1963, *Nature* 197, 1290.

BRIGGS, M. H. and MAMIKUNIAN, G.: 1963, *Space Sci. Rev.* **1**, 647.

CALVIN, M. and VAUGHAN, S. K.: 1960, *Space Research I,* North-Holland Publishing Co., Amsterdam.

CIERESKO, L. S., ATTAWAY, D. H., and KOONS, C. B.: 1963, Ninth Amer. Chem. Soc. Okla. Tetre-sectional Mtg., Tulsa, Okla., March 16; Abstr. in *Vapor Pressure* **33**, No. 3, 59.

COHEN, E.: 1894, *Meteoritenkunde,* E. Schwizerbarsche Verlag, Stuttgart.

COOPER, J. E. and BRAY, E. E.: 1963, Preprints Division of Petroleum Chemistry, Amer. Chem. Soc. **8**, No. 2, A 23.

COX, B. B.: 1946, Bull. Amer., Petrol. Geol. **30**, 645.

CRAIG, H.: 1963 Geochim. Cosmochim. Acta **3**, 53.

DEAN, R. A. and WHITEHEAD, E. V.: 1961, Tetrahedron Letters **21**, 768.

DEGENS, E. T. and BAJOR, M.: 1962, Submitted to *Naturwissenschaften.* Discussed in *Time Magazine,* March 2, 1962.

ECKELMANN, W. R. *et al.*: 1961, Paper presented Annual Meetings *Geological Society of America,* Cincinnati, Ohio.

ENGLER, C. and SINGER, L.: 1893, *Ber. deutsch. Chem. Ges.* **26**, 1449.

ENGLER, C.: 1897a, *Ber. deutsch. Chem. Ges.* **30**, 2358.

ENGLER, C. and LEHMAN, T.: 1897b, *Ber. deutsch. Chem. Ges.* **30**, 2365.

ENGLER, C., GRÜNING, H., and SCHNEIDER, C.: 1897c, *Ber. deutsch. Chem. Ges.* **30**, 2908.

ERDMAN, J. G.: 1961, *Geochim. Cosmochim. Acta* **22**, 16.

HEALD, K. C.: 1953, *Fundamental Research on Occurrence and Recovery of Petroleum* 1952–1953, Lord Baltimore Press., Baltimore, Md., p. 151.

HUNT, J. M.: 1953, *Bull. Amer. Assoc. Petrol. Geologists* **37**, 1837.

HUNT, J. M.: 1961, *Geochim. Cosmochim. Acta* **22**, 37.

HUNT, J. M. and JAMIESON, G. W.: 1956, *Bull. Amer. Assoc. Petrol. Geologists* **40**, 477.

KAPLAN, I. R., DEGENS, E. T., and REUTER, J. H.: 1963, *Geochim. Cosmochim. Acta.* In press.

KLEIN, H. P.: 1957, *J. Bacterial* **73**, 530.

LUMPKIN, H. E.: 1956, *Anal. Chem.* **28**, 1946.

MAIR, B. J. and BARNEWELL, J. M.: 1963, Preprints Division of Petroleum Chemistry, *Amer. Chem. Soc.* **8**, No. 4, C–5.

MAIR, B. J., KROUSKOP, N. C., and MAYER, T. J.: 1962, *J. Chem. Engrs. Data* **7**, 420.

MAIR, B. J. and MAYER, T. J.: 1963, Preprints Division of Petroleum Chemistry, *Amer. Chem. Soc.* **8**, No. 4, C–29.

MAIR, B. J. and MARTINEZ-PICO, J. L.: 1962, *Chem. Engr. News* **40**, No. 10, 54.

MARTIN, R. L., WINTERS, J. C., and WILLIAMS, J. A.: 1963, *Nature* **199**, 110.

MASON, B.: 1963a, *Space Sci. Rev.* **1**, 621.

MASON, B.: 1963b, *Scientific American* **208**, No. 3, 43.

MEINSCHEIN, W. G.: 1957, Abstracts. Petroleum Symposium, S.W. Regional Meeting, *Amer. Chem. Soc.* Tulsa, Okla.

MEINSCHEIN, W. G.: 1959, *Bull. Amer. Assoc. Petrol. Geologists* **43**, 925.

MEINSCHEIN, W. G. *et al.*: 1960, *Annual Meetings Geological Society of America,* Denver, Colo., p. 159.

MEINSCHEIN, W. G.: 1961a, *Geochim. Cosmochim. Acta* **22**, 58.

MEINSCHEIN, W. G.: 1961b, 'Origin of Petroleum', *Enciclopedia del petrolia e dei gas naturali,* Press of L. Instituto Chimico dell' Università Roma. In press.

MEINSCHEIN, W. G.: 1963, *Nature* 197, 833.

MEINSCHEIN, W. G. and KENNY, G. S.: 1957, *Anal. Chem.* **29**, 1153.

MEINSCHEIN, W. G., NAGY, B., and HENNESSY, D. J.: 1963, *Ann. N.Y. Acad. Sci.* **108**, 553.

MELANDER, L.: 1960, *Isotope Effects on Reaction Rates,* Ronald Press Co., New York **132**.

MOLD, J. D., STEVENS, R. K., MEANS, R. E., and RUTH, J. M.: 1963, *Nature* **199**, 283.

MUELLER, G.: 1953, *Geochim. Cosmochim. Acta* **4**, 1.

NAGY, B., MEINSCHEIN, W. G., and HENNESSY, D. J.: 1961, *Ann. N.Y. Acad. Sci.* **93**, 25.

NAGY, B., FREDRIKSSON, K., UREY, H. C., CLAUS, G., ANDERSON, C. A., and PERCY, J.: 1963, *Nature* **198**, 121.

OAKWOOD, T. S.: 1953, *Fundamental Research on Occurrence and Recovery of Petroleum 1952–1953*, Lord Baltimore Press, Baltimore, Md., p. 168.

ROBERTSON, R.: 1963, Nature **199**, 113.

SAGAN, C.: 1961, 'Extraterrestrial Organic Life', *Lunar Colloquium II*, North American Aviation, Downey, Calif., No. 4, p. 49.

SHARKEY, A. G., Jr., SCHULTZ, J. L., and FRIEDEL, R. A.: 1962, *Anal. Chem.* **34**, 826.

SILVERMAN, S. R.: 1960, Abstract Papers presented at *Amer. Assoc. Petrol. Geologists,* Atlantic City Meeting.

SILVERMAN, S. R. *et al.*: 1961, Paper presented at Annual Meetings of Geological Society of America, Cincinnati, Ohio.

SILVERMAN, S. R. and EPSTEIN, S.: 1958, *Bull. Amer. Assoc. Petrol. Geologists* **42**, 998.

SMITH, P. V., Jr.: 1952, *Bull. Amer. Assoc. Petrol. Geologists* **36**, 411.

SMITH, P. V., Jr.: 1954, *Bull. Amer. Assoc. Petrol. Geologists* **38**, 377.

SORENSEN, N. A. and MEHLUM, J.: 1948, *Acta Chim. Skand.* **2**, 140.

STEVENS, N. P., BRAY, E. E., and EVANS, E. D.: 1956, *Bull. Amer. Assoc. Petrol. Geologists* **40**, 975.

UNDERWOOD, A. J. V.: 1940, *Ind. Eng. Chem.* **32**, 449.

UREY, H. C.: 1962, *Science* **137**, 623.

VALLENTYNE, J. R.: 1962, *Arch. Hydrobiol.* **58**, No. 4, 423.

WHITMORE, F. C.: 1943, *Fundamental Research of Occurrence and Recovery of Petroleum 1943*, Lord Baltimore Press, Baltimore, Md., p. 124.

WHITMORE, F. C.: 1945, *Fundamental Research of Occurrence and Recovery of Petroleum 1944–1945*, Lord Baltimore Press, Baltimore, Md., p. 99.

WILSON, A. T.: 1962, *Nature* **166**, 11.

WOHLER, F.: 1858, *Sitzungsber. Akad. Wissensch., Wien, Math.-Naturwiss. Klasse* **33**, 205.

WOHLER, F.: 1959a, *Sitzungsber. Akad. Wissensch., Wien, Math.-Naturwiss. Klasse* **34**, 7.

WOHLER, F.: 1859b, *Sitzungsber. Akad. Wissensch., Wien, Math.-Naturwiss. Klasse* **35**, 6.

WOHLER, F.: 1860, *Sitzungsber. Akad. Wissensch., Wien, Math.-Naturwiss. Klasse* **41**, 565.

YANKWICH, P. E. and IKEDA, R. M.: 1959, *J. Amer. Chem. Soc.* **81**, 5054.

ZOBELL, C. E.: 1953, *Fundamental Research on Occurrence and Recovery of Petroleum 1952–1953*, Lord Baltimore Press, Baltimore, Md., p. 178.

ZOBELL, C. E.: 1963, *International Science and Technology* **20**, 42.