Carbon Isotopic Evidence for the Role of Lipids in Petroleum Formation

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Abstract

Data available on stable carbon isotope ratios (C^{13}/C^{12}) are reviewed. It is concluded that data for modern and ancient natural carbonaceous materials reveal consistently low C^{13}/C^{12} ratios for substances of biologic origin as opposed to the ratios for inorganic carbonate minerals deposited in the oceans. Ratios of modern marine organisms are about 1% higher than those of terrestrial organisms. The average C^{13}/C^{12} ratio of modern marine organisms is also about 1% higher than that of ancient organic matter in marine sediments. A similar relation exists between the ratios of terrestrial organisms and those of petroleums and other noncoaly organic matter genetically related to nonmarine sediments. Coals of all ranks have the same range of isotope ratios as those noted for terrestrial plants.

Lipid fractions of organisms have consistently lower C^{13}/C^{12} ratios than do the whole organisms. The average difference between nonlipid and lipid materials for all organisms studied is about 0.5% and ranges in individual species from as little as several hundredths to more than 1.5%. This suggests that petroleums and other noncoaly organic matter in ancient sediments are derived from lipids, or at least from certain components of the lipid fraction. In contrast, coal deposits apparently are derived from whole plants or from the cellulosic fraction of land plants, which is the major nonlipid constituent of plant tissues.

The isotopic compositions of narrow distillation fractions of petroleums suggest that the low-molecular-weight hydrocarbon components of the gas and gasoline fractions are formed by decomposition of higher-molecular-weight compounds during the post-depositional history of petroleum. Concurrently with the formation of low-boiling compounds, these transformation processes initiate the polymerization reactions responsible for the formation of some of the most complex petroleum components, such as the asphaltenes. New data obtained from distillates of Colombian crude oil are reported in this paper. The fraction with an average boiling point of 450C and average molecular weight of 420 had the lowest C^{13}/C^{12} ratio. This suggests that the fraction, which includes the boiling range of typical triterpenoids, contains a major proportion of the primary components from which the light and heavy ends of petroleum are derived. This implication is supported by other geochemical information, including the distribution of optical activity in petroleum fractions and the identification of specific petroleum components which are structurally related to lipid components of modern organisms.

Introduction

STABLE CARBON ISOTOPE abundance studies by many investigators during the past 27 years have established the typical C^{13}/C^{12} ratio ranges of many classes of natural carbonaceous materials. This information has improved understanding and recognition of the mechanisms and environmental conditions involved in the carbon cycle in nature.

Isotope Ratio Determination

The isotopic compositions presented and discussed throughout this paper were obtained by high precision mass spectrometric analyses. Details of the sample preparation and analytical procedures are given by Craig (1) and Silverman and Epstein (2). The C^{13}/C^{12} ratios are reported as δ-values, which are deviations, in parts per thousand (per mil), of the C^{13}/C^{12} ratios of the samples from that of a petroleum standard (N.B.S. No. 22). The δ-values are defined by the formula:

$$\delta \text{ in per mil } ‰ = \frac{C^{13}/C^{12}\text{ sample} - C^{13}/C^{12}\text{ standard}}{C^{13}/C^{12}\text{ standard}} \times 1000$$

The C^{13}/C^{12} ratio of the petroleum standard is 29.4 per mil lower than that of the Peedee belemnite standard used by the University of Chicago group (3). The precision of the reported analyses is of the order of ± 0.1 per mil.

Discussion of Data

Modern Biological Carbon

The C^{13}/C^{12} ratios of typical sedimentary marine carbonates are higher by about 1% to 3% than those of biologic carbon. This difference is attributed to the selective utilization of C^{12} during the photosynthetic fixation of carbon by green plants (4). Organisms living in marine environments have higher C^{13}/C^{12} ratios than those from terrestrial or fresh-water environments. This environmental distinction is accounted for by the fact that marine plants can utilize carbonate complexes in sea water for photosynthesis (5). Terrestrial plants and fresh-water aquatic plants must rely on atmospheric carbon dioxide for their source of carbon for photosynthesis, and the C^{13}/C^{12} ratio of atmospheric CO_2 is about 0.8% lower than that of the average carbonate.

These relations are summarized in Figure 1, in which the isotope ratios for the various categories of modern organisms represent data from many sources (1–2,4,6–15). Not included in this figure are the 13 plankton samples (14) collected in the high latitude (>40 S.) areas of the South Atlantic Ocean. Other evidence, which will be presented in a future publication, implies that these samples, from low-temperature environments and with abnormally low C^{13}/C^{12} δ-values (-1.2 to $+2.3$ per mil), probably are not representative of typical marine organisms. Included in Figure 1 are eight marine plant and animal samples belonging to the category of plankton, the isotope ratios of which fall between $+11.3$ and $+20.2$ per mil.

Petroleum Carbon

Petroleums as well as practically all solid organic matter in sediments of pre-Cambrian to Pleistocene ages and from world-wide localities have an isotope ratio range of about 1.2% (-4 to $+8$ per mil). Thus

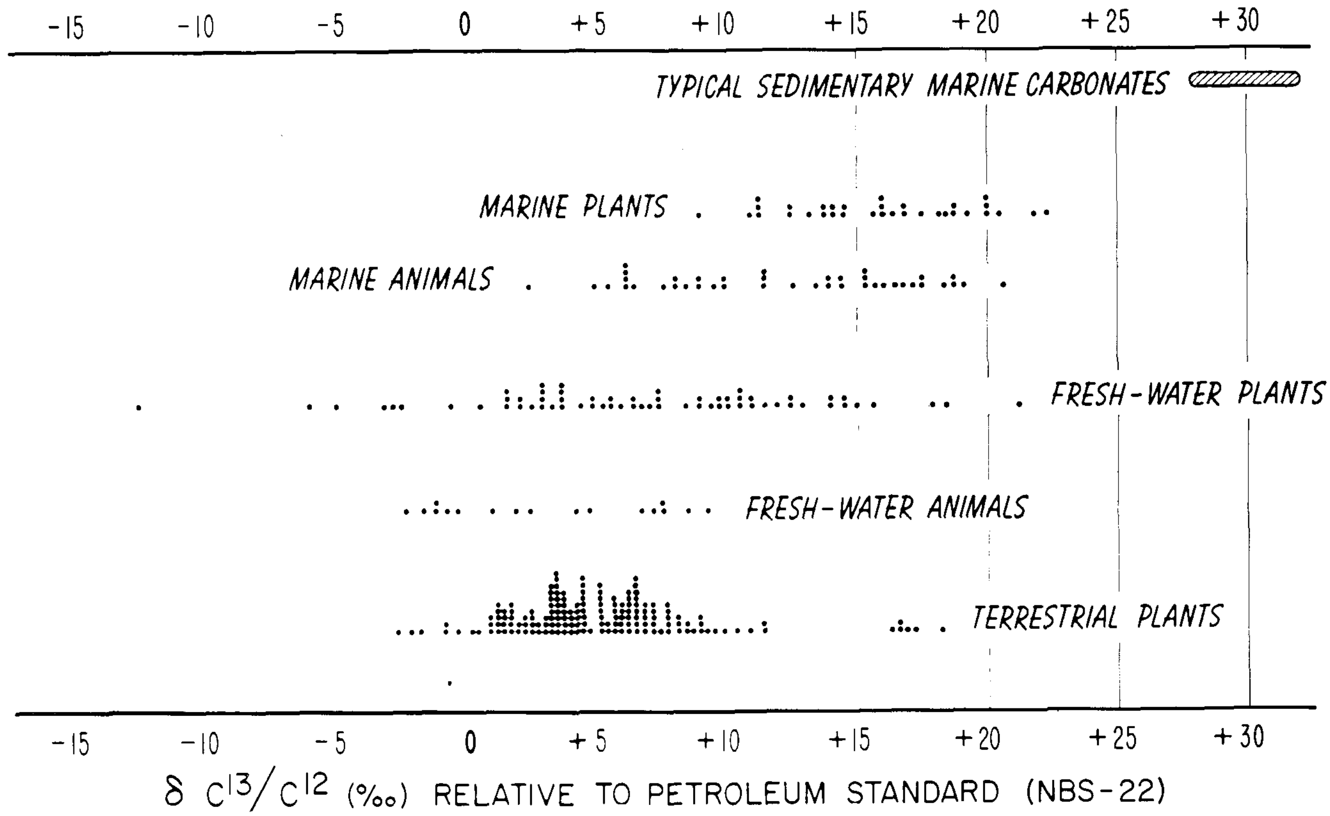

FIG. 1. The C^{13}/C^{12} ratio ranges of biologic carbon and marine carbonate.

the organic matter in ancient sediments is from 2% to 3.5% lower in C^{13}/C^{12} ratio than the average sedimentary marine carbonate. Carbon isotope ratios of petroleums supposedly derived from organic matter living in marine environments are higher than those of petroleums related to nonmarine source materials (2). This generalization does not hold for early Paleozoic petroleums, the C^{13}/C^{12} δ-values of which are typically low and often fall within the range of ratios noted for nonmarine petroleums. This overlap is believed to be caused by the gradual depletion of C^{12} in atmospheric CO_2 with decreasing geologic age (16,17).

The general relations among isotopic compositions of carbonate, atmospheric, and petroleum carbons are depicted graphically in Figure 2, in which average values, as well as typical ranges, for each of these categories are indicated. This form of comparison reveals that C^{13}/C^{12} δ-values of petroleums supposedly derived from ancient marine organisms are approximately 10 per mil lower, on the average, than those of modern marine biological carbon. A parallel relation exists between nonmarine petroleums and present-day nonmarine organisms, which show an average difference of about 8 per mil. These observations led Silverman and Epstein in 1958 (2) to conclude that either an isotope fractionation process is involved during the chemical conversion of total biologic carbon to petroleum or that not all biologic carbon is converted to petroleum.

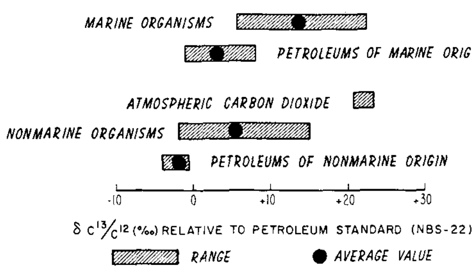

FIG. 2. The C^{13}/C^{12} ratio ranges in natural carbonaceous materials.

The first alternative, which implies that all organismal components are involved in petroleum formation through an isotope fractionation process, should result in the production of residual organic carbonaceous matter with markedly higher C^{13}/C^{12} ratios. Evidence of such products is lacking because the C^{13}/C^{12} ratios of all organic carbonaceous matter in ancient sediments are similar to those noted for petroleums.

Lipid Carbon

The second alternative, implying selective preservation of C^{12}-enriched biological components, requires that different varieties of organism-produced substances have different carbon isotopic compositions. Evidence of such differences has existed for more than 25 years, beginning with the work of R. O. Belkengren [cited by Murphy (18) and also by Craig (1)], who reported that the C^{13} content of plant fats is about 10 per mil lower than that of plant cellulose. Further investigations of modern plant and animal constituents have established that lipid components are consistently enriched in C^{12} relative to the remainder of the organism. A summary of available data, including published information (2,6,8,10–11,14) on C^{13}/C^{12} ratios of lipids relative to those of whole organisms is shown in Figure 3. The values plotted on this figure are the algebraic differences obtained by subtracting the C^{13}/C^{12} δ-value of the lipid fraction from the C^{13}/C^{12} δ-value of the whole organism for each specimen analyzed. The positive differences (Δ's) indicate that the C^{13}/C^{12} ratios of the lipid

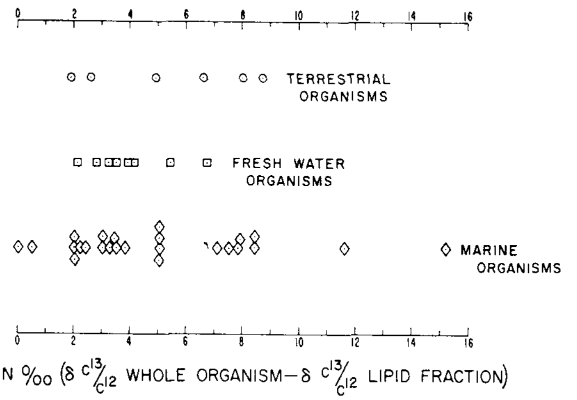

FIG. 3. Relations between Δ C^{13}/C^{12} of modern whole organisms and their lipid fractions.

fractions of modern terrestrial, fresh-water, and marine organisms are, on the average, 5.5, 3.8, and 5.0 per mil lower respectively than the C^{13}/C^{12} ratios of the entire organisms.

Thus the lipids, or at least certain specific components of the lipid fraction, may be the sole biologic sources of petroleum. Coal, on the other hand, regardless of rank or geologic age, is isotopically similar (1) to modern terrestrial plant carbon. This observation implies that coal is derived from whole plants or primarily from the carbon in the cellulosic fraction, which is the predominant constituent of terrestrial plant substance and is therefore a product of nonlipid biologic carbon. Lipids, as defined by Bergmann (19), constitute the class of biologically produced substances that are relatively insoluble in water but soluble in one or another of the so-called "fat-solvents," such as chloroform, carbon tetrachloride, ethers, aliphatic and aromatic hydrocarbons, and acetone. The most important types of lipid components, in the geochemical sense, are the fatty acids, fatty acid esters of higher aliphatic alcohols or glycerol, hydrocarbons, branched acyclic or cyclic compounds belonging to the terpenoid or steroid groups, and the more complex heterocyclic alkaloids, such as the steroid alkaloids.

Lipids are usually encountered as minor constituents of modern plants and animals relative to the more abundant carbohydrates and proteins; lipid concentrations of organisms, on a dry-weight basis, generally range from 0.5% to 5% although concentrations above 75% have been reported under certain unusual conditions. Bergmann (19) reviewed the evidence, suggesting that lipid content depends on the phylogenetic level of organisms and that it is influenced by environmental conditions.

The relative stability of lipids, as pointed out in Breger's review (20), enables them to survive adverse geological conditions whereas the nonlipid components, such as carbohydrates and proteins, are more readily hydrolyzed and dispersed as water-soluble products in the oceans. Chemically, on the basis of elemental compositions as well as structural molecular configurations, lipid components more closely resemble petroleum constituents than do any of the other biological components. Furthermore the identification of specific acyclic and cyclic terpenoids in petroleums and ancient sediments (21–25) and the recognition that low-molecular-weight hydrocarbons (aliphatics and aromatics) present in petroleum can be reasonably explained as decomposition fragments of terpenoids or as products of disproportionation reactions involving isoprenoids (21,24,26) favor the contention that lipids are the primary precursors of petroleum.

Carbon Isotope Ratios of Petroleum Fractions

Understanding of the mechanisms of petroleum evolution and the nature of petroleum source substances were further enhanced by isotopic measurements of petroleum distillation fractions (27). After it was established that typical gas-phase hydrocarbons separated from petroleums are about 15 per mil lower in C^{13}/C^{12} ratio than are the associated liquid phases, the ratios of progressively higher boiling fractions of a crude petroleum from the West Coyote field in California were determined. The C^{13}/C^{12} δ-value of the whole crude oil is +7.0 per mil. The gas phase was separated into individual hydrocarbon components in the C_1 to C_3 range and into isomeric mixtures in the C_4 to C_6 range by using a Podbielniak fractionation column. Eight fractions were separated from the liquid phase in a vacuum still; their average atmospheric boiling temperatures ranged from 115C to 288C. The distillation was terminated after the eighth fraction to avoid thermal cracking of the residual liquid. The isotope ratios of each of the separated fractions, shown in Figure 4, increase from methane through hexane, pass through a maximum in the vicinity of 115C, and decrease gradually from the 115C fraction through the 288C fraction. This pattern, which was found to be similar for fractions separated from other petroleums, was regarded (27) as evidence that the lowest-molecular-weight hydrocarbons (methane through pentanes) were formed by decomposition of high-molecular-weight components. Because these small molecular fragments are enriched in C^{12}, the residual molecules must be enriched in C^{13} and at the same time reduced to smaller molecular dimensions, as a result of the splitting off of these fragments, and consequently will have lower boiling temperatures.

Thus it is possible to explain, by this mechanism, the origin of the lightest petroleum constituents (C_1 through C_7), which are not present in Recent sediments (28) in significant concentrations, also the intermediate-molecular-weight components of the gasoline, kerosene, and gas-oil fractions.

It was also pointed out (27) that the proposed mechanism of light hydrocarbon formation is a dehydrogenation process, which, by inducing unsaturation and ring closure in the parent molecules, could account for the formation of low-molecular-weight aromatics and initiate polymerization processes to form the highly complex polycyclic components of petroleum, such as the asphaltenes. The C^{13}/C^{12} ratios of asphaltenes are consistently higher than the ratios of the whole crudes from which they are separated; thus, like the light gasoline components, asphaltenes are secondary products of the petroleum maturation

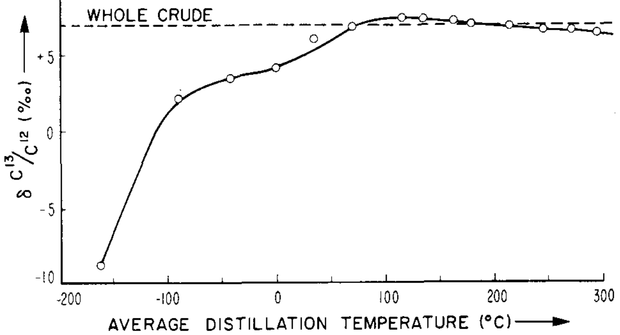

FIG. 4. Carbon isotope ratios of petroleum and gas fractions (West Coyote crude oil).

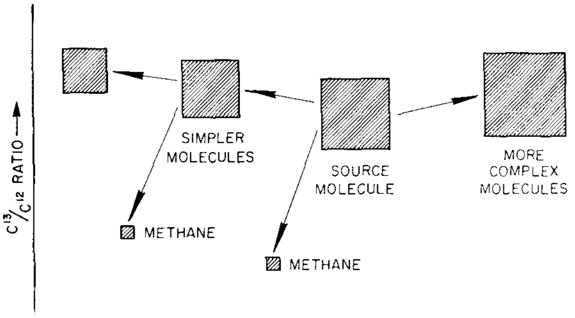

FIG. 5. Petroleum maturation reactions.

process, and both probably were formed as a result of natural alterations of the original mixture of primary biologic substances. This proposed mechanism is depicted diagrammatically in Figure 5, in which relative molecular dimensions are symbolized by the size of the squares; the vertical position of the squares denote relative C^{13}/C^{12} ratios. Thus the source molecule is depicted as becoming smaller and isotopically heavier after the loss of an isotopically light fragment (methane). Polymerization of residual molecules is shown in this diagram by the transformation to the right, which results in higher-molecular-weight compounds with higher C^{13}/C^{12} ratios. The more complex products are probably subject to additional or secondary decompositions to form simpler molecules, which subsequently polymerize into still more complex products. This natural cracking or maturation process continues until the hydrogen content of the residual molecules is insufficient to support further decompositions. The process can continue until all of the original organic source material is exhausted by complete conversion to methane and graphite or, as is more commonly encountered, by incomplete conversion to petroleum and kerogen. If this explanation is correct, then, by extending the isotope study of distillation fractions to higher boiling temperatures (without cracking the petroleum), investigators should find that the curve constructed in Figure 4 will eventually pass through a minimum C^{13}/C^{12} δ-value, which would identify the petroleum fraction containing the greatest concentration of primary components from which the light and heavy ends of petroleum are derived.

Such a study was made on fractions of a crude oil from Well No. 11 in the Rio Zulia field, Colombia. The fractions were separated by vacuum distillation, which achieved an atmospheric equivalent end-point of 635C without exceeding the cracking temperature of the petroleum. Results of analyses of 28 fractions with average atmospheric boiling temperatures ranging from 86.5C to 557.5C and the residuum after 635C are shown in Figure 6. The curve shows several distinct minima in the vicinities of 140C, 240C, 335C, and 420C, but the most pronounced C^{13}/C^{12} ratio minimum occurs in the vicinity of 450C. The average molecular weight of the latter fraction is approximately 420. This is within the range of values typical of the triterpenoids, important components of some lipid fractions and prominent components or sources of components of petroleums and other sedimentary organic substances (21,23–25).

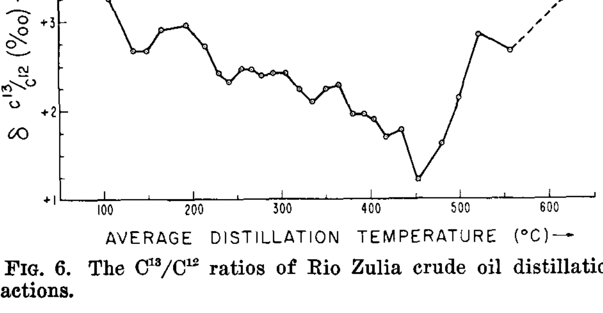

FIG. 6. The C^{13}/C^{12} ratios of Rio Zulia crude oil distillation fractions.

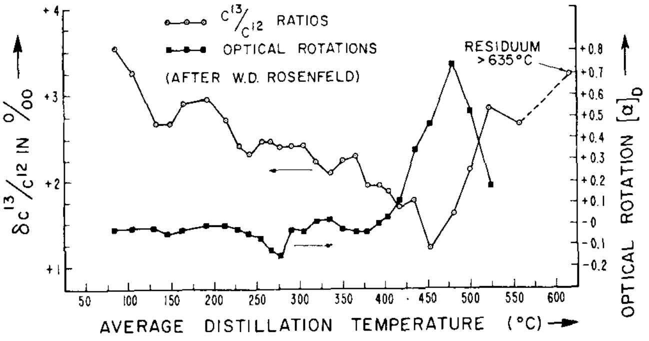

FIG. 7. Relation between C^{13}/C^{12} ratio and optical rotation in Rio Zulia crude oil distillation fractions.

Twenty-six of the Rio Zulia crude oil distillation fractions were analyzed for optical rotation by Rosenfeld (29), who found a distinct maximum in the 455C to 480C distillation range. Optical rotations are compared with carbon isotope ratios of the distillation fractions from the Rio Zulia crude in Figure 7, which indicates a close correspondence between the optical rotation maximum and the carbon isotope ratio minimum. Since optical activity in petroleums is undoubtedly related to remnants of biological source-materials and is apparently related to concentrations of steroidal substances in petroleums (29), this information provides additional evidence that lipids are important primary precursors of petroleum and that the triterpenoid class of such substances constitutes a major proportion of the source materials from which the heavy and light fractions of petroleum are derived.

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REFERENCES

1. Craig, H., Geochim. Cosmochim. Acta *3*, 53 (1953).
2. Silverman, S. R., and S. Epstein, Bull. Amer. Assoc. Petroleum Geologists *42*, 998 (1958).
3. Craig, H., Geochim. Cosmochim. Acta *12*, 133 (1957).
4. Park, R., and S. Epstein, Ibid. *21*, 110 (1960).
5. Smith, J. B., M. Tatsumoto and D. W. Hood, Limnology and Oceanography *5*, 425 (1960).
6. Abelson, P. H., and T. C. Hoering, Proc. Nat. Acad. Sci. *47*, 623 (1961).
7. Wickman, F. E., Geochim. Cosmochim. Acta *2*, 243 (1952).
8. Park, R., and S. Epstein, Plant Physiology *36*, 133 (1961).
9. Oana, S., and E. S. Deevey, Amer. J. Sci. *258-A*, 253 (1960).
10. Parker, P. L., Ann. Rept., Director, Geophysical Laboratory, 1962–63, p. 234.
11. Sondheimer, E., W. A. Dence, L. R. Mattick and S. R. Silverman, Science *152*, 221 (1966).
12. Deevey, E. S., and M. Stuiver, Limnology and Oceanography *9*, 1 (1964).
13. Broecker, W. S., and A. Walton, Geochim. Cosmochim. Acta *16*, 15 (1959).
14. Sackett, W. M., W. R. Eckelmann, M. L. Bender and A. W. H. Be, Science *148*, 235 (1965).
15. Damon, P. E., A. Long and D. C. Grey, J. Geophys. Res. *71*, 1055 (1966).
16. Silverman, S. R., reported at Geological Society of America Meeting, Cincinnati, 1961.
17. Nagy, B., Proc. Nat. Acad. Sci. *56*, 389, 397 (1966).
18. Murphy, B. F., M. A. thesis, University of Minnesota, (1941).

19. Bergmann, W., in "Organic Geochemistry," I. A. Breger, ed., The Macmillan Company, New York, 1963, p. 503.
20. Breger, I. A., JAOCS *43*, 197 (1966).
21. Meinschein, W. G., Bull. Amer. Assoc. Petroleum Geologists *43*, 925 (1959).
22. Bendoraitis, J. G., B. L. Brown and L. S. Hepner, Anal. Chem. *34*, 49 (1962).
23. Burlingame, A. L., P. Haug, T. Belsky and M. Calvin, Proc. Nat. Acad. Sci. *54*, 1406 (1965).
24. Mair, B. J., Geochim. Cosmochim. Acta *28*, 1303 (1964).
25. Hills, I. R., and E. V. Whitehead, Nature *209*, 977 (1966).
26. Andreev, P. F., A. I. Bogomolov, A. F. Dobryanskii and A. A. Kartsev, "Transformation of Petroleum in Nature," Gostoptekhizdat, Leningrad, 1958.
27. Silverman, S. R., in "Isotopic and Cosmic Chemistry," H. Craig, S. L. Miller, and G. J. Wasserburg, eds., North-Holland Publishing Company, Amsterdam, 1964, p. 92.
28. Dunton, M. L., and J. M. Hunt, Bull. Amer. Assoc. Petroleum Geologists *46*, 2246 (1962).
29. Rosenfeld, W. D., JAOCS *44*, 703–707 (1967).