May 27, 1969 E. E. BRAY ET AL 3,446,597

GEOCHEMICAL EXPLORATION

Filed July 18, 1966

FIG. 3

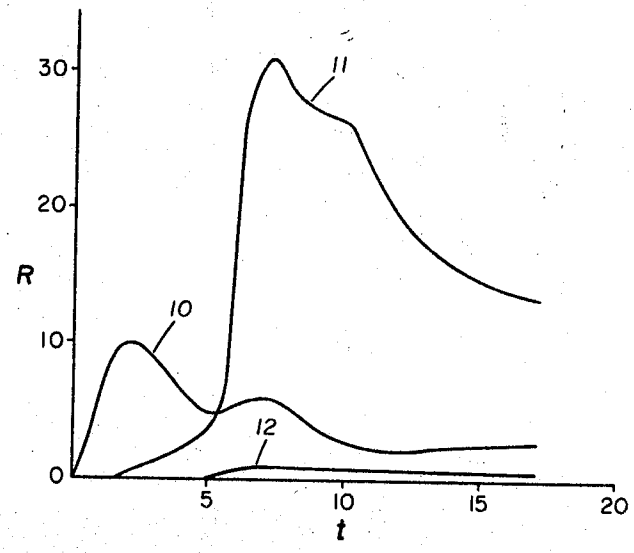


FIG. 2

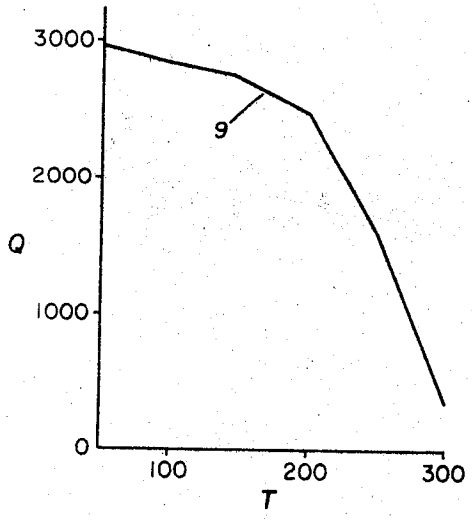


FIG. 1

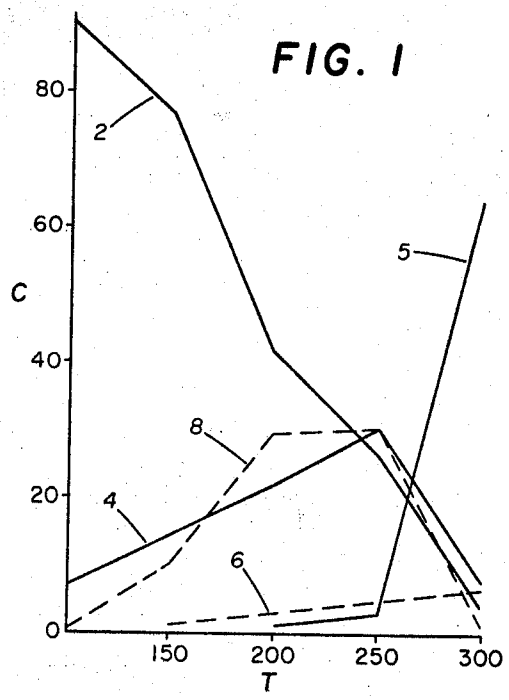
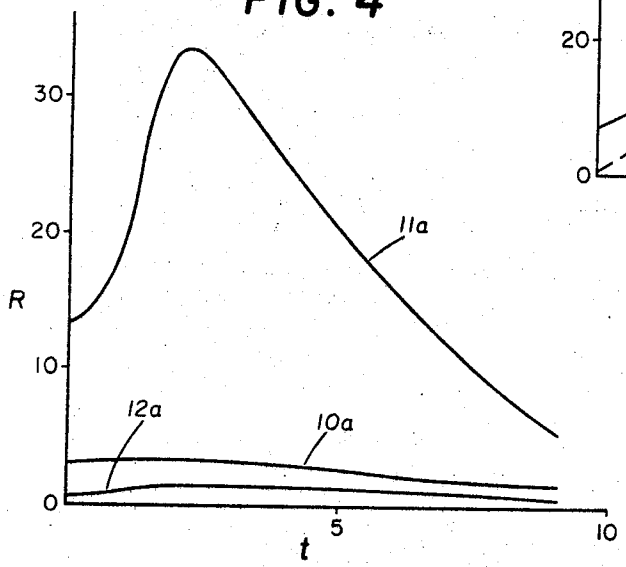


FIG. 4



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GEOCHEMICAL EXPLORATION

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23 Claims

This invention relates to geochemical exploration for petroleum hydrocarbons, and more particularly to a geochemical exploration method which involves the identification of source rocks of gaseous petroleum hydrocarbons.

Petroleum is found in commercial quantities in subsurface rock formations such as sandstones and limestones. The presence of a petroleum deposit in a subterranean formation is not ordinarily manifested by readily discernible indicia at the earth's surface. Accordingly, various techniques have been evolved in exploring for oil and gas. Among these are those which fall within the general classification of geochemical exploration.

In most geochemical exploration techniques, a search is made, usually at or near the surface of the earth, for components, precursors or derivatives of petroleum minerals. These procedures are based upon the theory that these materials may have migrated to or near the surface of the earth from an underlying petroleum reservoir. Thus, where materials such as hydrocarbons which are normally constituent components of petroleum are found, the presence of a subterranean reservoir of petroleum in the area is indicated.

While these techniques are extremely valuable in determining the presence of petroleum minerals within a general area, they usually give little indication of the location of the underlying reservoir. Other exploration procedures such as seismic surveying may be utilized to identify possible petroleum reservoirs at subterranean locations in the earth's crust. However, while such measures may give valuable information as to subterranean structures favorable to the accumulation of oil and/or gas, they leave much to be desired in regard to determining which, if any, of such structures actually contain such petroleum deposits.

In attempting to ascertain whether such structures contain petroleum hydrocarbons, geologists have in recent years turned to exploration techniques based upon the so-called "source rock" concept. Under this concept, it is assumed that petroleum hydrocarbons are formed during long periods of burial in sediments of high organic matter content, the petroleum hydrocarbons being derived from organic matter of biologic origin which was deposited with these sediments. The exact mechanism by which oil and/or gas are formed within such sediments, i.e., source rocks, is not known with certainty. After the hydrocarbon forming mechanism has taken place, it is thought that the petroleum hydrocarbons in the source rock then migrated to more permeable reservoir rocks where they accumulated in the concentrated deposits found today.

In previous geochemical exploration techniques utilizing the source rock concept, rock formations have been characterized as source rocks on the basis of the amount and kind of hydrocarbons contained in the formation. Exemplary of such techniques are the procedures disclosed in U.S. Patent No. 2,854,396 to Hunt et al. and the article by E. E. Bray et al., "Distribution of N-Paraffins as a Clue to Recognition of Source Beds," Geochimica et Cosmochimica Acta, 1961, vol. 22, pp. 2–15. While techniques such as those disclosed in Bray et al. are promising tools in exploration for oil, they possess certain limitations. Generally, relatively small quantities of hydrocarbons in a rock formation are presumed to indicate lack of generation of petroleum hydrocarbons and, thus, the likelihood that the rock formation under investigation is not a source rock for petroleum hydrocarbons. However, mild metamorphism of the sediment, which may be undetectable in the inorganic matrix, may have been sufficient to degrade hydrocarbons and other organic matter originally contained in the sediment into hydrocarbon gases. These gases may have escaped from the sediment, leaving behind only a carbonaceous residue which is depleted in hydrocarbon content. Conventional methods of source rock identification based upon analysis for hydrocarbons would fail to identify such a sediment as a source rock for gaseous petroleum hydrocarbons.

In accordance with the instant invention, there is provided a method for determining whether or not a sedimentary formation, which may be relatively barren of hydrocarbon content, is a likely source rock for petroleum hydrocarbons, particularly gaseous petroleum hydrocarbons, and also for determining the state of maturation for such a sediment. More particularly, there is provided, in accordance with the instant invention, a method of analyzing a sedimentary rock formation in order to ascertain the likelihood of the formation being a source rock for gaseous petroleum hydrocarbons.

It has heretofore been recognized that thermal action hastens the production of hydrocarbons from organic material. For example, in the article by J. D. Mulik et al., "Genesis of Hydrocarbons of Low Molecular Weight in Organic-Rich Aquatic Systems," Science, vol. 141, No. 3575 (July 5, 1963), pp. 806–807, there are described the results of investigation carried out with regard to recent marine sediments. In this work it was discovered that mild heat treatment of sediment samples resulted in the generation of certain aromatic compounds which were not originally present in the samples in detectable amounts.

In accordance with the present invention, a sample obtained from a formation in the earth's crust is subjected to thermal action in order to determine if organic matter originally present in the formation has, during the course of geologic history, undergone degenerative reactions yielding gaseous hydrocarbon products. As explained in detail hereinafter, by the analysis of certain gases produced during this treatment of the sample, it can be determined whether the formation from which the sample is taken is in a relatively early stage of maturation in which certain hydrocarbon gases have not been generated, or in a relatively late state of maturation where there is a strong possibility that such hydrocarbon gases have been generated during the course of its geologic history.

In carrying out one embodiment of the present invention, a sample obtained from an organic matter containing formation is disposed in a noncombustion supporting environment and heated over a plurality of time intervals at a temperature sufficient to produce gaseous matter from the organic matter in the sample. The gaseous matter thus produced is analyzed to determine for each of the time intervals the relative quantities of nitrogen or carbon dioxide, or both, produced from the organic matter during heating. Preferably, the gaseous matter also is analyzed to determine the relative quantities of methane produced during these time intervals. From this data, the state of maturation of the rock formation and the likelihood of its being a source rock for hydrocarbon gases may be determined.

The production during this thermal treatment of gases such as nitrogen and carbon dioxide, and in particular nitrogen, is associated with low activation energies. On the other hand, the production of hydrocarbon gases, and in particular methane, is associated with higher activation

energies. Thus, the production of relatively large amounts of nitrogen and carbon dioxide during the early stages of the thermal treatment is indicative of an early state of maturation. On the other hand, relatively low production of nitrogen and carbon dioxide during the early stages of thermal treatment is an indication of a late stage of maturation. The rock formation thus is indicated as a possible source rock, particularly where the production of significant quantities of methane is observed during the later stages of the thermal treatment.

In accordance with another embodiment of the instant invention, there is provided a procedure for determining the relative amount of gas which has been generated within a sedimentary formation during the course of its geologic history. In carrying out this aspect of the invention, a first sample from an organic matter containing formation is disposed in a noncombustion supporting environment and heated at a temperature sufficient to produce methane from the organic matter in the sample. The methane thus produced is analyzed with regard to the concentration therein of the carbon isotope C^{13}. Analysis also is carried out on a second sample obtained from the formation under investigation in order to determine the C^{13} concentration for the formation organic matter. These C^{13} concentrations then are correlated in order to ascertain the gas generation in history of the formation, with a C^{13} content in the methane approaching the C^{13} content for the formation organic matter indicating that a relatively large amount of gas has been generated within the formation.

For a more detailed description of the instant invention, reference may be had to the following detailed description, taken in conjunction with the accompanying drawings in which:

FIGURES 1, 2, 3 and 4 are graphs illustrating the results of certain experimental work carried out regarding the invention.

Before turning to a description of the instant invention, reference will be made to certain investigations carried out with regard to the kinetics involved in the degeneration of organic matter found in sedimentary rock formations. Many organic compounds decompose at rates which obey the following relationships:

$$k=\frac{2.303}{t}\log\frac{c_o}{c} \tag{1}$$

$$k=Ae^{-E/RT} \tag{2}$$

wherein:
t is the time of the reaction,
c_o is the original concentration of the reactant,
c is the concentration of the reactant after time t,
A is the frequency factor,
E is the activation energy,
R is the gas content,
T is the absolute temperature, and
k is the rate constant.

The above terms may be in any consistent units and k, of course, is expressed as the reciprocal of time in the same units as t. For a more complete description of Equations 1 and 2, reference may be had to F. Daniels et al., Physical Chemistry, 2nd ed., John Wiley & Sons, Inc., 1961; and Philip H. Abelson, Researches in Geochemistry, John Wiley & Sons, Inc., 1959. By substitution between Equations 1 and 2, the following relationships may be developed:

$$Ae^{-E/RT}=\frac{2.303}{t}\log\frac{c_o}{c} \tag{3}$$

$$\frac{t}{e^{ERT}}=A\ln\frac{c_o}{c} \tag{4}$$

$$\frac{T\ln t}{E}=\ln\frac{(A\ln c_{o/c})}{R} \tag{5}$$

For any fixed values of $c_{o/c}$ and A, the right-hand term of Equation 5 is a constant k. Thus:

$$\frac{T\ln t}{E}=k \tag{6}$$

From Equation 6, it can be seen that there is a linear relationship between the logarithm of time and the reciprocal of temperature at any stage in the degeneration reaction of a given organic compound. Thus, for a fixed amount of reaction, i.e., a fixed $c_{o/c}$, the product of temperature and the logarithm of time are constant; and for any given organic material of activation energy E, there will be a specified amount of reaction $c_{o/c}$ for each product of temperature and the logarithm of time. This product is referred to hereinafter as the "time-temperature equivalent."

In the degeneration of complex organic compounds originally deposited in a sediment, reactions involving the dissociation of low-energy bonds should proceed at lower activation energies than reactions involving the dissociation of high-energy bonds. Stated otherwise, the products of dissociation of low-energy bonds should appear predominantly at lower time-temperature equivalents than the products of dissociation of high-energy bonds. Thus, samples from relatively recent sediments which have not undergone extensive thermal action during the course of their geologic history should give off relatively large quantities of substances associated with low activation energies when the samples are subjected to heating. On the other hand, samples from older sediments normally should, when heated, give off lesser amounts of those substances associated with relatively low activation energies. Also, these older sediments should yield, during the course of thermal treatment, relatively larger quantities of dissociation products associated with higher activation energies.

To confirm these relationships, certain tests were carried out on samples obtained from organic matter containing sediments. One such sediment was a shale which, during the course of geologic history, had reached an intermediate stage of maturation of its contained organic matter. This was evidenced by the presence in the shale of significant quantities of petroleumlike hydrocarbons, i.e., relatively high molecular weight aromatics and saturated hydrocarbons. In carrying out this experiment, a sample from the shale formation was subjected to heating over progressively increasing temperature increments. The heating was started at a temperature of 100° C. and continued over temperature increments of 50° C. to a temperature of 300° C. The temperature at each increment was maintained constant for a period of four days and the gas produced during each increment was analyzed qualitatively and quantitatively for nitrogen, carbon dioxide, methane, ethane, propane, butane, and pentane. The results of this test are shown in FIGURE 1 which is a graph of percent composition, C, on the ordinate versus temperature, T, in °C. on the abscissa. In FIGURE 1, curves **2**, **4**, **5**, **6**, and **8** are plots, respectively, of the percent composition in the produced gas of nitrogen, carbon dioxide, methane, ethane and propane, and butane and pentane. From FIGURE 1 it can be seen that nitrogen and carbon dioxide were prominent constituents of the gas evolved at the lower temperatures; whereas, the hydrocarbon gases, and in particular methane, were present in significant amounts in the gas evolved at the higher temperatures.

In FIGURE 2, curve **9** is a plot of the amount Q, in micrograms per gram of shale of soluble organic residue retained in samples from this shale formation at the end of each temperature increment, as a function of temperature T. The organic matter was comprised primarily of high molecular weight saturated and aromatic hydrocarbons and asphaltic compounds. As shown in FIGURE 2, the amounts of organic matter remaining at the end of each of the temperature increments decreased with in-

creasing temperature. It can be seen from an examination of FIGURES 1 and 2 that the gaseous matter produced during heating was due to degradation of the organic matter originally present in the shale. It also will be recognized from an examination of FIGURE 1 that the production of nitrogen and, to a lesser extent, carbon dioxide is associated predominately with lower activation energies; whereas, the production of methane is associated predominately with somewhat higher activation energies. It will be recalled in examining the results shown in FIGURES 1 and 2 that the organic matter in the shale from which the samples were obtained had progressed to a state of having generated significant amounts of petroleum hydrocarbons.

Further experiments regarding the present invention were carried out on marine sediments of very recent origin and which did not contain discernible amounts of petroleumlike hydrocarbons. The results of these tests are shown in FIGURES 3 and 4 which are graphs of rates of production, R, of various substances produced during heating in milliliters per day at atmospheric pressure on the ordinates versus time, *t*, in days to the abscissas.

In the test illustrated in FIGURE 3, the temperature of the sample was maintained constant at 97° C. for the first five days and thereafter increased to a temperature of 110° C. for the remainder of the test. The gas produced during heating was analyzed qualitatively and quantitatively at the end of each day for nitrogen, carbon dioxide, and methane. The rates of production of nitrogen, carbon dioxide, and methane (increased tenfold) are shown by curves **10**, **11**, and **12**, respectively. From an examination of FIGURE 3 it can be seen that during the first two days of heating where the temperature was maintained constant at 97° C. the gas produced consisted almost entirely of nitrogen. Thereafter, increasing amounts of carbon dioxide were produced; and when the temperature was raised to 110° C., the carbon dioxide production rate increased sharply, with the maximum production rate occurring at about seven days. Only minor amounts of methane, as shown by curve **12**, were produced throughout the test.

It will be recognized that the procedure of FIGURE 3 was, in effect, a synthesis of thermal metamorphism of the organic matter contained in the sample as would occur during a period of geologic time. Thus, through the heating procedure, the sample was progressed from a very early state of maturation to some later state of maturation. This, of course, was accomplished in the test procedure through the application of temperatures higher than those which normally would be encountered by a sediment during the course of its geologic history.

This same sample then was subjected to heating at an increased temperature of 132° C. with the results shown in FIGURE 4. In FIGURE 4, curves **10***a*, **11***a*, and **12***a* are plots of rate of production versus time for nitrogen, carbon dioxide, and methane, respectively. From an examination of FIGURE 4, it can be seen that carbon dioxide was the predominant gas produced and that nitrogen was now produced in relatively small amounts. In addition, it can be seen that the rates of production of nitrogen, methane, and carbon dioxide all peaked at approximately the same time, thus, at approximately the same time-temperature equivalent; whereas, in the test of FIGURE 3, the nitrogen production rate first peaked well ahead of the production rates for the other substances.

On the basis of such experimental procedures, it is postulated that a possible source rock of petroleum hydrocarbons may be considered during its geologic history to pass through three general stages, arbitrarily designated as the "early stage," the "intermediate stage," and the "late stage." The intermediate stage is characterized by the presence of significant quantities of petroleumlike heavy hydrocarbons. This stage thus may be recognized by analysis of the rock for such hydrocarbons by known geochemical procedures. However, the early and late stages are both characterized by the absence, or the presence in only very small quantities, of petroleumlike heavy hydrocarbons. Therefore, in examining a sedimentary rock having little or no petroleumlike hydrocarbons, it is important to establish whether the rock is in an early stage of maturation, in which case it is not a likely source rock, or in a late stage of maturation, in which case it is a possible source rock of petroleum hydrocarbons and particularly gaseous petroleum hydrocarbons. This is accomplished in accordance with the instant invention by subjecting a sample obtained from such a formation to a thermal treatment in order to determine if the kind and relative amounts of products given off are those associated with low time-temperature equivalents (early stage) or high time-temperature equivalents (late stage).

As a first step in practicing the instant invention, one or more organic matter samples from the rock formation or formations under investigation are placed in a noncombustion supporting environment. It is preferred to carry out the invention utilizing a rock sample, containing the organic matter dispersed therein in its natural state, which is crushed in order to facilitate uniform heating and evolution of the produced gases.

The desired noncombustion supporting environment for the sample may be obtained by placing it in a suitable airtight chamber and thereafter diluting the air in the chamber by repeated injection and evacuation of nitrogen. The chamber then is evacuated to a vacuum, e.g. of about 2×10^{-4} p.s.i., and a small amount of water is added in order to provide a water vapor atmosphere in the chamber. The chamber is provided with any suitable means for heating the sample and also for measuring the temperature of the sample and controlling it at the desired value. Suitable means also are provided for collecting the gaseous matter produced during heating and for analyzing the gaseous matter for its components. For example, the produced gases may be collected over water and analyzed by mass spectrometry or gas chromatography. Since such systems and procedures for collection and analysis of gases are well known to those skilled in the art, they will not be described further.

A number of procedures may be followed in heating the organic matter sample. In any case, the sample is heated at a temperature sufficient to produce gaseous matter from the organic matter in the sample. The temperature of the sample may be maintained constant throughout the heating process or it may be varied, as will be explained hereinafter.

Analysis of the gaseous matter produced during heating may be made with regard to one or more designated index substances. Carbon dioxide and nitrogen are both associated with relatively low time-temperature equivalents, and therefore analysis is carried out with regard to at least one of these substances. Since nitrogen is the most consistent and reliable indicator of low time-temperature equivalents, it is preferred to carry out analysis of the gaseous matter with regard to this substance. In most cases, of course, it will be desirable to analyze the gaseous matter produced during heating for both nitrogen and carbon dioxide.

As noted previously, methane is associated with relatively high time-temperature equivalents. This condition also is indicated by the relative paucity of nitrogen and, to a lesser extent, carbon dioxide in the gaseous matter produced during heating. It is preferred to carry out analysis of such gaseous matter with regard to methane, as well as nitrogen and carbon dioxide. This will supplement the data obtained from analysis with regard to nitrogen and carbon dioxide and also will indicate to some extent the past potential of the organic matter for the generation of methane and other gaseous hydrocarbons. The higher gaseous hydrocarbons, specifically ethane, propane,

butane, and pentane, are associated with time-temperature equivalents intermediate those predominately associated with carbon dioxide and methane. Analysis also may be carried out for these heavier hydrocarbon gases although such analysis alone normally will not provide a basis for a conclusive determination of the state of maturation of organic matter in the formation under investigation.

In one embodiment of the invention, the sample is heated at a constant temperature, preferably within the range of 100° C. to 250° C., and the rates of production of the various index substances measured and recorded as a function of time. This may be accomplished by collecting the gaseous matter produced during heating and analyzing it for each of a plurality of suitable time intervals. For example, the time intervals each may be for a period of one day or less. The quantity of the index substances such as carbon dioxide, nitrogen, and methane produced during the several time intervals may be measured in order to determine the quantity of each index substance produced during each time interval relative to the quantity produced during the other of the time intervals. If the maximum production rate for nitrogen or carbon dioxide occurs ahead of the maximum production rate for methane, the organic matter and the sediment are likely to be in an early stage of maturation and, hence, the sediment is not a likely source rock for petroleum hydrocarbon gases. On the other hand, if the maximum rates of production for nitrogen and carbon dioxide occur at approximately the same time as the rate of production for methane, the organic matter contained in the rock sample is considered to be in a late stage of maturation, particularly if an initial analysis of the rock sediment showed only a very small amount of petroleum-like hydrocarbons. The sediment, thus, may be regarded as a likely source rock for gaseous petroleum hydrocarbons.

In heating the sample at constant temperature, the time-temperature equivalent changes only as a function of time. This results in a relatively low rate of increase in the time-temperature equivalent and allows the analysis of the gaseous matter produced during heating to be made on the basis of small incremental changes in the time-temperature equivalent. However, heating at a constant temperature usually requires that the process be carried out for a relatively long length of time, e.g., on the order of twenty days or more in order to provide sufficient data for evaluation of the formation.

In accordance with another embodiment of the invention, there is provided a procedure which may be completed within a shorter time and yet allows analysis to be made over a wide time-temperature equivalent range. In carrying out this embodiment of the invention, the sample is heated over a series of progressively increasing temperature increments. Preferably, the temperature at each of these increments is maintained constant in order to provide during such increments a relatively low rate of change in time-temperature equivalent. Each temperature increment encompasses at least one of the time intervals for which measurements of the produced gases are made. In carrying out this embodiment of the invention, it has been found suitable to initiate heating at a temperature of 100° C. and then proceed stepwise at temperature intervals of 50° C. until a maximum temperature of 300° C. is reached. Thus, the sample may be heated at temperature increments of 100° C., 150° C., 200° C., 250° C., and 300° C. In order to simplify the analysis of the results and to provide uniformity for correlation where a plurality of samples are analyzed, it usually will be preferred to extend each of the temperature increments for the same period of time. Preferably, the sample is heated for a period of at least one day at each of the temperature increments. It is preferred to extend each temperature increment at least past the occurrence of the maximum production rate for the index substance which is predominant in the gaseous matter produced at this temperature increment. Thus, if analysis is carried out with regard to nitrogen, carbon dioxide, and methane, and nitrogen is the predominant one of these index substances at the 150° C. increment, this temperature should be maintained until the maximum production rate for nitrogen is reached. Preferably, a given temperature increment will be maintained past the maximum production rates for all of the index substances produced at this temperature.

In carrying out this embodiment of the invention, temperature increments of values other than those noted above may be used. However, it is preferred to provide at least one temperature increment within the range of 100° C. to 150° C. and at least another temperature increment above 150° C. but not more than 300° C. Also, the temperature of the higher increment should be at least 15° C. greater than the temperature of the lower (100° C.–150° C.) temperature increment.

A number of factors may be taken into consideration, in evaluating, in accordance with the present invention, the probability of a formation being a source rock of petroleum hydrocarbons. The concentrations of the various index substances may be measured and recorded as a function of the time-temperature equivalent or some representative characteristic thereof. For example, where the stepwise heating procedure is utilized, as usually will be preferred, the percent composition of the index substances may be recorded as a function of temperature similarly as shown in FIGURE 1. Either a predominance of nitrogen and carbon dioxide at the lower temperatures or a significant decrease in percentage composition of nitrogen and carbon dioxide with increasing temperature is an indication that the sediment is in an early stage of maturation and, hence, is not a likely source rock of petroleum hydrocarbons and, in particular, gaseous petroleum hydrocarbons. On the other hand, an absence of significant amounts of nitrogen and carbon dioxide at the lower temperatures or the absence of any significant decrease in percentage composition of nitrogen and carbon dioxide with increasing temperature may be taken as an indication of a relatively late stage of maturation with the attendant increasing probability that the sediment is a probable source rock. This is particularly true where these conditions are accompanied by the occurrence of increasing amounts of methane at the higher temperatures.

The analysis for the various index substances also may be made in terms of the relative quantities of these substances produced at each of the several temperature increments. If most of an index substance, such as nitrogen, associated with a low time-temperature equivalent is produced at the lower temperature increments, e.g., at 100° C. and 150° C., the sediment may be considered to be an unlikely source rock. Conversely, if most of the nitrogen is produced at the higher temperatures, e.g., on the order of 200° C., 250° C., or 300° C., the sediment may be considered as a source rock.

As noted previously, a determination as to the relative amount of gas generated within a sedimentary formation may be made on the basis of the concentration of the carbon isotope C^{13} in the methane formed during heating of a formation sample and the C^{13} concentration in the organic matter originally present in the formation. This embodiment of the invention preferably is utilized in conjunction with one of the above-described heating procedures in order to further characterize sediments which have been identified as possible source rocks by such procedures. It is to be recognized, however, that this embodiment may alone be used to identify possible source rocks of hydrocarbon gases.

In carrying out this embodiment of the invention, analysis is made with regard to two samples obtained from a source rock type formation. Preferably, such samples are obtained from the same location within a formation. This

may be accomplished by obtaining a master sample from the formation and dividing it into two portions. Preferably, the sample is divided into two equal portions in order to simplify the subsequent evaluation of results. One of the samples is disposed in a noncombustion supporting environment and heated at a temperature sufficient to produce gaseous matter which includes methane as a component thereof. During the heating step, measurements may be made with regard to the various index substances in accordance with the criteria described above. For example, the sample may be heated within a range of 100° C. to 300° C. at increments of 50° C. and measurements made with regard to nitrogen, carbon dioxide, and methane. In any case, the sample should be heated at a temperature sufficient to produce methane from the contained organic matter. In order to produce such methane within a reasonable time, it usually will be desired to heat the sample at a temperature of at least 150° C. Preferably, the sample will be heated, during at least a portion of the heating procedure, at a temperature of at least 200° C.

After the heating step, the methane thus produced is analyzed to determine the concentration of the carbon isotope C^{13} therein. The C^{13} concentration for the methane may be measured and recorded on any suitable basis. It is preferred, however, to express the C^{13} concentration in terms of parts per million of C^{13} on the basis of total carbon content. Measurement of the C^{13} concentration may be accomplished by any satisfactory procedure. For example, the methane may be converted to carbon dioxide and water by combustion and the resulting carbon dioxide then analyzed for its C^{13} concentration through the use of a mass spectrometer. For a more complete description of a suitable analysis procedure to be followed, reference is made to H. Craig, "The Geochemistry of the Stable Carbon Isotopes," Geochimica et Cosmochimica Acta, Pergamon Press Ltd., London, 1953, vol. 3, pp. 53–92.

A similar procedure may be followed in measuring the C^{13} concentration in the original organic matter contained in the formation. Thus, the second sample from the formation under investigation may be crushed and then burned in order to convert the carbon in the organic matter to carbon dioxide. The carbon dioxide thus produced then may be subjected to analysis for its C^{13} concentration by the use of a mass spectrometer.

The ratio of the C^{13} concentration in the methane to the C^{13} concentration of the formation organic matter is an indicator of whether the formation is source rock of hydrocarbon gases. By way of example, a formation exhibiting a methane C^{13} concentration of 10,790 parts per million and an organic matter C^{13} concentration of 10,800 parts per million would be a more likely source rock of gas than a formation exhibiting a methane C^{13} concentration of 10,700 parts per million and an organic matter C^{13} concentration of 10,800 parts per million.

The invention may be utilized in various exploration procedures. For example, the invention may be utilized as a primary exploratory technique in order to determine the possibility of petroleum accumulations within a general geographic area of the earth's surface. In this case, it usually will be preferred to obtain samples from a relatively large number of locations in the earth's crust. The sampling stations may be chosen randomly or on the basis of a predetermined scheme and the samples may be obtained at the surface of the earth or by drilling to subsurface locations within the earth's crust.

The samples thus obtained are analyzed by one or more of the above-described heating procedures in order to ascertain the character of the gaseous matter produced during heating. As noted previously, analysis of the gaseous matter must be made at least with respect to carbon dioxide or nitrogen. Preferably, analysis will be made with regard to nitrogen, carbon dioxide, and methane and also the methane and formation organic matter C^{13} concentrations. The measurements taken for the respective samples then are correlated with each other and the locations in the earth's crust at which the samples are taken in order to ascertain possible source rocks of petroleum hydrocarbons in the area. This may be accomplished by plotting the significant gas generation and C^{13} characterisitcs for the samples at their respective location on a geographical map of the area surveyed.

The instant invention also may be utilized in carrying out supplemental exploration in areas within which other prospecting operations already have been carried out. For example, a seismic survey of a particular locality may indicate the presence of subsurface sedimentary structures favorable to the accumulation of petroleum hydrocarbons. In this instance, the present invention can provide a valuable tool in determining which of these subsurface structures may actually contain such hydrocarbons.

In this use of the invention, at least one and preferably a pair of samples may be obtained from each of the source rock type formations in the area. Source rock type formations usually may be considered to be sediments such as shales of not more than six percent by weight organic matter content and carbonates of not more than one percent by weight organic matter content, and which have permeabilities of not more than one millidarcy. The samples then are analyzed for one or more of the index substances, as described above, in order to identify possible source rock formations. C^{13} measurements also may be carried out in accordance with the instant invention in order to ascertain for each formation the ratio of the methane C^{13} concentration to the formation organic matter C^{13} concentration. These ratios then are correlated with each other and their respective rock formations in order to ascertain the formation having the highest such ratio, and a well is drilled into a reservoir rock formation which is in fluid communication with the designated source rock formation and which has a permeability greater than the designated source rock formation. Preferably, the well is drilled into a reservoir rock formation, at least a portion of which is in a contiguous relationship with at least a portion of the source rock formation. By contiguous relationship is meant a reservoir rock formation which lies next to the source rock formation and thus provides a ready acceptor for petroleum hydrocarbons formed in the source rock and migrating therefrom. However, in some cases it may be desirable to drill a well into a promising reservoir rock formation which is not in a contiguous relationship with the source rock formation, but which is in fluid communication therewith by other means such as through subterranean faults or joints.

Having described a specific embodiment of the instant invention, it will be understood that further modifications thereof may be suggested to those skilled in the art, and it is intended to cover all such modifications as fall within the scope of the appended claims.

What is claimed is:

1. In a method of geochemical exploration, the steps comprising:
   (a) disposing in a noncombustion supporting environment a sample obtained from an organic matter containing formation in the earth's crust;
   (b) heating said sample at a temperature sufficient to produce gaseous matter from organic matter in said sample; and
   (c) measuring for each of a plurality of time intervals during said heating the quantity of at least one substance selected from the class consisting of carbon dioxide and nitrogen in said gaseous matter relative to the quantity of said at least one substance for the other of said time intervals to determine the maturation of said formation.

2. The method of claim 1 wherein said sample is from a formation having an organic matter content of not more

than six percent by weight and a permeability of not more than one millidarcy.

3. The method of claim 1 further comprising the step of measuring for each of said time increments the quantity of methane in said gaseous matter relative to the quantity of methane for the other of said time increments.

4. The method of claim 3 further comprising the steps of measuring the concentration of the carbon isotope C^{13} in said methane and measuring the concentration of the carbon isotope C^{13} in the organic matter in a second sample obtained from said formation.

5. The method of claim 3 wherein the measurement carried out in step (c) of claim 1 is of nitrogen.

6. The method of claim 3 wherein the measurement carried out in step (c) of claim 1 is of nitrogen and carbon dioxide.

7. The method of claim 6 wherein said sample is heated at an essentially constant temperature for a period encompassing a plurality of said time increments.

8. The method of claim 1 wherein said sample is heated over a plurality of progressively increasing temperature increments each of which encompasses at least one of said time intervals, the temperature at each of said increments being constant.

9. The method of claim 8 further comprising measuring for each of said time intervals the quantity of methane in said gaseous matter relative to the quantity of methane for the other of said time intervals.

10. The method of claim 9 further comprising the steps of measuring the concentration of the carbon isotope C^{13} in said methane and measuring the concentration of the carbon isotope C^{13} in the organic matter in a second sample obtained from said formation.

11. The method of claim 9 wherein the measurement carried out in step (c) of claim 1 is of nitrogen.

12. The method of claim 9 wherein the measurement carried out in step (c) of claim 1 is of nitrogen and carbon dioxide.

13. The method of claim 12 wherein the temperature of at least one of said increments is within the range of 100° C.–150° C. and the temperature of at least another of said increments is above 150° C. but not more than 300° C. and at least 15° C. greater than the temperature of said at least one increment.

14. In a method of geochemical exploration, the steps comprising:

(a) disposing in a noncombustion supporting environment a sample obtained from an organic matter containing formation in the earth's crust;

(b) heating said sample over a plurality of progressively increasing temperature increments, the temperature at each of said increments being essentially constant and sufficient to produce gaseous matter from organic matter in said sample; and

(c) measuring for each of said increments the relative concentration in said gaseous matter of at least one substance selected from the class consisting of carbon dioxide and nitrogen to determine the maturation of said formation.

15. The method of claim 14 further comprising the step of measuring for each of said temperature increments the relative concentration of methane in said gaseous matter.

16. The method of claim 15 further comprising the steps of measuring the concentration of the carbon isotope C^{13} in said methane and measuring the concentration of the carbon isotope C^{13} in the organic matter in a second sample obtained from said formation.

17. The method of claim 15 wherein the measurement carried out in step (c) of claim 14 is of nitrogen.

18. The method of claim 15 wherein the measurement carried out in step (c) of claim 14 is of nitrogen and carbon dioxide.

19. The method of claim 18 wherein the duration of each of said temperature increments is at least one day.

20. In a method of geochemical exploration, the steps comprising:

(a) disposing in a noncombustion supporting environment a first sample obtained from an organic matter containing formation in the earth's crust;

(b) heating said first sample at a temperature sufficient to produce gaseous matter including methane from organic matter in said sample;

(c) measuring the concentrations of the carbon isotope C^{13} in said methane; and

(d) measuring the concentrations of the carbon isotope C^{13} in the organic matter in a second sample obtained from said formation.

21. The method of claim 20 wherein said sample is from a formation having an organic matter content of not more than six percent by weight and a permeability of not more than one millidarcy.

22. The method of claim 20 wherein a pair of first and second samples from each of a plurality of organic matter containing formations in the earth's crust are treated in accordance with steps (a), (b), (c), and (d) to determine for each of said pairs of samples the ratio of the concentration of C^{13} in said methane to the concentration of C^{13} in said organic matter and further comprising correlating said ratios with each other and said formations to ascertain the one of said formations having the highest of said ratios, and drilling a well into a subsurface reservoir formation in fluid communication with said one of said formations and having a permeability greater than the permeability of said one of said formations.

23. The method of claim 22 wherein at least a portion of said reservoir formation is in a contiguous relationship with at least a portion of said first-named formation.

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