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Generation, Accumulation, and Resource Potential of Biogenic Gas[1]

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ABSTRACT

Biogenic gas is generated at low temperatures by decomposition of organic matter by anaerobic microorganisms. More than 20% of the world's discovered gas reserves are of biogenic origin. A higher percentage of gases of predominantly biogenic origin will be discovered in the future. Biogenic gas is an important target for exploration because it occurs in geologically predictable circumstances and in areally widespread, large quantities at shallow depths.

In rapidly accumulating marine sediments, a succession of microbial ecosystems leads to the generation of biogenic gas. After oxygen is consumed by aerobic respiration, sulfate reduction becomes the dominant form of respiration. Methane generation and accumulation become dominant only after sulfate in sediment pore water is depleted. The most important mechanism of methane generation in marine sediments is the reduction of CO_2 by hydrogen (electrons) produced by the anaerobic oxidation of organic matter. CO_2 is the product of either metabolic decarboxylation or chemical decarboxylation at slightly higher temperatures. The factors that control the level of methane production after sediment burial are anoxic environment, sulfate-deficient environment, low temperature, availability of organic matter, and sufficient space. The timing of these factors is such that most biogenic gas is generated prior to burial depths of 1,000 m.

In marine sediments, most of the biogenic gas formed can be retained in solution in the interstitial (pore) waters because of higher methane solubility at the higher hydrostatic pressures due to the weight of the overlying water column. Under certain conditions of high pressures and (or) low temperatures, biogenic methane combines with water to form gas hydrates.

Biogenic gas usually can be distinguished from thermogenic gas by chemical and isotopic analyses. The hydrocarbon fraction of biogenic gas consists predominantly of methane. The presence of as much as 2% of heavier hydrocarbons can be attributed to admixture of minor thermogenic gas due to low-temperature degradation of organic matter. The amounts of hydrocarbon components other than methane generally are proportional to temperature, age, and organic-matter content of the sediments. Biogenic methane is enriched in the light isotope ^{12}C ($\delta^{13}C_1$ lighter than -55 ppt) owing to kinetic isotope fractionation by methanogens. The variations in isotopic composition of biogenic methane are controlled primarily by $\delta^{13}C$ of the original CO_2 substrate, which reflects the net isotopic effect of both addition and removal of CO_2. The methane isotopic composition also can be affected by mixing of isotopically heavier thermogenic gas. The possible complicating factors require that geologic, chemical, and isotopic evidence be considered in attempts to interpret the origin of gas accumulations.

Accumulations of biogenic gas have been discovered in Canada, Germany, Italy, Japan, Trinidad, the United States, and USSR in Cretaceous and younger rocks, at less than 3,350 m of burial, and in marine and nonmarine rocks. Other gas accumulations of biogenic origin have undoubtedly been discovered; however, data that permit their recognition are not available.

INTRODUCTION

For effective exploration, a better understanding of processes that lead to the origin, migration, and accumulation of hydrocarbons is necessary. Geologic and geochemical evidence indicates that hydrocarbons are generated from organic matter disseminated in fine-grained sedimentary rocks by a series of complex chemical reactions. The extent of nonbiologic reactions is controlled primarily by temperature and duration of heating (geologic time). The quantity and molecular size of hydrocarbons (liquid or gaseous) generated are influenced by the concentration and type of organic matter preserved in the source rock, and by the stage of thermochemical alteration (maturity).

The generation and occurrence of hydrocarbons can be related to three main stages of thermal maturity of organic matter in sedimentary rocks (Fig. 1):

1. *Immature stage (diagenesis)*—Biologic activity and chemical rearrangement are responsible for converting organic matter to kerogen, an insoluble residue, which is the source of most hydrocarbons. Although small

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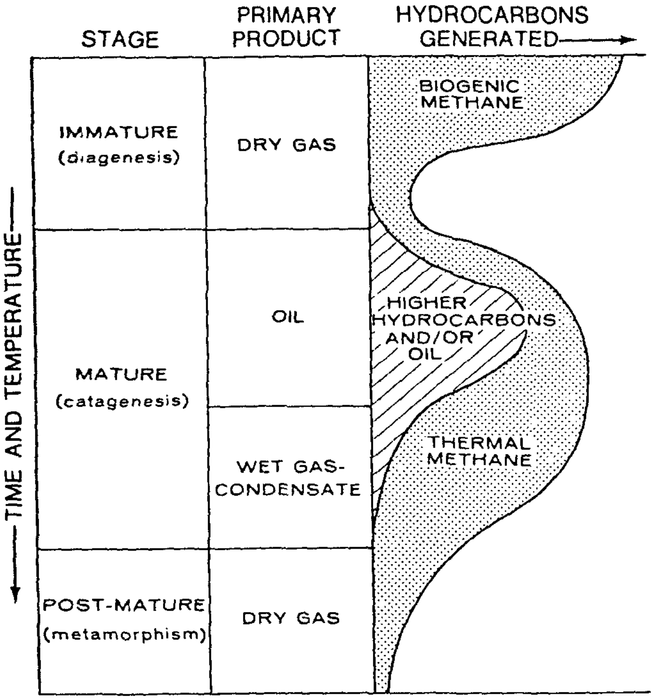

FIG. 1—Diagram showing generation of hydrocarbons with increasing temperature and time.

amounts of hydrocarbons are present which are inherited from or produced by mild degradation of organic tissues, biogenic methane is the only hydrocarbon actually generated in significant volumes during this stage.

2. *Mature stage (catagenesis)*—With increasing temperature and advancing geologic time, the full range of hydrocarbons is produced from kerogen and other nonhydrocarbon precursors by thermal degradation and cracking reactions. Depending on the concentration and type of organic matter, oil generation occurs during this stage accompanied by the production of significant amounts of natural gas. As temperatures increase, lighter hydrocarbons are formed preferentially, owing to breaking of carbon-carbon bonds, affecting both the residual kerogen and the hydrocarbons previously formed. Wet gas and condensate are the primary products of the later part of the stage.

3. *Postmature stage (incipient metamorphism)*—At the end of the mature stage, the kerogen becomes highly polymerized, condensed in structure, and chemically stable. The main hydrocarbon generated is methane which results from the cracking of the existing hydrocarbons. Hydrocarbons larger than methane are destroyed much more rapidly than they are formed.

This paper discusses the methane-rich gas generated in accumulating sediments during the immature stage (diagenesis) by the metabolic activity of anaerobic bacteria. Hereafter, this gas will be referred to as biogenic gas to emphasize that microorganisms are responsible for its formation. We emphasize that biogenic gas not only is generated, but has accumulated in economically significant quantities and warrants consideration in future exploration. Our objectives are to: (1) describe the conditions required for generation of biogenic gas with an emphasis on marine sediments because many ancient accumulations were generated in this environment; (2) discuss the factors favoring the accumulation of biogenic gas; (3) characterize biogenic gas and distinguish it from natural gas of the other stages of hydrocarbon generation; (4) document major ancient occurrences; and (5) estimate potential resources of biogenic gas.

ORIGIN OF BIOGENIC GAS

Biogenic gas is produced during the decomposition of organic matter by microorganisms. Under present-day conditions, biogenic methane formation is controlled by certain physiologic and ecologic restraints. First, methane-producing microorganisms are strict anaerobes and cannot tolerate even traces of oxygen. Second, biogenic methane does not accumulate in significant amounts in the presence of high concentrations of dissolved sulfate. These restrictions confine the activity of methane-producing microorganisms to certain environments such as: dung heaps and anaerobic-sewage digestors (Toerien and Hattingh, 1969); digestive tracts of animals (Bryant, 1965); poorly drained swamps, bays, paddy fields, and anoxic freshwater lake bottoms (Oana and Deevey, 1960; Koyama, 1963; Kim and Douglas, 1972); landfills (Colonna, 1977); glacial drift (Coleman, 1976; Coleman et al, 1977); and marine sediments beneath the zone of active sulfate reduction (Emery and Hoggan, 1958; Atkinson and Richards, 1967; Nissenbaum et al, 1972).

Methane production is readily observable in bogs, swamps, and marshes because it occurs close to the surface and bubbles are released from the sediment. In marine sediments, sulfate reduction is the dominant process of anaerobic bacterial respiration at shallow depths of burial (ZoBell and Rittenberg, 1948). Evidence for significant methane production is usually not detected until dissolved sulfate is almost completely removed from the interstitial water (Nissenbaum et al, 1972). In many recent marine environments, complete removal of sulfate does not occur until sediments have been buried to depths of some tens of meters (Sayles et al, 1973; Waterman et al, 1973; Manheim and Sayles, 1974). Consequently, the geochemical effects of methanogenesis in open marine sediments have been difficult to observe. However, with the advent of deep coring procedures by the Deep Sea Drilling Project (DSDP), information on the nature and distribution of methane generation in marine sediments has become available.

MICROBIAL METABOLISM IN MARINE SEDIMENTS

Microorganisms require energy for growth and cell maintenance which is obtained by metabolizing organic matter by a series of coupled oxidation-reduction reactions. These metabolic processes result in the production of gases including methane. Two general types of metabolic processing by microorganisms in the marine environment are (1) respiration (both aerobic and anaerobic) which utilizes inorganic compounds as electron acceptors, and (2) fermentation in which electron transfer occurs within or between organic compounds.

The metabolic processes yield differing amounts of energy which, along with the environmental constraints, determine the nature of the microbial population. Relative energy yields indicate selective advantage gained by microorganisms capable of catalyzing the various processes. This advantage results in the dominance of certain microbial-population members which obtain the greatest amount of energy when two or more are competing in the same ecologic niche for the same organic substrate. Consequently, an ecologic succession of metabolic processes is established and varies with time and depth in the sediment column, with less efficient organisms being at greater depths. A more detailed account of the succession of diagenetic environments in marine sediments was given by Claypool and Kaplan (1974).

Figure 2 is a cross section through an open-marine, organic-rich sedimentary environment and illustrates the succession of microbial ecosystems. The interactions between sedimentologic and ecologic factors result in three distinct biochemical environments, each of which is characterized by a dominant form of respiratory metabolism. The three resulting zones are: the aerobic zone; the anaerobic sulfate-reducing zone; and the anaerobic carbonate-reducing (methane production) zone. The presence of these zones, which are characterized by successively less efficient modes of respiratory processes, can be inferred in the sediments and interstitial waters by systematic changes in the concentration and isotopic composition of the respiratory metabolites. In each of the zones, the dominant microbial population exploits the environment and eventually creates a new environment that favors a different population. Therefore, the transitions between the various zones are a geochemical consequence of environmental changes induced by microorganisms.

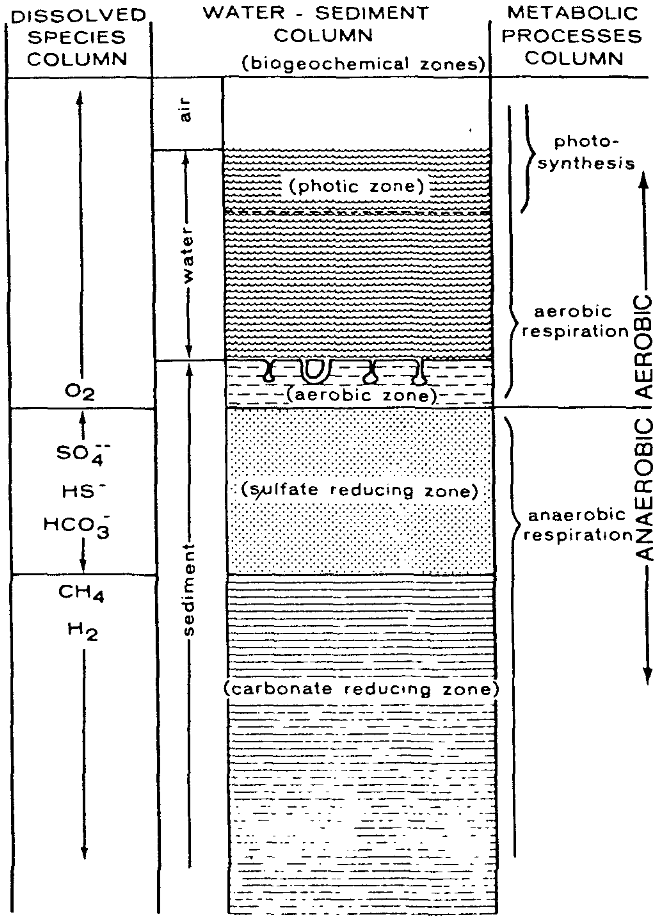

FIG. 2—Diagrammatic cross section of organic-rich, open-marine environment showing succession of microbial ecosystems that lead to methane generation.

When the ecologic succession in Figure 2 is established, the biochemical zones move upward with time, keeping pace with the addition of new sediments at the sediment-water interface. Likewise, the sediments move downward through the succession of diagenetic environments.

Aerobic respiration using organic matter is the most efficient energy-yielding metabolic process. The aerobic zone in the marine environment is normally developed in the water column and uppermost part of the sediment column. During aerobic respiration, oxygen is rapidly used and the demand often exceeds the rate at which the dissolved gas can be introduced from the atmosphere or overlying water column, particularly in areas of high sedimentation rates. When the oxygen is depleted, obligatory aerobic organisms cannot grow. Facultative anaerobes can switch from aerobic respiration to fermentation or anaerobic respiration using electron acceptors, but these are not abundant in marine sediments and have negligible effect on decomposition of organic matter.

In the marine environment, sulfate reduction becomes the dominant form of respiration after the onset of anaerobic conditions because of the relatively high concentration of sulfate (0.028 M) in normal sea water. In addition, only a few other microbial species can tolerate H_2S which is the end product of sulfate reduction. Sulfate-reducing bacteria are restricted in their range of oxidizable substrates (Postgate, 1965) and these compounds are probably present in limited amounts at a given time. Therefore, active sulfate-reducing bacteria require a symbiotic association with an anaerobic fermenting population to provide a source of oxidizable carbon substrate.

Below the sulfate-reduction zone, CO_2 reduction becomes the dominant process of anaerobic respiration and results in the formation of methane. The extent to which sulfate reduction and methanogenesis are mutually exclusive in marine sediments is currently under investigation (Martens and Berner, 1974, 1977; Oremland and Taylor, 1978; Kosiur and Warford, 1979). Only minor concentrations of methane are present in marine sediments containing dissolved sulfate (Whelan et al, 1975, 1978; Bernard et al, 1978), and rapid methane production appears to begin immediately after (or below the depth where) dissolved sulfate reaches low concentration and sulfate reduction is essentially complete (Nissenbaum et al, 1972; Claypool et al, 1973; Claypool, 1974; Claypool and Kaplan, 1974). However, several studies suggest that methane is consumed in the overlying sulfate-reducing zone (Barnes and Goldberg, 1976; Reeburgh, 1976; Martens and Berner, 1977; Reeburgh and Heggie, 1977; Kosiur and Warford, 1979). Thus it is likely that the balance between production and consumption of methane is an important factor controlling the distribution of methane in marine sediments (Bernard, 1979).

Methane-producing microorganisms also are even more restricted than sulfate reducers with respect to substrates utilizable for growth. Hydrogen and CO_2 are the preferred substrates studied in pure culture, whereas formate, methanol, and acetate can be used, but the reactions are probably much less energy-efficient (Wolfe, 1971; Zeikus and Wolfe, 1972; Winfrey et al, 1977; Belyaev and Laurinavichus, 1978). CO_2 reduction is energetically the most favorable mechanism of biogenic methane production and probably accounts for most of the methane produced in the marine environment, although other pathways are available.

ISOTOPIC INDICATORS

The progression of metabolic processes that results in methane production in the marine environment can be followed by monitoring the changes in the concentration and stable isotope ratios of the residual reactants or the accumulating products with increasing depth. Where the principle of "steady-state diagenesis" (Berner, 1975) is applicable, the changes with increasing depth are equivalent to the changes with respect to advancing time at the same depth.

The effects of in-situ sulfate reduction by bacteria can be traced in an example from sediments of DSDP hole 148 in the Caribbean Sea (Presley et al, 1973; Claypool, 1974). As illustrated in Figure 3, the sulfate dissolved in the interstitial water is depleted with increasing depth. At the same time, the ^{34}S is relatively enriched in the residual sulfate at any depth as a result of preferential ^{32}S removal in the sulfide with increasing depth.

Sampling techniques commonly have not permitted measurement of the concentration of methane in sediments. Where such measurements are not possible, the effects of methane generation can be examined by the changes in the concentration of $\delta^{13}C$ of bicarbonate dissolved in the interstitial water. Figure 4 is an example of the effects of methane production on the concentration and stable isotope ratio of dissolved bicarbonate from the Gulf of California (Goldhaber, 1974). In these sediments, sulfate concentration goes to zero at a depth of about 2 m. The onset of methane production at this point is reflected in decreased titration alkalinity and increased $\delta^{13}C$ of total dissolved CO_2. However, the interpretation of changes with depth in the concentration and $\delta^{13}C$ of the dissolved bicarbonate due to methane formation is more complex than with sulfate. The complexity results from dissolved bicarbonate at any depth reflecting the net of both addition and removal of CO_2. Metabolic CO_2 added to the interstitial water of anoxic sediments has about the same $\delta^{13}C$ as organic matter, or about −22 ppt (Presley and Kaplan, 1968). The CO_2 removed to form methane is about 70 ppt lighter than the $\delta^{13}C$ of the CO_2 dissolved in the interstitial water at the time of its formation, owing to a large kinetic isotope effect (Rosenfeld and Silverman, 1959).

Possible isotope effects of CO_2 addition and removal during biogenic methane production are illustrated in

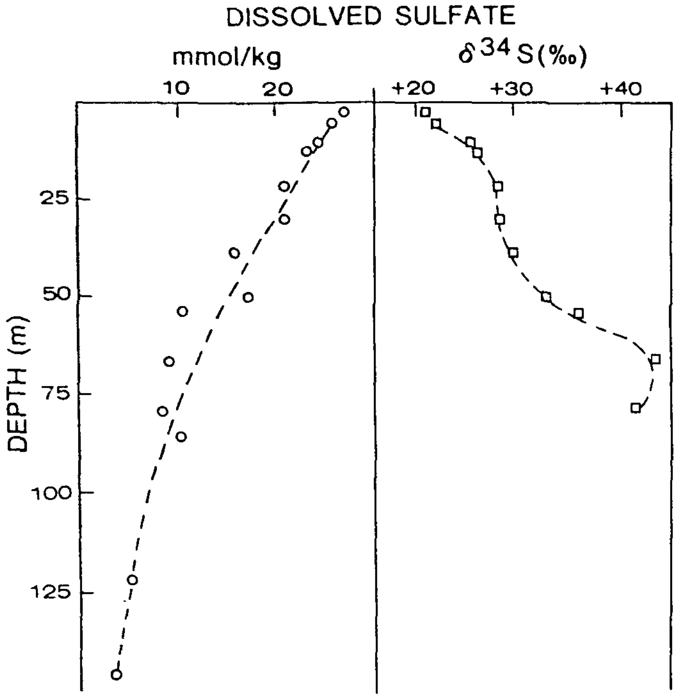

FIG. 3—Changes with depth in concentration and sulfur isotope ratio ($\delta^{34}S$) of dissolved sulfate in interstitial water of Aves Ridge (DSDP Site 148) sediments, caused by bacterial sulfate reduction.

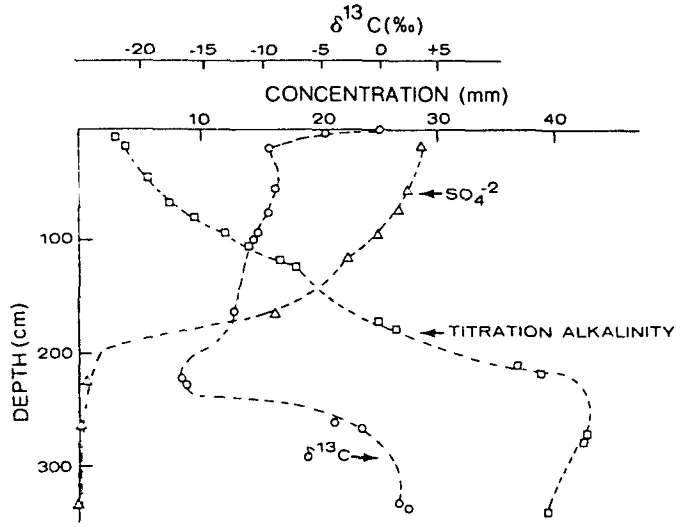

FIG. 4—Changes with depth in concentration of sulfate and titration alkalinity and $\delta^{13}C$ of total dissolved CO_2 in interstitial water of South Guymas basin sediments (Goldhaber, 1974). Shallowest occurrence of methane in these sediments is at depth of 2 m where trends in plotted pore-water constituents reverse.

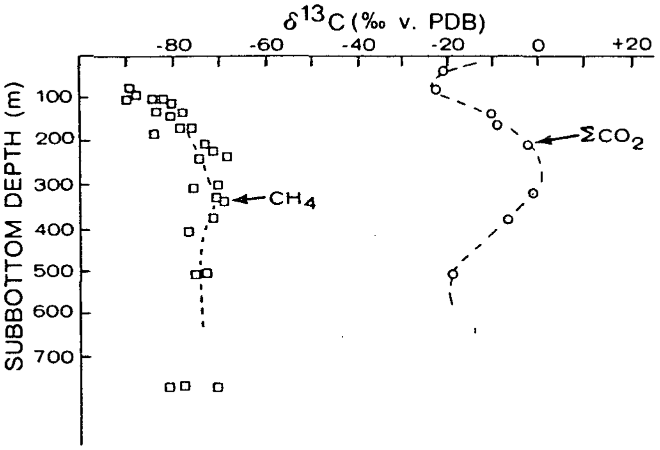

FIG. 5—Parallel changes with depth in $\delta^{13}C$ of dissolved carbonate and methane in sediments of Astoria fan (DSDP Site 174A).

Figure 5 for sediments of the Astoria fan at the mouth of the Columbia River from DSDP hole 174A (Claypool and Kaplan, 1974). Trends of $\delta^{13}C$ of dissolved carbonate and methane are shown with depth. In these sediments, sulfate is present to a depth of about 80 m (Waterman et al, 1973). Just below this depth, biogenic methane with $\delta^{13}C$ of -90 ppt is present. At the onset of methane formation, the concentration of dissolved CO_2 in the interstitial water is relatively high (0.022 M) and has $\delta^{13}C$ of -22 ppt reflecting input of metabolic CO_2 as a result of sulfate reduction. With net removal of isotopically light CO_2 to form methane, the concentration of CO_2 decreases and the $\delta^{13}C$ of the residual CO_2 increases. In such circumstances, methane also becomes isotopically heavier with increasing depth of burial reflecting ^{12}C depletion in the residual dissolved CO_2 from which the methane is being produced. This complementary relation between dissolved bicarbonate and methane is the principal evidence that microbiologic methane production in marine sediments proceeds mainly by the mechanism of CO_2 reduction. These changes also indicate that microbial methane generation can continue for 2 m.y. to depths of 500 m or more in the Astoria fan and probably longer and deeper elsewhere.

In the Astoria fan, the net addition of isotopically light CO_2 causes the $\delta^{13}C$ of both the methane and dissolved CO_2 to shift to more negative values (isotopically lighter) below depths of about 300 m (Fig. 5). Profiles of $\delta^{13}C$ for other sites also reflect a similar trend in which the heaviest values are obtained at intermediate depths with a trend toward lighter values at greater depths (Claypool and Kaplan, 1974). We interpret this to mean that isotopically light CO_2 was being added faster than its removal by methane production. Increases in the concentration of CO_2 over the depth interval in which this trend occurs support this conclusion. Although the early increase in CO_2 content is related to sulfate reduction, this later stage of CO_2 production probably represents a different process. CO_2 production after sulfate reduction has stopped appears to be controlled by the thermal history and age of the sediment as supported by first-order kinetic models (Claypool, 1974). This indicates that low-temperature nonbiologic decarboxylation of organic matter (Johns and Shimoyama, 1972; Tissot et al, 1974; Bray and Foster, 1980) is the most likely mechanism. This later diagenetic CO_2 is isotopically light ($\delta^{13}C$ of -20 to -25 ppt) and serves as a source for continued methane generation as indicated by the shift toward lighter $\delta^{13}C$ values of methane in deeper samples.

REQUIREMENTS FOR METHANE PRODUCTION

Production of biogenic methane is controlled by several critical factors. These requirements must be met not only to commence generation, but also to maintain production over a period of time so that large quantities can accumulate.

1. *Anoxic environment*—Methanogenic microorganisms are obligate anaerobes and cannot tolerate even traces of oxygen.

2. *Sulfate-deficient environment*—In environments where the sulfate concentration of the water is low, such as brackish or fresh water, methane production begins immediately after the oxygen is depleted. However, in the marine environment, sulfate must be reduced almost completely before significant amounts of methane can accumulate.

3. *Temperature*—Methane generation by microorganisms can occur at depths that are equivalent to temperatures between 0 and 75°C (Buswell and Mueller, 1952; Zeikus and Wolfe, 1972). Although methanogens can function over a wide temperature range, the optimum for a specific population generally is confined to several degrees. For example, the optimum temperature for growth of *Methanobacterium thermoautotrophicus*, an extreme thermophile, is 65 to 70°C. In shallow aquatic environments of northern latitudes, seasonal variations in temperature generally confine the maximum methane production to summer months (Koyama, 1963; Barber, 1974; Zeikus and Winfrey, 1976; King and Wiebe, 1978). However, in the deeper marine waters, temperatures and therefore methane-generating rates should remain more constant throughout the year. At the upper end, increasing temperatures lead to denaturation of bacterial tissues and transformation of organic matter to a form (humin/kerogen) which is less susceptible to attack by microorganisms.

4. *Presence of organic matter*—Organic matter is required for methanogenesis and the various metabolic processes that precede and support it. A minimum of metabolizable organic matter equivalent to about 0.5% organic carbon is required to support methane production in marine sediments (Claypool and Kaplan, 1974; Rashid and Vilks, 1977). Organic matter is generally concentrated in finer grained sediments (Hunt, 1972).

5. *Space*—A minimal amount of space is required for bacteria to function, particularly in fine-grained sediments where the organic nutrients are concentrated. Typical shale pores have a median size of 1 to 3 nm (Momper, 1978). However, bacteria have an average size of 1 to 10 μ m (Momper, 1978) indicating that they

saturation of the waters above the 82°C minimum solubility isotherm, the waters will become supersaturated with further burial and will produce a free gas state. At very shallow depths of burial, free gas will probably bubble to the surface and eventually will enter the atmosphere. This is a situation similar to nonmarine and (or) brackish-water environments.

A free gas phase in marine sediments leading to the accumulation of large quantities of biogenic methane can result from either generation of gas in excess of the solubility, or exsolution of gas brought about by a reduction of hydrostatic pressure. Gas generation in excess of solubility commonly is observed in shallow water sediments. Exsolution by reduction of hydrostatic pressure also may be a frequent cause of a free gas phase available for migration and accumulation, and could result from lowering of sea level, uplift and erosion, or upward migration of gas-bearing waters to zones of lower hydrostatic pressures.

A reservoir, seal, and trap must be present prior to release of gas from solution to insure its retention. These conditions probably are not met until sediments have been buried to depths greater than 500 m. At these depths, the sediments are at least partly dewatered, compacted, and the initial porosity and permeability reduced drastically. A large amount of biogenic methane is probably trapped stratigraphically, at least initially, in rocks of low porosity and permeability. At shallow depths, porous and permeable reservoirs are often flushed with fresh water, and natural gas accumulates only in closed structural traps.

In the marine-shelf environment, the deposition of discontinuous and relatively impermeable silt and sand enveloped by organic-rich mud and clay provides extremely favorable conditions for both in-situ generation and entrapment of biogenic methane. In the Cretaceous section of the northern Great Plains, bentonite beds, which are composed of montmorillonitic clays derived from volcanic ash, are numerous and extensive in marine-shelf sequences and are excellent seals for the widespread gas accumulations.

Another key trapping mechanism of biogenic methane may be the formation of early diagenetic carbonate cements as either layers or concretions; obviously the layers are more effective traps.

Early diagenetic carbonates can be formed in two ways. First, when CO_2 is removed from the dissolved bicarbonate reservoir of interstitial waters by reduction and formation of methane, the pH increases which can result in the precipitation of authigenic carbonates in anoxic sediments. Examples for this type of carbonate from deep-sea sediments (Claypool, 1974) are the Miocene Monterey Shale (Friedman and Murata, 1979), the Upper Cretaceous of Montana (D. L. Gautier, personal commun., 1979), and the Upper Jurassic of England (Irwin et al, 1977).

A second major mechanism for precipitation of isotopically anomalous (−30 ppt) carbonate layers is from CO_2 generated from oxidation of methane (Hathaway and Degens, 1969; Deuser, 1970; Roberts and Whelan, 1975). This process can result from periodic exsolution of methane associated with marine shoreline regressions, escape of the methane upward, and oxidation of methane to CO_2 under aerobic conditions (Hutton and ZoBell, 1949). The isotopically light CO_2 from the oxidation of methane first must be neutralized by reaction with the sediment to form bicarbonate, which is then available for precipitation of carbonate cement.

Under certain conditions of high pressure and low temperature, such as those of deep-sea sediments or areas of permafrost, biogenic methane will combine with water to form hydrates. The hydrates can serve both as a trap for the methane enclosed in the clathrate structure, and also as a seal for hydrocarbons, including biogenic methane generated below the hydrate, or liberated at the base of a gas hydrate zone subsiding into a region of temperature instability. Gas hydrate reservoirs have the potential of trapping greater volumes of gas than free gas trapped in the same space. However, current technology does not permit economic production of the hydrated gas.

During the Pleistocene, large areas of the world were covered with permafrost, and gas hydrates were more widespread because of generally cooler temperatures. Since that time, the areas of permafrost have been retreating and associated hydrates have been decomposing which has resulted in the formation of free gas accumulations. Gas fields in Siberia were cited by Makogon et al (1972) as examples of gas hydrate-involved accumulations.

Finally, most recognizable biogenic gas accumulations have low reservoir pressures because of their shallow depth of burial. However, they are also underpressured in relation to normal hydrostatic pressure gradients. This underpressuring, which is probably related to the removal of overburden and thus may coincide with exsolution of the gas, helps to trap the gas. The subnormal pressures have probably resulted from dilation of pore volume and from a decrease of reservoir temperature associated with uplift and erosion (Barker, 1972; Dickey and Cox, 1977).

CHARACTERISTICS OF BIOGENIC GAS

Gaseous hydrocarbons produced during the three main stages of thermal maturity have distinct chemical compositions and stable carbon isotope ratios (Fig. 7) that enable one, in theory, to distinguish between the products of each stage. However, in most examples, complicating factors require that geologic evidence must also be considered in interpreting the origin of natural gas occurrences.

Biogenic gas consists predominantly of methane, except in nonmarine and (or) brackish-water (low pH) environments where biologically formed CO_2 also may be a major component. Davis and Squires (1954) and Kim and Douglas (1972) demonstrated that trace amounts of the higher alkanes (ethane, propane, butane, and pentane) were generated in laboratory-conducted fermentation studies. Only traces being detected illustrates the usual occurrence of higher hydrocarbons in trace amounts with biogenic methane in recent sediments (Weber and Maximov, 1976).

Accumulations of natural gas of predominantly biogenic origin are usually associated with even greater concentrations of heavier hydrocarbons than are present in laboratory fermentation experiments. Their presence probably indicates a contribution of early thermogenic gas.

Analyses of gas samples from the DSDP indicate that gas of predominantly biogenic origin contains higher hydrocarbons in amounts which are directly proportional to: (1) temperature history, (2) age of the sediments, and (3) organic-matter content of the sediments from which the gas originates (Claypool, 1974; Doose et al, 1978; Whelan and Hunt, 1978). These relations suggest that the higher hydrocarbons are generated in situ by low-temperature degradation of the organic matter. In Figure 8, the ratio of ethane to methane is plotted as a function of depth of burial for a variety of depositional settings. Generally, there is an exponential increase in ethane content with increasing depth of burial. At any given locality, the amount of ethane is proportional to the temperature and age of the sediment. In the Cariaco basin (Fig. 8), the approximate 10-fold increase in the ethane concentration is due to a similar 10-fold enrichment in the organic-matter content as compared with typical sediments (Claypool, 1974). This exponential increase in ethane content with increasing depth of burial continues to depths where gas with composition typical of thermogenic gas associated with liquid petroleum should be generated.

Thus, although methane is the primary hydrocarbon product of anoxic microbial breakdown of organic matter, heavier hydrocarbons amounting to as much as 2% can be expected to be associated with the methane because of early low-temperature degradation. With the cessation of methanogenesis by microorganisms and increasing levels of maturation, the full range of hydrocarbons, typical of the mature stage, including liquid petroleum, are produced. With further increases in temperature, methane-rich gas again becomes the main product in the postmature stage resulting from thermal cracking of the carbon-carbon bonds. However, this gas can be distinguished from biogenic gas by heavier methane carbon isotope ratios.

Two main mechanisms are responsible for carbon isotope fractionation of methane in natural gas biogenic enrichment and thermal cracking. The isotope composition of biogenic methane is the result of the enrichment of the light isotope ^{12}C by microorganisms in the product relative to the substrate (Rosenfeld and Silverman, 1959). In the marine environment where CO_2 reduction is the primary mechanism of methane generation, the isotopic composition of the earliest methane formed is controlled by the $\delta^{13}C$ of the original CO_2 substrate. The isotopic composition of subsequent methane formed reflects the net effect of both addition and removal of CO_2. One of the major sources of CO_2 for reduction is anaerobic oxidation of organic matter during sulfate reduction. The $\delta^{13}C$ of the CO_2 is about -22 ppt (Presley and Kaplan, 1968). Another important source

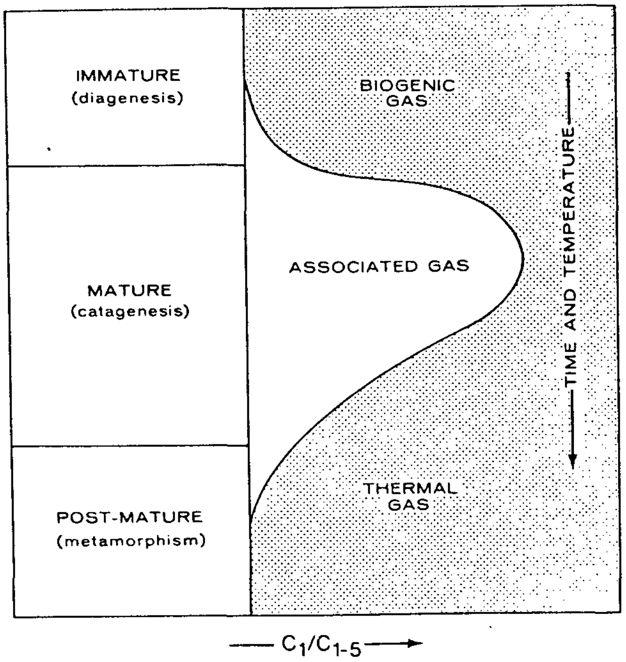

FIG. 7—Diagram showing characteristics of natural gas with increasing temperature and time.

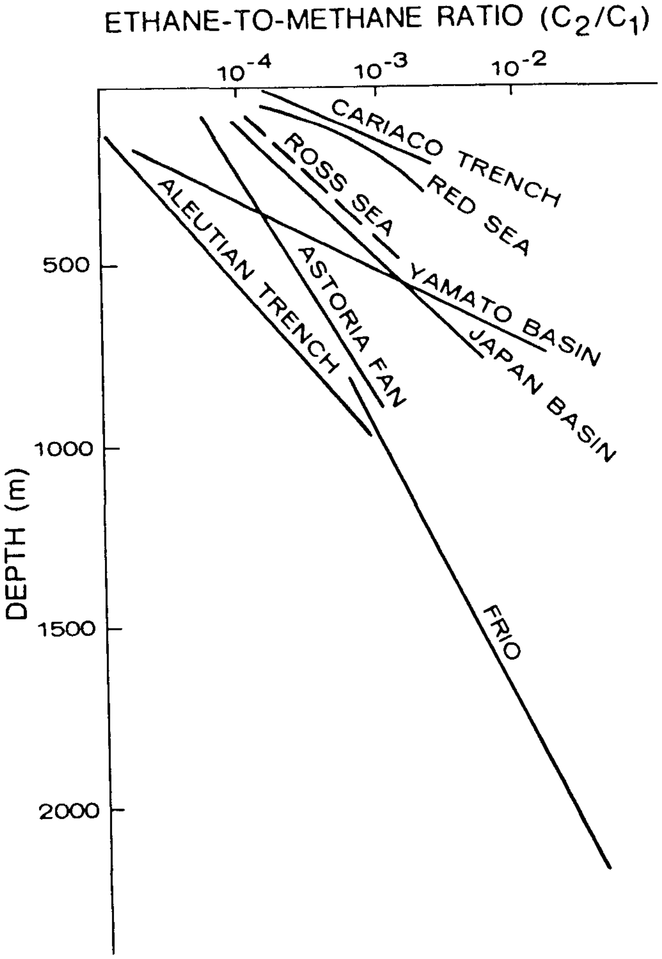

FIG. 8—Ethane-to-methane ratios of natural gas from selected DSDP sites.

of CO_2 at slightly higher temperatures results from decarboxylation which also provides isotopically light CO_2 ($\delta^{13}C$ = −20 to −25 ppt).

In general, the $\delta^{13}C$ of the residual dissolved CO_2 becomes isotopically heavier as isotopically light CO_2 is removed from the interstitial waters for methane formation. Consequently the methane produced from this remaining CO_2 also becomes isotopically heavier with depth. This general trend of isotopically heavier methane resulting from removal of isotopically light CO_2 is typical for DSDP sediments buried to depths of 1 km and is illustrated in Figure 5. The $\delta^{13}C$ values over this depth interval range from −90 to −65 ppt. However, if another source of CO_2 is added, such as from the thermogenic decarboxylation, an intermediate trend toward lighter $\delta^{13}C$ values of the methane may result.

An additional mechanism responsible for carbon isotope fractionation of methane is the kinetic isotope effect of thermal cracking. When methane is produced by nonbiologic decomposition or organic matter, ^{12}C-^{12}C bonds are broken at a faster rate than ^{13}C-^{12}C bonds (Stahl, 1974). As a result, gases generated by thermal processes become isotopically heavier with increasing levels of maturation. Gases associated with oil generation have $\delta^{13}C$ values in the range of −50 to −40 ppt; gases in the wet gas-condensate stage have $\delta^{13}C_1$ values of −40 to −35 ppt; and postmature gases are isotopically heaviest with $\delta^{13}C$ values heavier than −35 ppt.

The earliest formed thermogenic methane is isotopically light ($\delta^{13}C$ = −55 ppt) because of a kinetic isotope effect (Sackett, 1978; Stahl et al, 1979). However, significant quantities of thermogenic methane are not generated until temperatures of about 100°C are reached (Frank et al, 1974; Hunt, 1979). Minor amounts of thermogenic methane that are generated at low temperatures are mixed with and secondary to biogenic gas previously generated at shallow depths. The addition of minor amounts of thermogenic methane has the effect of gradually increasing the $\delta^{13}C$ of the methane at depths greater than about 1 km to depths of burial where thermogenic processes account for major quantities of gas. Sediments capable of supporting the production of biogenic methane generally contain sufficient quantities of organic matter so that they are also capable of generating thermogenic gas at elevated temperatures. As a result, early formed biogenic gas commonly contains a significant component of later formed thermogenic gas that cannot be distinguished because of compositional changes resulting from mixing.

Because of the effects of the isotopic composition of the initial or residual CO_2 and mixing with thermogenic methane, an absolute lower limit for the isotopic composition ($\delta^{13}C$) of predominantly biogenic methane cannot practically be assigned. However, for classifying ancient accumulations, in which many of these effects are impossible to determine, an arbitrary lower $\delta^{13}C_1$ value of −55 ppt is used, recognizing the fact that biogenic methane can be heavier, although thermogenic methane rarely is lighter.

Table 1 lists the isotopic composition of natural gases of biogenic origin. Although most of the gases are isotopically lighter than −55 ppt, some are as heavy as −45 ppt. Isotopically heavier methane can result from partial microbial oxidation in near-surface sediments. The residual methane after partial oxidation would be enriched in ^{13}C compared with the starting material because of preferential oxidation of $^{12}CH_4$ as discussed by Lebedev et al (1969).

Migration may be a mechanism of carbon isotope fractionation such that methane could either become enriched or depleted with ^{12}C (Galimov, 1967; Columbo et al, 1969; Lebedev and Syngayevski, 1971). Although these effects have been demonstrated in laboratory experiments and may be significant when migrating small quantities of gas, migration has not been shown to produce consistent or significant isotope effects under

Table 1. Isotopic Composition of Natural Gases of Biogenic Origin*

Source and Location	$^{13}C_1$(‰)	References
1. Marsh gas (Delaware, Louisiana, and Minnesota)	−70.2 to −52	Fuex, 1977
2. Lake sediments (Africa)	−45	Deuser et al (1973)
3. Lake sediments (Utah)	−45.8	This report
4. Lake sediments (Connecticut)	−80.2 to −57.2	Oana and Deevey (1960)
5. Marsh gas (USSR)	−69 to −52	Ovsyannikov and Lebedev (1967)
6. Sludge gas (California)	−47.1	Nissenbaum et al (1972)
7. Marsh gas (USSR)	−74 to −52	Lebedev et al (1969)
8. Marine sediments (DSDP, Leg 41)	−73.7 to −51.7	Doose et al (1978)
9. Marine sediments (DSDP, Leg 42B)	−72 to −63	Hunt and Whelan (1978)
10. Marine sediments (Alaska)	−80	Kvenvolden et al (1979)
11. Marine sediments (Gulf of Mexico)	−65.5 to −58	Bernard et al (1976)
12. Marine sediments (DSDP, Leg 15)	−76.3 to −59.6	Lyon (1973)
13. Marine sediments (DSDP, Legs 10, 11, 13, 14, 15, 18, 19)	−88.7 to −47.1	Claypool et al (1973)
14. Marine sediments (British Columbia)	−55.6	Nissenbaum et al (1972)
15. Solution gas (Montana)	−65.32 to −63.94	This report
16. Solution gas (North Dakota)	−71 to −69.2	This report

*Gases isotopically heavier than −50 ‰ may be due to microbial oxidation.

natural conditions (Bernard et al, 1977; Coleman et al, 1977; Stahl et al, 1977).

In addition to the chemical and isotopic characteristics of biogenic methane, the geologic setting must be considered in making the final interpretation of the gas origin. Gases of obvious biogenic origin occur at relatively shallow depths, at low temperatures, and in relatively young sediments and sedimentary rocks. Although most biogenic gases are generated at depths of less than 1 km, subsequently they can be buried as deep as gas of thermal origin. However, deeply buried gas of original biogenic origin invariably will be mixed with gas of later thermogenic origin so that recognition on the basis of chemical and isotopic composition will be difficult. In rare conditions, biogenic gas can be associated with oil if the oil was undersaturated in thermogenic gas and migrated into an immature sedimentary section.

ANCIENT ACCUMULATIONS OF BIOGENIC GAS

Although recent occurrences of biogenic gas are numerous, data that permit recognition of ancient accumulations are available only for those accumulations listed in Table 2. Because a combination of chemical and isotopic composition plus geologic setting has been used to make the interpretations, there are undoubtedly many accumulations that we have not identified.

In general, ancient accumulations of biogenic gas occur in relatively young rock sequences (Cretaceous and younger) that have had a low-temperature history. Although known accumulations occur as deep as 3,350 m, most are at depths of less than 1,800 m. These accumulations are present in both marine and nonmarine rocks. However, the newly documented accumulations occur strictly in marine sequences.

Several known areas containing biogenic gas accumulations listed in Table 2 are reviewed in the following. Detailed data for more than 30 fields are presented in Tables 3, 4, and 5. Locations of newly described fields in the United States and Canada, and fields in northwest Siberia, USSR, are shown in Figures 9 and 12.

Niobrara Formation, Colorado and Kansas

Natural gas was discovered more than 50 years ago in chalks of the Niobrara Formation of Late Cretaceous age in eastern Colorado, but commercial development did not begin until the early 1970s. There are now more than 30 such gas fields in eastern Colorado and northwestern Kansas. Natural gas, much of which is interpreted to be of biogenic origin, is produced from chalk beds that are characterized by high values of porosity, but low values of permeability at depths ranging between about 270 and 850 m. Lockridge and Scholle (1978) indicated that commercial production of hydrocarbons at depths greater than 1,200 m from Niobrara chalk reservoirs will require significant natural fracturing because of greatly reduced porosity and permeability. Thus, the interpreted occurrence of

Table 2. Worldwide Accumulations of Biogenic Gas

Location	Reservoir Age	Depth (m)	$^{13}C_1C^0/_{00})$	Reference
United States				
Cook Inlet, Alaska	Tertiary	910-1,650	−63 to −56	Claypool et al (1980)
Offshore Gulf of Mexico	Pleistocene	460-2,800	−69 to −55	This report
Rocky Mountains (Colorado, Kansas, Montana, Nebraska, New Mexico, South Dakota)	Cretaceous and Tertiary	120- 840	−72 to −55	This report
Illinois	Pleistocene	40	−84 to −72	Wasserberg et al (1963)
Japan	Tertiary	100-1,000	−75 to −65	Nakai (1960)
Italy	Tertiary	400-1,830	−71 to −55	Colombo et al (1966)
Germany	Tertiary	900-1,800	−72 to −64	Schoell (1977)
Canada	Cretaceous	300-1,000	−68 to −60	This report; Fuex (1977)
USSR				
North Aral	Tertiary	320- 350	−72 to −64	Avrov and Galimov (1968)
Siberia	Cretaceous	700-1,300	−68 to −58	Yermakov et al (1970)
Stravapol	Cretaceous and Tertiary	200-1,200	−75 to −57	Alekseyev et al (1972)
North Priaral	Tertiary	300- 500	−72 to −63	Galimov (1969)
Trinidad	Tertiary	980-3,350	−71 to −64	B. D. Carey (personal commun., (1980)

biogenic gas coincides with the development of reservoir properties suitable for development.

Gas samples were collected at seven wells along a southeast-northwest belt that trends as shown in Figure 9. Current depths of burial increase northwestward along this belt from 328 to 842 m. An isopach map of reconstructed thicknesses of the Pierre Shale, the youngest Cretaceous unit exposed at the beginning of the Tertiary, indicates a similar increase in burial depths in an east to west direction. Porosity versus depth plots of the Niobrara and other chalk reservoirs suggest that the Niobrara was probably subjected to greater burial than indicated by present-day burial or that can be accounted for by the thickness of Pierre Shale (Lockridge and Scholle, 1978).

Gases from wells along the trend reflect the increasing depth of burial by becoming isotopically heavier (Fig. 10). We interpret the gases to be of predominantly biogenic origin because of chemical and isotopic composition, reconstructed maximum depths of burial, and source rocks studies by Swetland and Clayton (1976) that indicate that older Cretaceous rocks in this region are immature.

The biogenic gas probably was generated in situ

Table 3. Biogenic Gas Fields in Rocky Mountains, United States

State	Field	Producing Unit[1]	Depth (m)	$^{13}C_1$(⁰/oo)	$C_1/C_{1\text{-}5}$
Colorado	Armel	Niobrara Fm.	482	−62.5	0.981
	Beecher Island	Niobrara Fm.	491-518	−60.8 to −60.1	0.982 to .981
	Republican	Niobrara Fm.	691	−59.7	0.981
	San Luis basin	Alamosa Fm.	300	−70.2 to −69.7	0.999 to .998
	Vernon	Niobrara Fm.	647	−58.8	0.98
	Whisper	Niobrara Fm.	842	−54.7	0.976
Kansas	Wildcat	Niobrara Fm.	328	−65.4	0.993
Montana	Bell Creek	Muddy Ss.	1,387	−65.1	0.98
	Black Coulee	Eagle Ss.	349	−66	0.996
	Bowdoin	Bowdoin and Phillips ss.[2]	224-445	−72.3 to −68.6	0.997 to .995
	Cassady	Eagle Ss.	385	−70	0.998
	Cedar Creek	Eagle Ss.	517	−69.7	0.996
	Guinn	Eagle Ss.	171	−65.2	0.987
	Hardin	Frontier Fm.	253	−65.9	0.989
	Leroy	Eagle Ss.	470	−68.7	0.996
	Liscom Creek	Shannon Ss. Mbr. of Gammon Shale	829	−64.8	0.992
	Lohman	Eagle Ss.	318	−68.1	0.997
	Tiger Ridge	Eagle Ss.	347-432	−65.5 to −63.5	0.997 to .991
Nebraska	Wildcats	Niobrara Fm. and Dakota Ss.	394-655	−66.5 to −62.8	0.956 to .998
New Mexico	Wagon Mound	Dakota Ss.	119-134	−59.8 to −55.3	0.999
South Dakota	West Short Pine Hills	Shannon Ss. Mbr. of Gammon Shale	417-605	−70.0 to −69.7	0.996 to .998

[1] Cretaceous age except Pliocene or Pleistocene Alamosa Fm.

[2] Subsurface usage.

Table 4. Biogenic Gas in Suffield Block, Southeastern Alberta, Canada

Depth (m)	Producing unit	$^{13}C_1$ (⁰/oo)	$C_1/C_{1\text{-}5}$
334	Milk River Fm. equivalent	−68	0.997
338	Milk River Fm. equivalent	−67.5	0.997
350	Milk River Fm. equivalent	−68.3	0.993
416	Medicine Hat Ss.	−67.8	0.997
433	Medicine Hat Ss.	−68	0.997
436	Medicine Hat Ss.	−68	0.997
471	Medicine Hat Ss.	−67.1	0.996
563	Second White Specks ss.	−65.7	0.995
564	Second White Specks ss.	−65.3	0.995
566	Second White Specks ss.	−65.4	0.9950
643	Second White Specks ss.	−65.4	0.996
758	Bow Island Formation	−66	0.994
783	Bow Island Formation	−66	0.995
831	Basal Colorado Ss.	−60.2	0.963

Table 5. Biogenic Gas Fields of Pleistocene Age in Offshore Gulf of Mexico

Field	Depth (m)	$\delta^{13}C_1$ (‰)	C_1/C_{1-5}
Ship Shoal 271	1,818 - 1,876	−59.9 to −56.9	0.989 to .987
East Cameron 245	458 - 983	−69.4 to −65.9	0.999
West Cameron 513	2,224 - 2,312	−57.2 to −56.9	0.997 to .972
West Cameron 533	917	−64.3	0.999
West Cameron 543	2,498 - 2,573	−58 to −56.7	0.98 to .978
West Cameron 587	1,355 - 1,562	−58.7 to −58.1	0.981
West Cameron 639	1,414 - 1,512	−63.2 to −57.9	0.996 to .985
West Cameron 643	1,391 - 1,399	−55.4 to −55.3	0.974
High Island A302	2,721 - 2,786	−65.1 to −61.7	0.999 to .997
High Island A309	1,390 - 2,208	−61.5 to −57.4	0.986 to .982
High Island A330	1,456 - 2,430	−66.5 to −64.5	0.997
High Island A343	1,829 - 1,916	−67 to −66.8	0.999 to .998
High Island A370	1,270 - 2,393	−65.3 to −60.6	0.998 to .96

because of low permeability of the chalks that inhibited migration and of the organic-rich laminae within the Niobrara that served as a source for the gas. Organic carbon values generally exceed 1% and some samples contain as much as 5.8%. Additionally, the Niobrara is overlain by a thick section of shale with many bentonite beds in the lower part that served as a seal preventing leakage of the gas from the Niobrara.

Northern Great Plains, Montana and South Dakota

Biogenic gas is being produced from widely spaced fields developed in Lower and Upper Cretaceous marine rocks at depths of less than 800 m (Table 3). However, maximum depths of burial were greater than present-day because most of the Tertiary and some of the Cretaceous section have been removed by erosion. All available evidence, including vitrinite reflectance, thermal alteration index (TAI), pyrolysis, clay mineralogy, and reconstructed depths of burial, suggests that temperatures necessary for thermal generation of significant amounts of hydrocarbons have not been achieved in the organic-rich shales that enclose the reservoirs.

In recent marine environments, biogenic gas is commonly found in sediments accumulating at rates greater than about 50 m/m.y. (Claypool and Kaplan, 1974). The average rate of sedimentation was more than 30 m/m.y. during Late Cretaceous time in the northern Great Plains (Gill and Cobban, 1973). However, the rate of sedimentation for Cretaceous rocks was probably greater than the rate for recent sediments after compensating for compaction, and undoubtedly was sufficiently rapid to insure the maintenance of anoxic conditions necessary for the generation of biogenic gas.

In modern sediments, organic carbon values generally exceed 0.5% where geochemical effects of methane-producing microorganisms are observed (Claypool and Kaplan, 1974; Rashid and Vilks, 1977). Many subsurface samples collected over a 100-m interval in the biogenic gas-productive Bowdoin Dome area and Cedar Creek anticline generally contain more than 0.5% and some samples contain as much as 8.7% organic carbon.

The biogenic gas is trapped in two distinct types of reservoirs and traps as exemplified by productive intervals in the Bearpaw Mountains and Bowdoin Dome. In the Bearpaw Mountains, the primary trapping mechanism is gravity-induced faulting and the reservoirs are porous and permeable marine sandstones enclosed by offshore marine shales (Rice, 1980). Petrographic studies indicate that extensive early mineral diagenesis in the reservoirs has taken place as a result of migrating waters (Gautier, in press). This interpretation suggests that the gas was held in solution in formation waters of the surrounding shales during diagenesis. Subsequent exsolution of the gas during uplift and erosion resulted in a free-gas phase that migrated to and accumulated in the sandstone because of capillary pressure differentials between the shale and sandstone beds.

In the Bowdoin Dome area, biogenic gas is stratigraphically entrapped over a large area (1,500 sq km) in thin (commonly less than 3 cm), discontinuous sandstone and siltstone laminae (Nydegger et al, 1979). Here, laminae are enclosed by organic-rich shales, containing numerous bentonite beds, that served as both a source and a seal for the gas. Because the reservoirs typically exhibit low permeability, stimulation is required to provide flow rates sufficient for economic development. However, this type of reservoir is developed over large areas of the northern Great Plains and structure is not required for trapping the gas.

Suffield Block, Southeastern Alberta

A widespread accumulation of gas covering more than 20,700 sq km was developed in the 1970s in southeastern Alberta. Most of the gas is entrapped in shallow, low-permeability marine reservoirs of Late Cretaceous age similar to those of the Bowdoin Dome area of north-central Montana.

The age occurs at depths of less than 600 m, although maximum depths of burial were greater. Uplift and erosion during the Tertiary probably resulted in the exsolution of the previously formed biogenic gas which was subsequently moved by capillary-pressure differentials from the immature, organic-rich shale to interlaminated

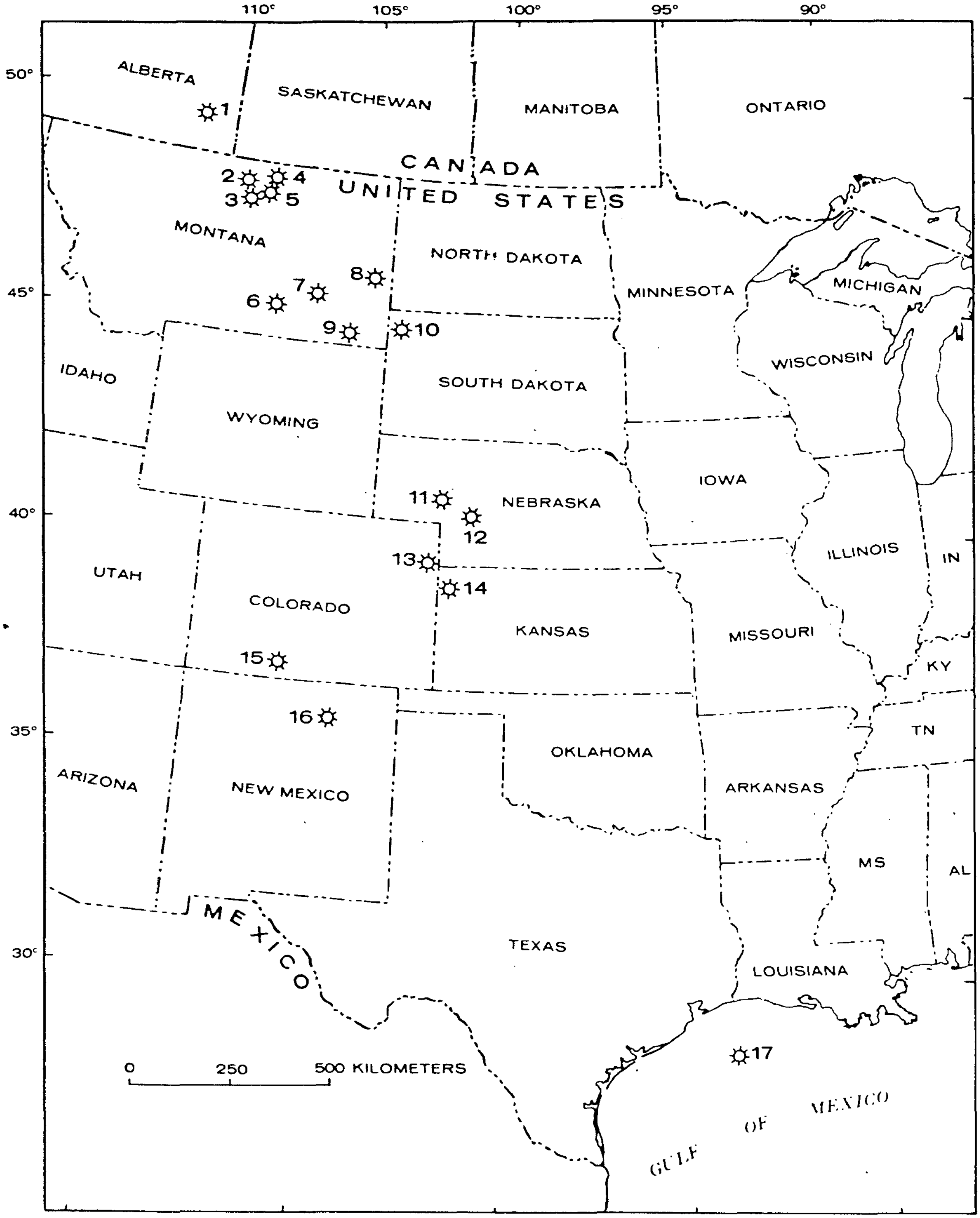

FIG. 9—Map showing location of biogenic gas fields in United States and Canada: (1) Suffield Block; (2) Tiger Ridge, Lohman, Black Coulee, and Cassady; (3) Leroy; (4) Bowdoin; (5) Guinn; (6) Hardin; (7) Liscom Creek; (8) Cedar Creek; (9) Bell Creek; (10) West Short Pine Hills; (11) Wildcat, Sec. 22, T19N, R39W; (12) Wildcat, Sec. 14, T16N, R33W; (13) Armel, Beecher Island, Republican, Vernon, and Whisper; (14) Wildcat, Sec. 10, T95N, R40W; (15) San Luis basin; (16) Wagon Mound; (17) Offshore Gulf of Mexico. Fields are listed in Table 5.

siltstone and sandstone reservoirs.

Gas samples were analyzed from the Suffield Block, a 2,600-sq km area within the large productive area. These gas samples are considered to be typical of the entire productive area. The samples were collected from five stratigraphic units and are arranged in Table 4 in order of descending age and increasing depth of burial. The deeper examples of a particular stratigraphic unit are in the northern part of the block.

The chemical and isotopic compositions, plus the immature stage of the enclosing sediments (Hacquebard, 1977), indicate that the gases of the Suffield Block are of predominantly biogenic origin. Gases in the Milk River Formation equivalent, Medicine Hat Sandstone, Second White Specks sandstone, and Bow Island Formation are distributed over about 400 m of stratigraphic section and have similar chemical and isotopic compositions (Table 4). A sample of gas from the basal Colorado Sandstone of the Colorado Group, which is approximately 120 m below the Bow Island, has a distinctly different chemical and isotopic composition, which may indicate a greater rate of mixing of thermogenic gas than can be explained by the increased depth of burial at the same geothermal gradient.

Offshore Gulf of Mexico

The Gulf of Mexico province lies offshore the states of Louisiana and Texas. It is one of the major hydrocarbon-producing regions of the United States. Many studies, including those of Dow (1978) and Lafayette and New Orleans Geological Societies (1968), have concluded that, because of the young age of the rocks, many of the hydrocarbon accumulations have resulted from extensive vertical migration from deeper, thermally mature source rocks.

Our studies indicate that the generation of biogenic gas at shallow depths in accumulating sediments has made a major contribution to many accumulations, particularly those of Pleistocene age. The gas fields of predominantly biogenic origin (Table 5) occur as deep as 2,800 m, which is much deeper than other documented accumulations (Table 2). In addition, the accumulations are overlain by as much as 200 m of water. However, in this region, temperatures in excess of about 160°C (equivalent to depths of burial of 5,600 m) must be reached before thermal generation of hydrocarbons becomes dominant in sediments of Pleistocene age (Dow, 1978).

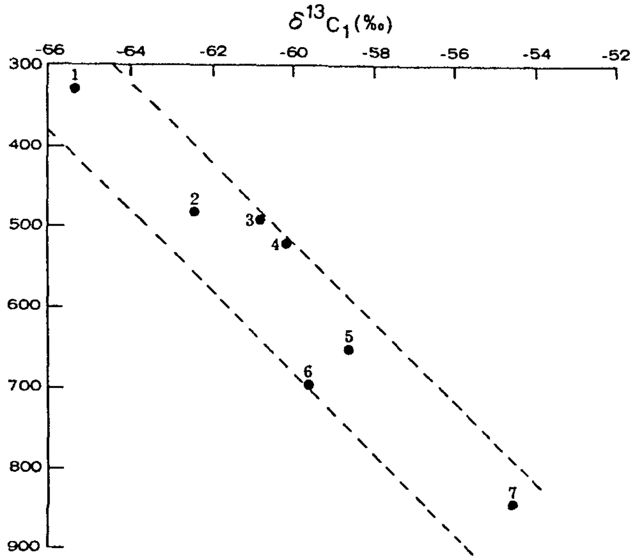

FIG. 10—Changes with depth in $\delta^{13}C_1$ of natural gases from Niobrara Formation in Colorado and Kansas. Numbers and dots correspond to wells located in Figure 11.

Although gases from the fields listed in Table 5 are predominantly of biogenic origin, many other accumulations, some with reservoirs older than Pleistocene, contain gas with biogenic methane as a major component. However, because of localized migration near growth faults and salt domes, these gases are isotopically heavier and (or) contain concentrations of heavier hydrocarbons greater than would be expected from systematic mixing of thermal gas with increasing time and temperature (Rice et al, 1979). Therefore, many accumulations with a significant biogenic gas component are not shown in Table 5.

Buckley et al (1958) conducted a study of water-bearing formations with dissolved hydrocarbon gases in the Gulf of Mexico. They determined that (1) dissolved gas is widespread, (2) the dissolved gas is chiefly methane with concentrations of CO_2 and heavier hydrocarbons ranging from traces to as much as 2% near oil accumulations, and (3) total quantity of dissolved gas probably exceeds known reserves in the area. Although some of the dissolved gas is of thermogenic origin, the dry gases associated with young reservoirs at shallow depths are undoubtedly of predominantly biogenic origin. The dissolved gas is present in quantities ranging from about 30 to 110 mmol/kg with higher concentrations occurring with increasing depth. These concentrations are generally greater than those reported for most deep-sea sediments and probably are analogous to the occurrence of accumulations of free biogenic gas in Gulf Coast Pleistocene reservoirs.

Cook Inlet, Alaska

Two types of natural gas occurrences have been documented in the Cook Inlet. The major reserves are in shallow (generally less than 1,600 m) nonassociated dry gas fields (C_1/C_{1-5} >0.99) that contain methane with $\delta^{13}C$ values in the range of −65 to −56 ppt (Claypool et al, 1980). The gas is trapped in nonmarine sandstones interbedded with coals of Miocene and Pliocene age and is considered to be of biogenic origin. The coals are bituminous or lower in rank (70 to 75% carbon, ash-free). Significant production of thermogenic gas from coal does not occur until higher ranks are attained and the coal-bed gas generated initially is generally wetter than the Cook Inlet nonassociated gas.

Lesser amounts of associated gas and oil are present in nonmarine Oligocene and Paleocene reservoirs. This gas is isotopically heavier ($\delta^{13}C_1$ values in the range of

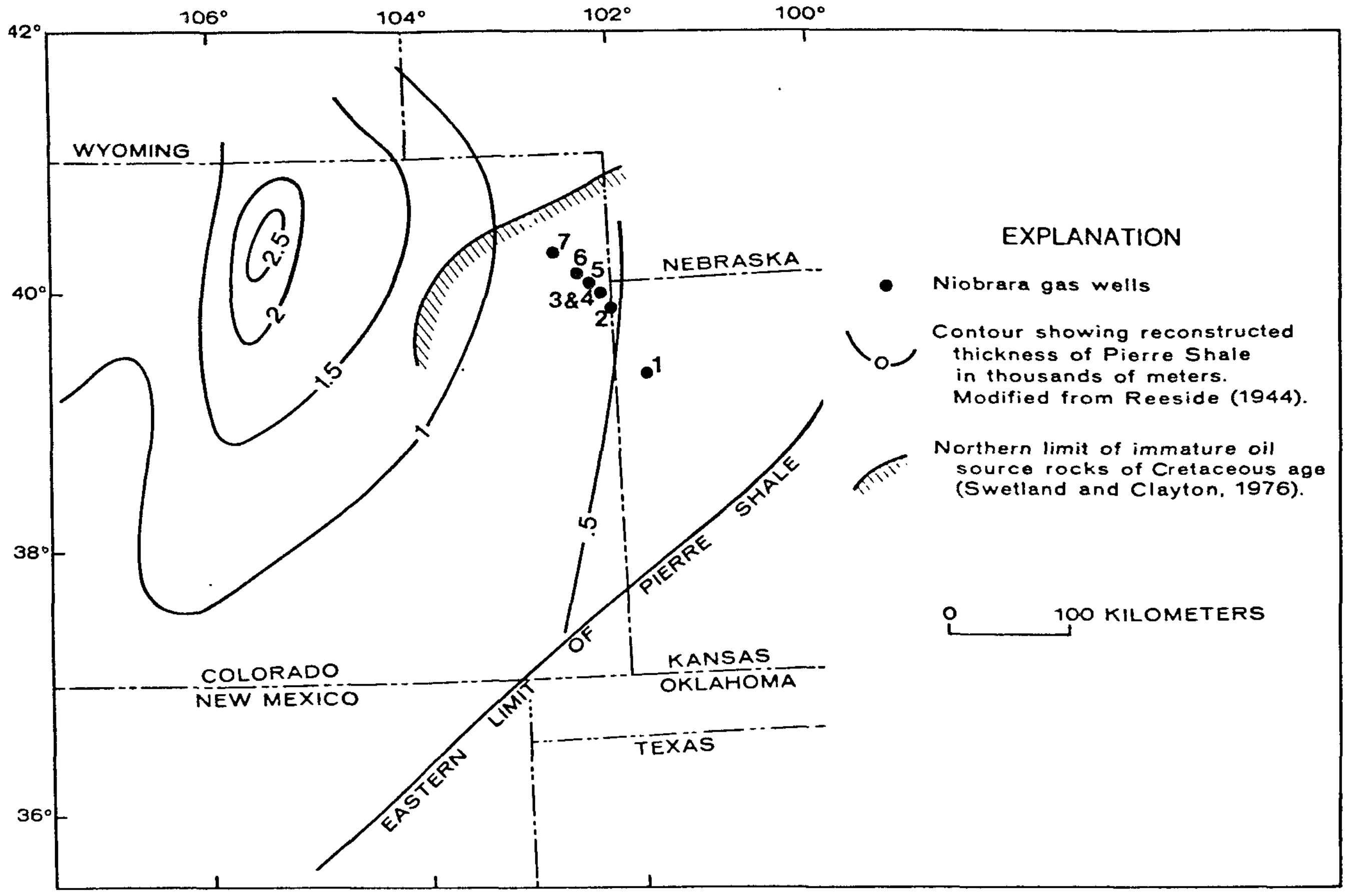

FIG. 11—Map showing location of Niobrara gas wells (Fig. 10), reconstructed thickness of Pierre Shale, and limit of immature oil source rocks.

−49 to −44 ppt) and contains appreciable amounts of heavier hydrocarbons (C_1/C_{1-5} >0.69 to 0.90; Claypool et al, 1980). This gas is interpreted to be of thermogenic origin and to have migrated with the oil from underlying, thermally mature, marine shale source rocks of Jurassic age (Magoon and Claypool, 1979).

Northwest Siberia, USSR

Yermakov et al (1970) studied gases from Jurassic and Cretaceous reservoirs from several giant fields in northwest Siberia. Location and data on these fields are presented in Figure 12 and Table 6. Gases from reservoirs that range in age from Aptian through Cenomanian are extremely dry (C_1/C_{1-5} >0.99). They have carbon isotope values in the range of other ancient biogenic accumulations ($\delta^{13}C$ = −68 to −58 ppt). Nesterov et al (1978) concluded in a study using argon isotopes that these gases were generated in situ.

These Cretaceous gases are interpreted to be dominantly of a biogenic origin. They occur at depths of less than 1,300 m, and are associated with organic-

Table 6. Biogenic Gas Fields in USSR*

Field	Estimated Reserves $10^{12}m^3$ (Tcf)	Depth of Production (m)	$\delta^{13}C_1$ C°/oo)	C_1/C_{1-5}
Arkticheskoye	0.18 (6.4)	683 - 2,500	−61.7	0.999
Gubkinskoye	0.35 (12.5)	745 - 780	−61.1	0.999
Komsomolskoye	0.46 (16.2)	929 - 985	−64.7	0.998
Medvezhye	1.55 (54.7)	1,057 - 1,207	−58.3	0.999
Severo-Stavropolskoye	0.23 (8.1)	180 - 1,050	−68.7 to −66.5	0.999
Urengoiskoye	5.04 (177.8)	1,043 - 3,160	−59.2 to −59	0.998
Vyngapurskoye	0.29 (10.3)	987 - 1,091	−60	0.998
Zapolyarnoye	2.66 (94.1)	1,120 - 1,300	−60.3	0.999
Total	10.8 (380.1)			

*Data from Alekseyev et al (1972); McCaslin (1977); Yermakov et al (1970). All fields except Severo-Stavropolskoye are in northwest Siberia.

rich rocks at a low level of maturation (lignite to initial cannel coal; Yermakov et al, 1970). During deposition, the area was a swampy lowland which favored the accumulation of organic matter; organic carbon values range between 3 and 6%. This area was along the southern edge of extensive permafrost cover during the Pleistocene. Larger quantities of biogenic gas were initially trapped as hydrates. The permafrost front has since retreated and associated hydrates have decomposed to form free gas (Makogon et al, 1972). Free gas has subsequently accumulated in large structural traps.

In comparison, the gases associated with deeper and older Jurassic reservoirs are different, both chemically and isotopically. The contrasting gases contain more than 6% heavier hydrocarbons and are enriched in ^{13}C ($\delta^{13}C$ values range from −46 to −38‰). The stratigraphic and compositional separation of these two groups of gases, together with the presence of oil in the Jurassic rocks, suggests a thermal origin for the Jurassic gases.

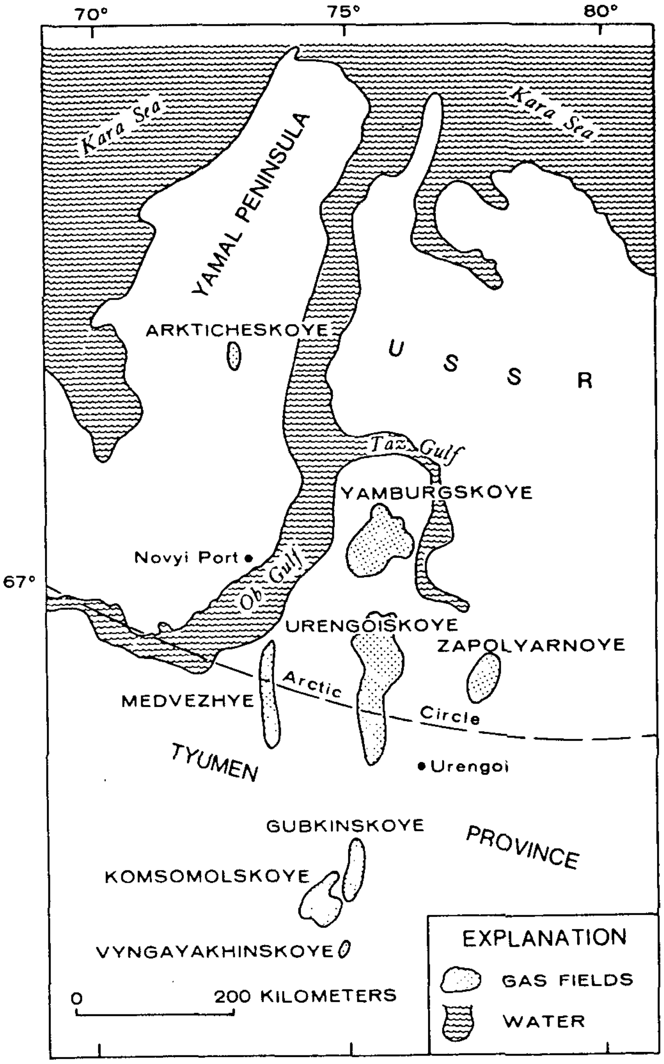

FIG. 12—Map showing location of biogenic gas fields in northwest Siberia. Although chemical and isotopic data are not available for Yamburgskoye and Vyngayakhinskoye fields, their geologic setting suggests that produced gases are of biogenic origin.

Illinois

Biogenic gas is present both in a free state and in solution in Pleistocene glacial drift of Illinois. Although free gas accumulations are not of commercial significance, many produce sufficient gas for domestic use (Meents, 1960, 1968). Local accumulations are composed primarily of methane, are at an average depth of 40 m, and have $\delta^{13}C_1$ values in the range of −84 to −72 ppt (Wasserburg et al, 1963). Radiocarbon dating of several gas samples indicates that the gas resulted from the microbial degradation of organic matter in the Robein Silt, which dates from 22,000 to 28,000 radiocarbon years B.P. (Coleman, 1976). The sands and gravels just above and below provide the reservoir, and the overlying till serves as the seal.

Coleman et al (1977) analyzed many gas samples in an effort to distinguish gas leaking from underground storage reservoirs from indigenous shallow biogenic gas in solution. They found that migration of gas resulted in chemical fractionation by removal of the heavier hydrocarbons from the gas that leaked out of the injected storage reservoir so that it became methane enriched in a manner similar to biogenic gas. This migration did not significantly affect the isotopic composition. They concluded that the two types of gases can be distinguished by isotopic composition: storage reservoir gas has $\delta^{13}C_1$ values in the range of −46 to −40 ppt whereas biogenic gas in solution is isotopically lighter ($\delta^{13}C_1$ = −90 to −64 ppt).

Japan

Biogenic gas dissolved in formation waters was the main source of natural gas production in Japan from the 1920s to 1960s. The gas is produced from brines confined to the lower part of marine or lagoonal basins by updip meteoric waters. The reservoirs are highly permeable sands and gravels of mostly Pliocene to Pleistocene age. Although the maximum depth of production is 2,000 m, most gas comes from depths of less than 1,000 m.

The initial gas-to-water ratio is close to the maximum solubility of methane in water at reservoir temperatures and pressures (Marsden and Kawaii, 1965). Because the depth of burial controls the pressure, the gas-water ratio is a function of depth. The ratio is about 1.2 m^3/m^3 at 500 m and 2 m^3/m^3 at 1,000 m. Most wells flow water naturally with the dissolved gas initially, but need artificial lift before long. The gas generally is released from the water as it flows to the surface and hydrostatic pressure is reduced. However, there are large quantities of water for disposal.

Biogenic origin of the dissolved gas was interpreted by Nakai (1960, 1962) and Sugisaki (1964). Carbon isotope values of gases from several fields range from −75 to −65 ppt (Nakai, 1960). The gas is predominantly methane, although as much as 0.08% ethane has been

Table 7. Estimated Volumes of Biogenic Gas, $10^{12}m^3$ (Tcf)*

	Discovered Volumes		Undiscovered Volumes	
Area	Reserves	Initial In-Place		Reference
Cook Inlet, Alaska	0.21 (7.5)[1]			Blasko (1974); Alaska Div. Oil and Gas (1976)
Gulf of Mexico		0.34 (12)[2]		U.S. Geol. Survey Resource Appraisal Group (unpub. data)
Japan	0.13 (4.7)			Marsden and Kawaii (1965)
Northern Great Plains, United States			2.83 (100)	Rice and Shurr (1980)
Southeast Alberta, Canada		0.42 (15)		Energy Resources Conservation Board (1977)
USSR	13.0 (460)[3]			Alekseyev (1975); McCaslin (1977)

*Total discovered estimate 21.3%; total discovered plus undiscovered estimate 25.5%.

[1] Includes cumulative production of 0.28 × $10^{12}m^3$ (1 Tcf).

[2] 75% of total estimated volumes because approximately 25% of gas is of thermal origin and has migrated from deeper, mature source rocks.

analyzed in a few rare examples (Marsden and Kawaii, 1965). The isotopic and chemical compositions are typical of biogenic gases. Sugisaki (1964) was able to make a distinction between dissolved biogenic gas and associated gas using nitrogen-argon ratios. Nakai (1962) noted that methane production was preceded by an increase in total CO_2 and concluded that the gas was produced in situ by fermentation in the formation waters.

Italy

Detailed studies on the chemical and isotopic compositions of Italian natural gases, interpreted by us to be of possible biogenic origin, were conducted by Colombo et al (1966, 1969; Table 2). Gases were collected from a thick turbidite sequence of Pliocene age in southern Italy at depths less than 1,600 m below sea level. They found that the $\delta^{13}C$ of the methane fraction became heavier as the C_2/C_1 ratio increased and proposed that this relation could be explained by two mechanisms: (1) mixing of biogenic and thermal gas or (2) migration fractionation of thermal gas from greater depths. They discounted the mixing mechanism because they believed that most biogenic gas is lost to the atmosphere and concluded that the distribution of gases was the result of migration fractionation. However, we believe that the *distribution and composition of gases can best be explained* by the mixing of predominantly biogenic gas with thermal gas. Early formed biogenic gas was gradually mixed with minor amounts of thermal gas which is generated in amounts proportional to temperature and age of the sediments.

ESTIMATED VOLUMES OF BIOGENIC GAS

Undoubtedly, there are many large areas, both discovered and undiscovered, where conditions were favorable for both the generation and accumulation of biogenic gas. However, in only a few areas are data available for identifying biogenic gas and for estimating volumes, as shown in Table 7. These estimated volumes probably represent only a part of the total resources of biogenic gas. A brief discussion follows on the areas where data are available.

Cook Inlet

Reserves of 0.21 × 10^{12} (7.5 Tcf) of biogenic gas, which include cumulative production of 0.028 × 10^{12} m^3 (1 Tcf) have been estimated for the Cook Inlet basin of Alaska (Blasko, 1974; Alaska Div. Oil and Gas, 1976). These reserves are significant because biogenic gas was generated in sediments containing low-rank coal beds of Tertiary age. Minor amounts of associated gas (0.011 × 10^{12} m^3 or 0.4 Tcf) are entrapped in older deeper Tertiary rocks, but this gas and accompanying oil are interpreted to have migrated from thermally mature Jurassic marine shales (Magoon and Claypool, 1979).

Gulf of Mexico

More than 0.8 × 10^9 m^3 (5 billion bbl) of oil and condensate, and 1.1 × 10^{12} m^3 (40 Tcf) of gas have been produced to date from the offshore Gulf of Mexico. Reservoirs of Pleistocene age contain major volumes of predominantly gas. The U. S. Geological Survey Resource Appraisal Group (unpub. data) estimated that rocks of Pleistocene age contain discovered in-place volumes of about 0.45 × 10^{12} m^3 (16 Tcf). Although some oil and thermal gas have migrated from deeper, mature source rocks, we estimate that about 75% of the gas in Pleistocene reservoirs is of predominantly biogenic origin. Therefore, the Pleistocene rocks may contain about 0.34 × 10^{12} m^3 (12 Tcf) of discovered biogenic gas. In addition, accumulations of both associated and nonassociated gas in older Tertiary reservoirs are interpreted to have had a predominantly biogenic origin locally.

Japan

Major quantities of dissolved gas of biogenic origin have been produced in Japan. The gas was adequate for local domestic use and in chemical manufacturing from the 1920s through the 1960s. However, because of production costs, the dissolved gas could not compete with residual oil as a fuel. Marsden and Kawaii (1965) described the three main fields from which biogenic gas is produced (Niigata, Southern Kanto, and Mobara) and estimated the reserves to be about 0.13 × 10^{12} m^3 (4.7 Tcf).

Northern Great Plains (Canada and United States)

The government of Alberta made a detailed evaluation in the early 1970s of the gas reserves of the Suffield Block located in the southeastern part of the province. The block covers an area of approximately 2,600 sq km and is part of a larger productive area of shallow biogenic gas that covers more than 20,700 sq km. The Suffield Block was assigned an in-place gas reserve figure of 0.10 × 10^{12} m^3 (3.7 Tcf) and a recoverable reserve figure of 0.076 × 10^{12} m^3 (2.7 Tcf; Suffield Evaluation Comm., 1974). Most of the gas (94%) is trapped in low-permeability reservoirs of Late Cretaceous age. For the entire productive area of southeastern Alberta, the initial in-place reserves of gas from low-permeability reservoirs of Late Cretaceous age are estimated to be 0.42 × 10^{12} m^3 (15 Tcf; Energy Resources Conservation Board, 1977). This per-section figure is lower than that assessed for the Suffield Block because of the various stages of technology and of different gas prices when the gas was developed. The ultimate size and recoverable reserves for this area in Canada will be controlled by economics and technology.

Similar thin, discontinuous, low-permeability reservoirs are developed over a large part of the northern Great Plains in both Canada and the United States. Rice and Shurr (1980) concluded that their study area of about 300,000 sq km in eastern Montana, western North and South Dakota, and northeastern Wyoming probably contained resources of biogenic gas in excess of 2.8 × 10^{12} m^3 (100 Tcf). They stated that the development of the shallow biogenic gas would depend on gas prices and recovery technology.

USSR

About 40% (26.0 × 10^{12} m^3 or 928 Tcf) of the world's reserves are present in the USSR (McCaslin, 1977). A large part of these gas reserves (10.8 × 10^{12} m^3 or 380 Tcf) has been identified as being of biogenic origin (Table 6). Alekseyev (1975) estimated that about 50% of the total Russian reserves is of biogenic origin; this amounts to 13.0 × 10^{12} m^3 (460 Tcf) on the basis of the figure given by McCaslin (1977). This figure appears accurate because there are several other fields with large reserves which are in the same geologic setting as those identified as being of biogenic origin.

Biogenic gas accounts for more than 20% of the world's gas reserves of 66.4 × 10^{12} m^3 (2,343 Tcf; Table 7). We believe that gas of biogenic origin will make an even greater contribution to future reserves for several reasons. First, natural gas has generally been underpriced as compared with other energy sources. This means that gas, until recently, has not been a major target of hydrocarbon exploration. Next, biogenic gas occurs in shallow reservoirs which are commonly underpressured. Also, much undiscovered biogenic gas is probably trapped in low-permeability marine reservoirs similar to those of the northern Great Plains. Sophisticated evaluation methods and advanced recovery technology are required to detect these accumulations and to provide commercial flow rates. A combination of low pressures and low permeability has resulted in many of these accumulations being uneconomic and unrecoverable in the past. Additionally, large volumes of biogenic gas are either dissolved or in hydrate structures (see Buckley et al, 1958; Claypool and Kaplan, 1974; Trofimuk et al, 1975; Cherskii and Tsarev, 1977; Tucholke et al, 1977; Shipley et al, 1979). Biogenic gas occurring in these phases is a large part of our undeveloped gas resource base. Major technologic advances and increases in gas prices will be required if these potential resources of dissolved and hydrated biogenic gas are to contribute to our energy needs in the future. However, a significant quantity of conventional gas of biologic origin probably has been underestimated and overlooked in past exploration.

SUMMARY AND CONCLUSIONS

Methane-rich gas is a product of low-temperature diagenesis of organic matter in sedimentary rocks. The gas is generated by the degradation of organic matter in rapidly accumulating sediments by anaerobic microorganisms. The gas is referred to as biogenic gas to emphasize that biologic processes are directly responsible for its formation. Biogenic gas is generated in immature sediments and can accumulate in large quantities. Thus it should be considered in future exploration efforts for hydrocarbons. The following conclusions are made about biogenic gas:

1. A succession of sedimentary ecosystems is established in the sediment column with lower energy-yielding metabolic process. In marine sediments, subsequent to oxygen depletion, sulfate reduction becomes the dominant form of respiration. Methane production replaces sulfate reduction only after the high concentrations of sulfate in sea water are reduced. The most important mechanism of methane generation is CO_2 reduction. The CO_2 can be a product of metabolic activity or

later thermal decarboxylation of the organic matter.

2. The succession of metabolic processes that result in methane production can be followed in modern sediments by monitoring the changes in concentration and stable carbon isotope ratios of the residual reactants or accumulating products with depth.

3. Major factors that control methane production after sediment burial are: anoxic environment, sulfate-deficient environment, low temperatures, organic matter, and sufficient space.

4. In marine sediments, most of the biogenic gas is formed in solution in the interstitial (pore) waters because of the limited amount of methane that is generated and the high solubility resulting from hydrostatic pressure due to the weight of the overlying water column. Under conditions of high pressure and (or) low temperature, the methane can combine with water to form gas hydrate compounds.

5. The dissolution of gas in interstitial waters can serve as a holding mechanism until the sediments are compacted, and traps and seals are available. Free gas is formed either when the solubility minimum is exceeded or by exsolution brought about by a reduction in hydrostatic pressure. Possible trapping mechanisms are: structure when the reservoirs are porous and permeable; low-permeability reservoirs; bentonites; early diagenetic carbonate cements, hydrates, and subnormal pressures.

6. The most useful characteristics in distinguishing biogenic gas are the chemical and isotopic compositions. Biogenic gases characteristically are composed almost entirely of methane ($C_1/C_{1-5}>0.98$). Minor amounts of heavier hydrocarbons can be attributed to low-temperature thermal generation. The most useful criteria for distinguishing biogenic gas are carbon isotope ratios. Biogenic gas is enriched in the light isotope ^{12}C resulting from fractionation during methane generation by anaerobic microorganisms. The $\delta^{13}C_1$ values of biogenic gas are generally lighter than -55 ppt. In making interpretations of gas origin, possible ambiguities in chemical and isotopic evidence are usually resolved by consideration of the geologic setting.

7. Accumulations of biogenic gas are documented from Cretaceous and younger rocks, at depths less than 3,350 m and in both marine and nonmarine rocks. Commercial accumulations are demonstrated from Canada, Germany, Italy, Japan, Trinidad, USSR, and the United States. Other accumulations of biogenic origin are undoubtedly present, but data that permit their recognition are not available.

8. Gas of predominantly biogenic origin has made major contributions to the world's reserves (more than 20%). We predict that biogenic gas will make an even greater contribution to world energy needs in the future.

9. Finally, biogenic gas is an important target for future exploration because it is widespread, shallow, and has been shown to accumulate in commercial quantities.

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