

**GEOCHEMICAL ASSESSMENT OF GASEOUS HYDROCARBONS:
MIXING OF BACTERIAL AND THERMOGENIC METHANE
IN THE DEEP SUBSURFACE PETROLEUM SYSTEM,
GULF OF MEXICO CONTINENTAL SLOPE**

A Thesis

by

ERCIN OZGUL

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

August 2002

Major Subject: Geology

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ABSTRACT

Geochemical Assessment of Gaseous Hydrocarbons: Mixing of Bacterial and
Thermogenic Methane in the Deep Subsurface Petroleum System,

Gulf of Mexico Continental Slope. (August 2002)

Ercin Ozgul, B.S., Middle East Technical University

Chair of Advisory Committee: Dr. Roger Sassen

Mixtures of bacterial and thermogenic methane are found both at vents at the seafloor and in reservoirs in the deep subsurface of the Gulf of Mexico continental slope. The C₁-C₅ gas that most recently charged reservoirs of Joliet (GC 184), Genesis (GC 160/161) and Petronius (VK 786) fields is estimated to include 17%-28%, 31%-51%, 31%-49% bacterial methane, respectively.

Geochemical assessment of the reservoir gas in the fields show that the gas may be the product of thermal cracking of Upper Jurassic crude oil before final migration to the reservoirs. The gas from three different fields is of similar thermal maturity levels. In contrast to oil in reservoirs in the fields, which shows biodegradation effects, the C₁-C₅ reservoir gas is unaltered by biodegradation. Late gas migration may have occurred at or near present burial depth and flushed the reservoir system of previously biodegraded hydrocarbon gas to include any previous bacterial methane.

Molecular and isotopic properties of reservoir gas and oil suggest that bacterial methane mixed with thermogenic hydrocarbon gas before entering the reservoirs. Thus the source of the bacterial methane is logically deeper than the present depth (>~4 km)

and temperatures of the reservoirs. High sedimentation rate and low geothermal gradient may offer conditions favorable for generation and preservation of bacterial methane in deep subsurface petroleum system of the Gulf slope. Bacterial methane dispersed across the large drainage areas of the deep subsurface petroleum system may have been swept by migrating fluids at >4 km, and then charged both vents (GC 185, GC 233 and GC 286) at the seafloor and reservoirs in the deep subsurface. The volume of bacterial methane from geologically significant depth in rapidly subsiding basins may be underestimated.

To my mother, Ruhiye Turhan, and my father, Mustafa Turhan

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CHAPTER I

INTRODUCTION

Natural gas may be detected in the subsurface either as traces in sediment or as accumulations in oil and gas reservoirs worldwide. Natural gas systems are becoming increasingly important as conventional liquid hydrocarbon energy sources are depleted. In this context, gas geochemistry has become an increasingly sophisticated tool for understanding the geologic history of hydrocarbons from their generation in source rocks to their accumulations in reservoirs, and their behavior in sedimentary basins.

The Gulf of Mexico Salt Basin that formed during Late Triassic rifting is one of the more important hydrocarbon producing areas in the world. The oil and gas in reservoirs beneath the Gulf of Mexico continental slope originated from prolific Mesozoic source rocks (e.g. Sassen et al., 2001a, b, c). The structural style of the Gulf slope was strongly influenced by active salt movement and faulting driven by rapid loading by siliciclastic sediment (e.g. Cook and D'Onfro, 1991; Wenger et al., 1994; Rowan, 1995; Schuster, 1995; Diegel et al., 1995, Sassen et al., 2001c).

The actively moving salt bodies and active faults provide efficient conduits of vertical migration of hydrocarbons along the rims of the salt withdrawal basins (e.g. Sassen et al., 2001a, b, c). There are many sites of active gas and oil seepage, authigenic

This thesis follows the style and format of the Bulletin of the American Association of Petroleum Geologists.

carbonate precipitation (mediated by microbial activity), gas hydrate crystallization and chemosynthetic communities in the Gulf slope (e.g. Anderson et al., 1983; Kennicutt et al., 1985; Brooks et al., 1987; Sassen et al., 1993a, 2001b, c).

Bacterial and thermogenic gas accumulations have been noted in the vent sites and shallow reservoirs of the Gulf slope (e.g. Kennicutt et al., 1992; Sassen et al., 1993a, 1999a, b, 2001a, c). Recent studies in applied geochemistry help to supply a considerable amount of crucial geochemical data that bear on bacterial and thermogenic gas generation, migration, accumulation, and alteration in such a dynamically active, and geochemically complex system (e.g. Kennicutt et al., 1992, 1993; Thompson, 1996; Sassen et al., 2001c).

Mixing of bacterial and thermogenic methane is common in shallow reservoirs and natural seeps in the Gulf of Mexico shelf (e.g. Rice, 1980; James, 1990; Rice and Threlkeld, 1990; Walters, 1990; Sassen et al., 2001c). However, in deep subsurface petroleum system of the Gulf slope, mixing of bacterial and thermogenic methane, and their relative abundances have not been studied.

Bacterial methane depleted in ^{13}C is microbially generated either by reduction of CO_2 or by acetate fermentation in shallow, low temperature sediment, and may be characterized by low concentrations of C_{2+} hydrocarbons. (e.g. Rice and Claypool, 1981; Schoell, 1983; Whiticar et al., 1986; Clayton, 1991; Coleman et al., 1996). Thermogenic gas is generated at greater depths and temperatures by thermal degradation of organic matter and of hydrocarbon liquids. The geochemistry of thermogenic gas is strongly dependent on source character and maturity, but it is generally characterized by high

concentrations of C₂₊ hydrocarbons and methane enriched in ¹³C (e.g. Schoell, 1983; Clayton, 1991; Whiticar, 1994)

In this study, the database on distribution and geochemistry (molecular and isotopic properties) of natural gas from representative hydrocarbon fields and associated vent sites across the Gulf slope compiled at the Geological Environmental Research Group of Texas A&M University has been used to understand the behavior of natural gas on the basin scale. The primary objectives of this study are to understand the mixing of bacterial and thermogenic methane and to constrain probable source of bacterial methane in deep subsurface petroleum system of the Gulf slope. Within this scope, specific objectives of this study are the following:

1. To document the molecular and isotopic properties of the gas, interpret its origin, and document the occurrence of mixed-source gas in the Gulf basin.
2. To understand the origin of gas and associated crude oil including source, thermal maturity, non-thermal alteration, migration pathways, and mixing.
3. To determine the mixing ratio of two end members thermogenic and bacterial methane, and calculate the relative contribution of bacterial methane versus thermogenic methane in the gas mixtures.
4. To integrate the information from geochemical interpretations with geologic insight of the basin and to reconstruct the filling histories of oil and gas fields.

Because this study is in an unknown territory of the Gulf basin the results will be in the hypothetical level and should not be generalized to other areas of the Gulf basin.

CHAPTER II

NATURAL GAS

This chapter briefly describes reviews on geochemistry of natural gas. The chapter defines natural gas types encountered, explains their mechanisms of generation, and documents their geochemical characteristics.

Natural gas, the gaseous phase of petroleum, is a naturally occurring mixture of hydrocarbon gases that is highly compressible and expansible. Typically, a reservoir gas contains methane (CH_4) as a major constituent (70-100%), ethane (C_2H_6) (1-10%), lower percentages of higher hydrocarbons “propane (C_3H_8), butane (C_4H_{10}), pentane (C_5H_{12})” through hexanes (C_6H_{14}), and traces up through nonanes (C_9H_{20}) (Tissot and Welte, 1978). Natural gas may also contain varying amounts of nonhydrocarbon gases such as carbon dioxide (CO_2), hydrogen sulfide (H_2S), nitrogen (N_2) and helium (He).

Origin, Generation and Types of Natural Gas

Geological and geochemical evidence indicates that hydrocarbons are generated from organic matter preserved in sedimentary rocks by a series of complex reactions. Quantity of organic matter is expressed as total organic carbon (TOC). TOC content may vary in different lithologies of source rock. Sandstones and red shales have very low TOC values (e.g. 0.04 in Chugwater, Colorado; Huc, 1988). Many limestones have low

TOC content (e.g. 2.1 in Austin Chalk, Texas; Huc, 1988). However, black and calcareous shales, and argillaceous limestones include very high amount of TOC values (18 in Green River, Wyoming; Huc, 1988).

Organic matter in the source rock is converted to liquid and gaseous hydrocarbons by partial conversion of the kerogen into bitumen (Barker, 1979). Insoluble, high molecular weight part of organic matter is called kerogen. The solvent soluble part of organic matter is called bitumen. The conversion reactions are controlled by temperature and time during burial of source rocks (e.g. Tissot and Welte, 1978; Hunt, 1996). Upon increasing temperature and depth of burial, increasing quantities of bitumen are formed and the residual kerogen becomes more mature.

Sedimentary organic matter represents the carbon-rich remains of terrestrial and marine organisms. Various types of organic matter are defined according to their chemical structure (e.g. carbohydrates, lipids, proteins, etc.) but an alternate classification scheme that is based on the chemical composition and structure of kerogen is widely used by petroleum geoscientists. Van Krevelen (1950) identified three main types of kerogen (called Types I, II, and III) based on H/C and O/C atomic ratios (Fig. 1). Subsequent investigations have added Type IV kerogen, and identified the type organisms from which kerogens are derived (e.g. French Petroleum Institute; Durand, 1980). Type I, II and III kerogen represent organic matter produced by algal, planktonic, and terrestrial plant sources, respectively (Tissot and Welte, 1978).

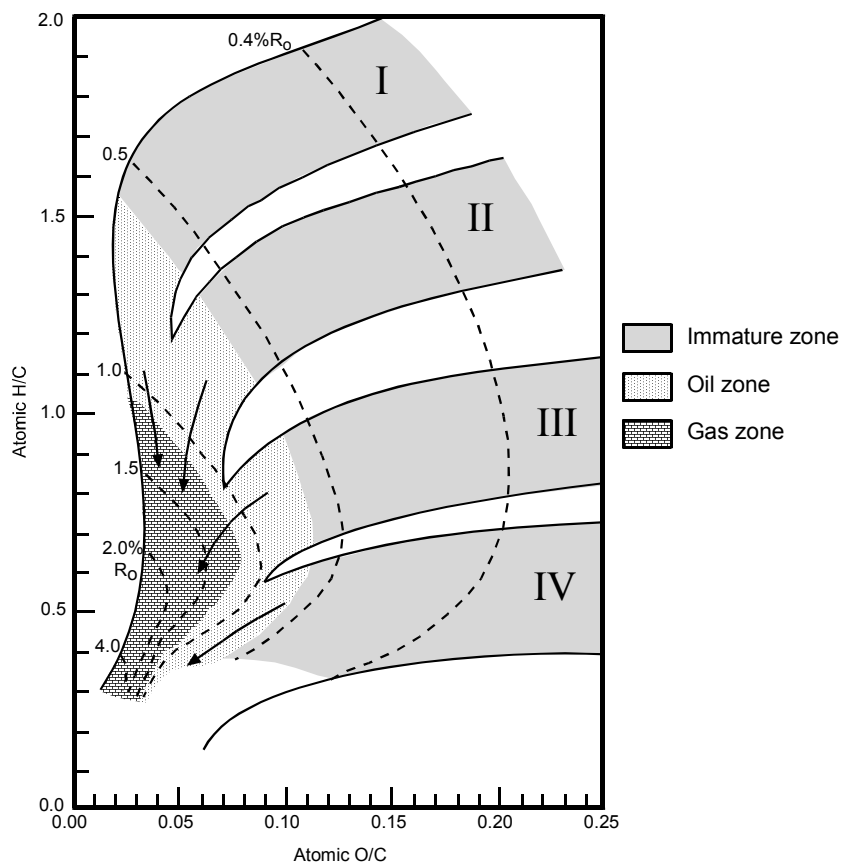


Figure 1. Types and chemical evolution of kerogen in response to increased levels of burial and thermal maturity presented on Van Krevelen's diagrams (arrows indicate increasing maturity) (after Tissot et al., 1974).

The generation and occurrence of primary type hydrocarbon gases (Table 1), which are generated directly by a simple source rock (Whiticar, 1994), are mainly dependent on the type of the kerogen, burial history (temperature and time), and geothermal gradient. Most commercial quantities of oil form from sapropelic (Type I and II kerogen) organic matter, whereas gas forms from humic (Types III and IV kerogen) source (Fig. 2). Primary hydrocarbon gas generation profiles from humic Type

III kerogen are different from sapropelic Type I and II kerogen. During their maturation history, sapropelic kerogens generate a significant volume of C₂₊ hydrocarbons (e.g. Hunt, 1996). Humic kerogens result in high amounts of thermogenic methane relative to C₂₊ components, yielding mostly CO₂ at low thermal maturity levels.

Primary type hydrocarbon gases include bacterial methane and thermogenic gas (Table 1). Bacterial methane is formed in shallow marine environments by microbial reduction of CO₂ and in freshwater environments by near-surface microbial acetate fermentation (e.g., Whiticar et al., 1986; Whiticar, 1999).

Table 1. Natural gas types (after Whiticar, 1994).

Type	Notes
Primary	
1) Bacterial gas:	
a) CO ₂ reduction	<i>Marine</i>
b) Microbial fermentation	<i>Freshwater</i>
2) Thermogenic gas:	<i>Wet and dry</i>
Immature	
Mature	<i>Hydrocarbon window</i>
Overmature	
Secondary	
Mixed gas	
Microbially oxidized	<i>Biodegradation</i>
Gas or water washed	
Migration fractionation	

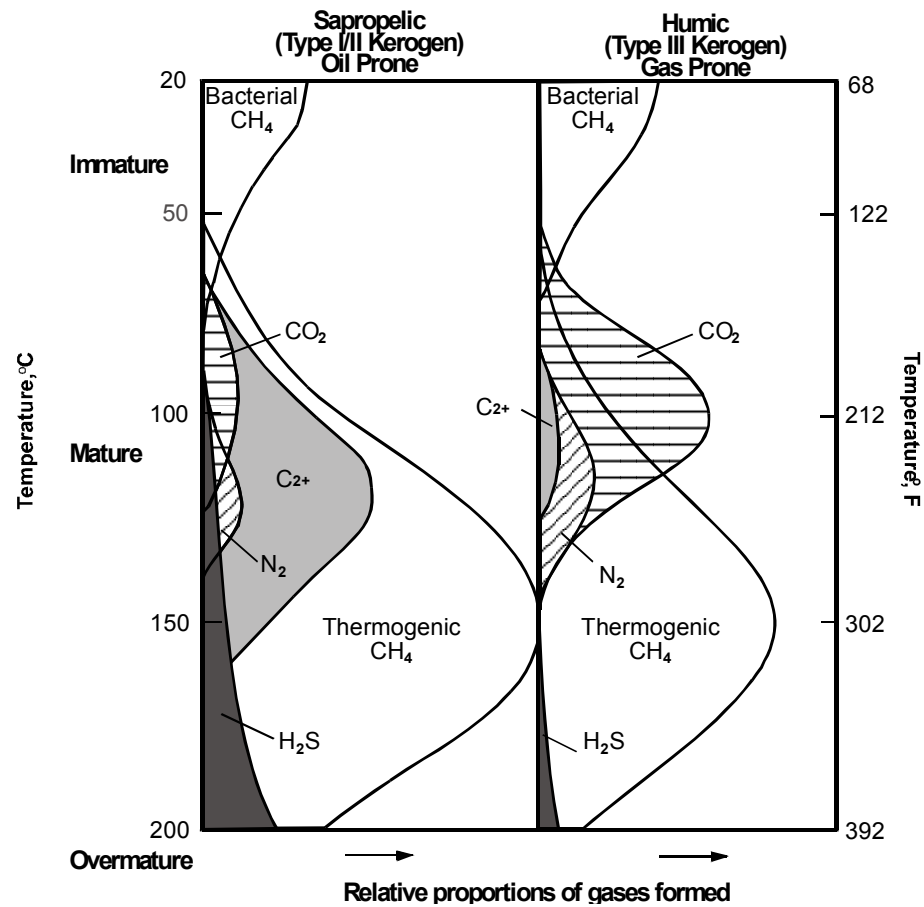


Figure 2. Relative proportions of natural gas generated from different types of organic matter (after Hunt, 1996).

Major factors that control bacterial methane production after sediment burial are an anoxic environment, sulfate-depleted environment, low temperatures and presence of organic matter (e.g. Rice and Claypool, 1981). Microbial production of gaseous hydrocarbons occurs in immature stage through chemical transformation of organic matter (e.g. Berner, 1989). This anaerobic process has been widely documented in

aquifers and shallow subsurface sediments with the thermal regimes $< \sim 70^{\circ}\text{C}$ (e.g. Hunt, 1996) (Fig. 3).

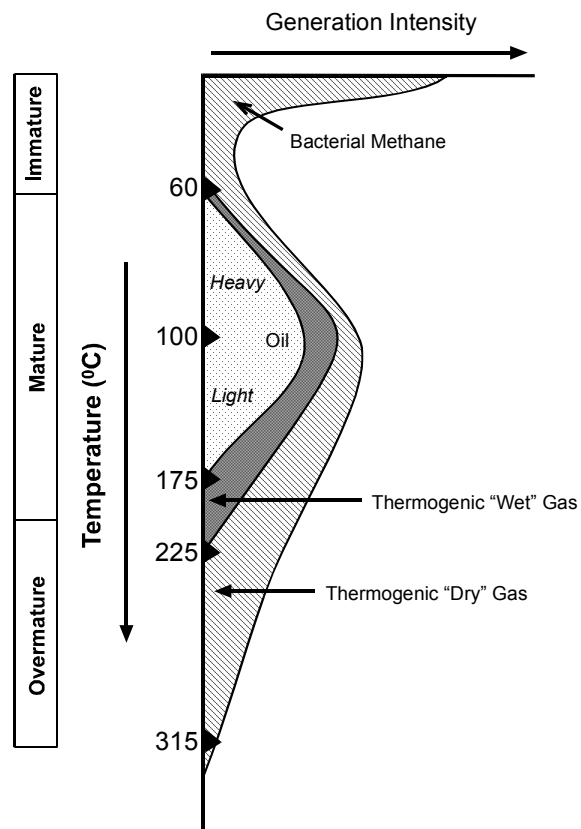


Figure 3. Diagram showing generation of natural gas and its types with increasing temperature (after Rice and Claypool, 1981).

The biogenic gases are almost exclusively methane, with less than 0.5% C_{2+} gases (e.g. Stahl, 1974; Whiticar et al., 1986). The occurrence of bacterial methane under extreme conditions of temperature (-1.2 to 110°C) and depth (>1 kbar) has also been

documented (Whiticar, 1992). In addition to surface environments, methane formed by microbes has been detected in oil reservoirs as a common component of oil field gas (Whiticar, 1994). Roughly 20% of the worldwide natural gas reservoirs are estimated as originated from microbial sources (Rice and Claypool, 1981; Rice, 1992).

Thermogenic gas may be formed by thermal degradation of kerogen or thermal cracking of crude oil with increasing maturity (e.g., Schoell, 1980, 1983; Hunt, 1996; Whiticar, 1999). Thermogenic gas may be wet or dry. Gas wetness is defined by the formula of $(C_2+C_3+i-C_4+n-C_4)/(C_1+C_2+C_3+i-C_4+n-C_4)*100$. Wet thermogenic gases are main products of the mature stage (between $\sim 70^\circ\text{C}$ and 150°C , with peak generation $\sim 120^\circ\text{C}$) (Hunt, 1996) (Fig. 2 and Fig. 3). They are formed from sapropelic (Type I and II) kerogen and thermal cracking of oil (e.g. Tissot and Welte, 1978; Hunt, 1996). Moreover, wet thermogenic gas in limited amount may also be derived from humic Type III kerogen. Dry thermogenic gas is formed by all kerogen types during overmature stage from $\sim 150^\circ\text{C}$, to over 200°C (e.g. Stahl, 1977; Schoell, 1983). At temperatures beyond 150°C , wet thermogenic gases decreases to very low values and dry thermogenic methane becomes dominant gas type (Fig. 2).

Other factors, such as time and pressure, affecting generation of hydrocarbon gases are less effective than temperature and type of the kerogen. However geothermal gradients strongly affect the burial history of organic matter and thus depth of generation of gaseous hydrocarbons. Geothermal gradients vary (world average is considered to be $25^\circ\text{C}/\text{km}$, Tissot and Welte, 1978). The variation in geothermal gradients in sedimentary

basins is typically in the range of 15°C/km to 50°C/km, although gradients as low as 5°C/km and as high as 77°C/km have been observed (Tissot and Welte, 1978).

Secondary type gases do not represent a single source, and are modified after generation by mixing of gases from different sources, by microbial alteration (biodegradation), gas or water washing, or by migration fractionation (e.g. James and Burns, 1984; Whiticar and Faber, 1986; Thompson and Kennicutt, 1990; Coleman et al., 1996) (Table 1). In the literature, the complex history of natural gas evolution has been elucidated by using geochemical fingerprinting parameters such as concentration, molecular composition and ratios, and stable isotopic properties of hydrocarbons (e.g. Rice and Claypool, 1981; Schoell, 1983; Chung et al., 1988; Hunt, 1996). Although natural gas contains fewer compounds and lesser structural diversity in comparison to oils, molecular and isotope compositions provide useful information on their history.

Mixing of two or more natural gases, an important post-generative process, frequently involves a contribution of bacterial methane or humic-sourced gas to a sapropelic-sourced thermogenic gas (e.g. Schoell, 1983; Chung et al., 1988; Whiticar, 1994) (Table 1). Biodegradation of natural gas normally refers to an alteration process at which living microorganisms oxidize hydrocarbons (preferentially the wet gas components in most instances) particularly when a reservoir is unroofed or when petroleum seepage migrates to near the surface (James and Burns, 1984). Migration fractionation is another alteration process from which a natural gas suffers during migration. Although there is no substantive evidence that gaseous hydrocarbons are

subjected to isotope fractionation during migration (Stahl, 1974), evaporative fractionation of hydrocarbons appears to be significant (Thompson, 1979).

Geochemical Characteristics of Natural Gas

Geochemical information obtained from samples of natural gas has been used in petroleum exploration and production. Widely used applications of geochemical information are the following: Source potential of gaseous hydrocarbons are determined (Sassen and Chinn, 1990). Maturity profiles, and cracking from the kerogen or crude oil are examined (e.g. Chung et al., 1988; Clayton, 1991). Migration pathways are modeled (e.g. Sassen et al., 1993a; Prinzhofer et al., 2000). Geochemical properties of natural gas have also been used for mixing (e.g. Prinzhofer and Huc, 1995; Sassen et al., 2002) and alteration diagnosis (e.g. James and Burns, 1984). Therefore, geochemical signatures are now considered to be a crucial criterion for the understanding of gaseous hydrocarbon history and behavior in sedimentary basins.

The molecular and isotopic properties of gas samples are controlled by a complex succession of processes (Prinzhofer and Huc, 1995) (Fig. 4). Following organic diagenesis which forms kerogen from organic matter in sediments, thermal degradation leads the formation of gas molecules along two different pathways: (1) a direct generation of gas from the kerogen, and (2) gas resulting from the cracking of crude oil. These pathways produce isotope fractionation, which is a major factor controlling the composition of hydrocarbon gases. After formation of the gas within the source rock, it

is subjected to expulsion and to migration towards the reservoir. During migration and in the reservoir, the natural gas composition is affected secondary (post-genetic) fractionation. These processes are called “non-thermal alteration”.

All geochemical applications assume that there are significant and systematic compositional variations among various gas types (e.g. Schoell, 1984; Hunt, 1996). It is generally more simple and reliable to relate primary type gas to the source by using geochemical fingerprinting. However, geochemical fingerprinting is also possible for the secondary type gas by recognition of the affects of secondary processes.

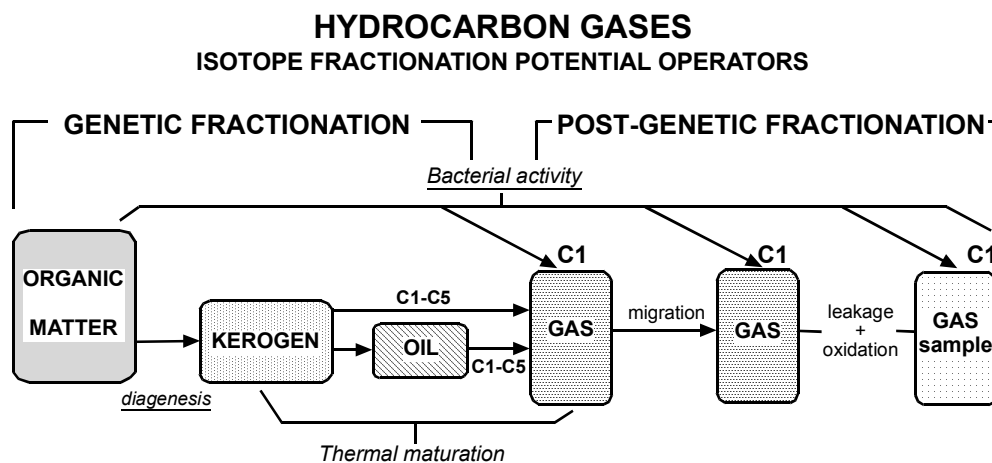


Figure 4. Schematic diagram showing potential factors controlling molecular and isotopic properties of hydrocarbon gases (after Prinzhofer and Huc, 1995).

Molecular and isotopic properties of hydrocarbon gases are sufficiently large in range and specific to provide indicative information on the sources even though the

number of chemical compounds of natural gas is restricted (Schoell, 1983; Chung et al., 1988; Whiticar, 1999).

Molecular Properties of Natural Gas

The amount of information contained in molecular composition of gaseous hydrocarbons is limited to seven saturated aliphatic compounds: methane (C_1), ethane (C_2), propane (C_3), isobutane ($i-C_4$), normal butane ($n-C_4$), isopentane ($i-C_5$) and normal pentane ($n-C_5$). The relative proportions of C_1 - C_5 hydrocarbons in a gas sample provide an initial classification of natural gas type (bacterial versus thermogenic) (e.g. Bernard et al., 1978; Schoell, 1983). Because methane is found both in bacterial and thermogenic gas, relative abundance of C_{2+} gases or ratios are useful in interpretation. The literature contains many molecular properties that distinguish primary gas types such as

1. Gas wetness (vol%) = $[(C_2+C_3+i-C_4+n-C_4)/(C_1+C_2+C_3+i-C_4+n-C_4)]*100$
2. $\sum C_{2+} = C_2+C_3+i-C_4+n-C_4+ i-C_5+n-C_5$
3. Bernard parameter = $C_1/(C_2+C_3)$ (Bernard et al., 1978)
4. C_1/C_2 (Claypool, 1974)
5. $1/\sum C_{2+}$ (Faber and Stahl, 1984)

Isotopic Properties of Natural Gas

The stable isotopic properties of specific hydrocarbons are useful in characterizing different natural gas type. Although molecular composition data on a natural gas may be used broadly to characterize its type, stable isotopic properties, such

as carbon and hydrogen isotopic properties of C₁-C₅ hydrocarbons, provide distinctive classification information illustrating common secondary alteration affects (e.g. Schoell, 1980). Moreover, the carbon and hydrogen isotopic properties of natural gas in reservoirs may provide detailed information about source and kerogen types (sapropelic or humic) (e.g. Prinzhofer and Huc, 1995). Carbon isotopic properties may be used to estimate the level of thermal maturity (e.g. James, 1983; Clayton, 1991). In addition, the combination of molecular and isotopic properties of gas may distinguish altered (secondary) gases or define gas mixtures (e.g. Faber and Stahl, 1984; Chung et al., 1988; Prinzhofer et al., 2000).

For practical reasons, stable isotope data are given as a ratio, such as ¹³C/¹²C and are reported in parts per thousands (‰) relative to a known standard isotope ratio. The isotopic composition is reported in the usual δ-notation;

$$\delta (\text{‰}) = (R_{\text{sample}} - R_{\text{standard}}) / R_{\text{standard}} * 1000$$

R is the isotope ratios of ¹³C/¹²C or D/H referenced relative to the PDB (Peedee Belemnite) or SMOW (Standard Mean Ocean Water) standards, respectively (Craig, 1957).

Various factors control isotopic properties of natural gas (e.g. Whiticar, 1999) (Fig. 4). The δ¹³C and δD of the source, and isotope effects associated with the process of generation, expulsion, migration and alteration of the natural gas are critical controlling factors (Hunt, 1996).

Equilibrium isotope effects have been proposed to explain the distribution of carbon isotopes in thermogenic hydrocarbons (e.g. Galimov and Ivlev, 1973; James,

1983). Galimov (1985) modified the equilibrium isotope effect to a “thermodynamically ordered distribution”, which approaches the more accepted view kinetic isotope effects (KIE), controlling the redistribution of isotopes. KIE theory is based on the assumption that the petroleum forming processes are related to carbon-carbon bond breakages of complex kerogen molecules (e.g. Stahl, 1973; Sackett, 1978; Chung et al., 1988). A ^{12}C - ^{12}C bond is easier to break than a ^{12}C - ^{13}C bond. This more frequent breakage results in gaseous products depleted in isotopic properties and in residue enriched in isotopic properties during thermal cracking. Similar KIE considerations also apply to bacterial methane (Whiticar, 1992). When microbes form methane they preferentially consume ^{12}C rather than the ^{13}C resulting in depleted ^{13}C values (e.g. Chung et al., 1988; Clayton, 1991).

Carbon isotopic properties of methane are commonly used to classify natural gases (Colombo et al., 1965; Stahl, 1973; Schoell, 1980,1988). However, methane has many sources and may be altered by secondary processes. Thus, in the last decade, carbon isotopic properties of C_{2+} gases have been widely used (James, 1983; Chung et al., 1988; Clayton, 1991). The hydrogen isotopes (δD) of methane may also be diagnostic parameter in classifying the type of gas (Schoell, 1980). In contrast to carbon isotopic properties, the hydrogen isotopic properties of methane do not appear to show a clear thermal maturity dependency (Schoell, 1980; Whiticar, 1994). Hydrogen isotopic properties provide details on the depositional environment and formation pathways such as microbial reduction of CO_2 or acetate fermentation (Whiticar, 1994).

Isotopic Properties of Bacterial Methane

Bacterial gas may be recognized by unique molecular and isotopic properties. Bacterial gas may be defined as exclusively methane depleted in ^{13}C , with less than 0.5% higher C_{2+} components (e.g. Stahl, 1974; Whiticar, 1994). The stable isotopes of both the hydrogen and carbon of the methane in bacterial methane may be fractionated by bacterial processes (microbial reduction of CO_2 or acetate fermentation). It is possible to differentiate bacterially formed methane from “thermogenic dry gas” formed by thermal cracking reactions by carbon isotopic properties.

Bacterial methane has a wide range of carbon and hydrogen isotopic properties. The isotopic properties vary from -60‰ to -110‰ PDB and from -150‰ to -400‰ SMOW (Schoell, 1983; Hunt, 1996; Whiticar, 1999). Anomalous values may occur outside these ranges because of variable sources of ^{13}C and D, and because of secondary processes such as migration or microbial alteration.

Schoell (1983) notes that the isotopic properties in bacterial gas from marine sediment throughout the world are relatively uniform, ranging between -60‰ and -75‰ PDB, and -170‰ and -190‰ SMOW (Fig. 5). Schoell (1980) emphasizes that carbon isotopic properties of bacterial gas do not change depending on the generation environment even though δD may vary widely ranging from -150‰ to -250‰ SMOW. Bacterial methane derived from continental environments (from -150‰ to -190‰ SMOW) is depleted in δD relative to bacterial methane derived from marine environments (from -190‰ to -250‰ SMOW) (e.g. Schoell, 1980, Whiticar et al.,

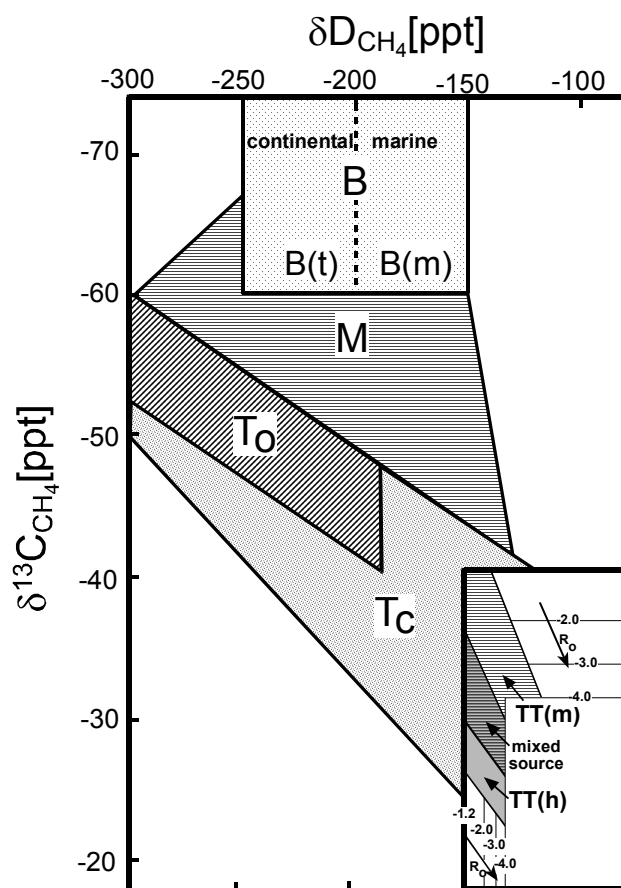


Figure 5. Genetic characterization of natural gas by variation in D and ^{13}C in methane. B(m): Bacterial gas derived from marine sediments; B(t): Bacterial gas derived from continental environments; M: Mixed gases; T_0 : Oil associated thermogenic wet gas; T_c : Condensate associated thermogenic wet gas; TT(h): Thermogenic dry gas derived from humic organic matter; TT(m): Thermogenic dry gas derived from liptinitic organic matter (after Schoell, 1983).

1986). The methane produced by fermentation processes in fresh water environments is more depleted in deuterium (from -250‰ to -400‰ SMOW) (Woltemate et al., 1984).

Whiticar (1999) constructed an empirical carbon versus hydrogen isotope diagram by delineating its fields according to the assumption that methane formed by

microbial fermentation in freshwater environments and methane that is generated by CO_2 reduction in marine sedimentary environments have distinct carbon and hydrogen isotopic properties. Two bacterial methane fields (microbial reduction of CO_2 and acetate fermentation) using approximate boundaries of $\delta^{13}\text{C}$ of -60‰ PDB and δD of -250‰ SMOW are differentiated (Fig. 6). Although it was assumed that methane

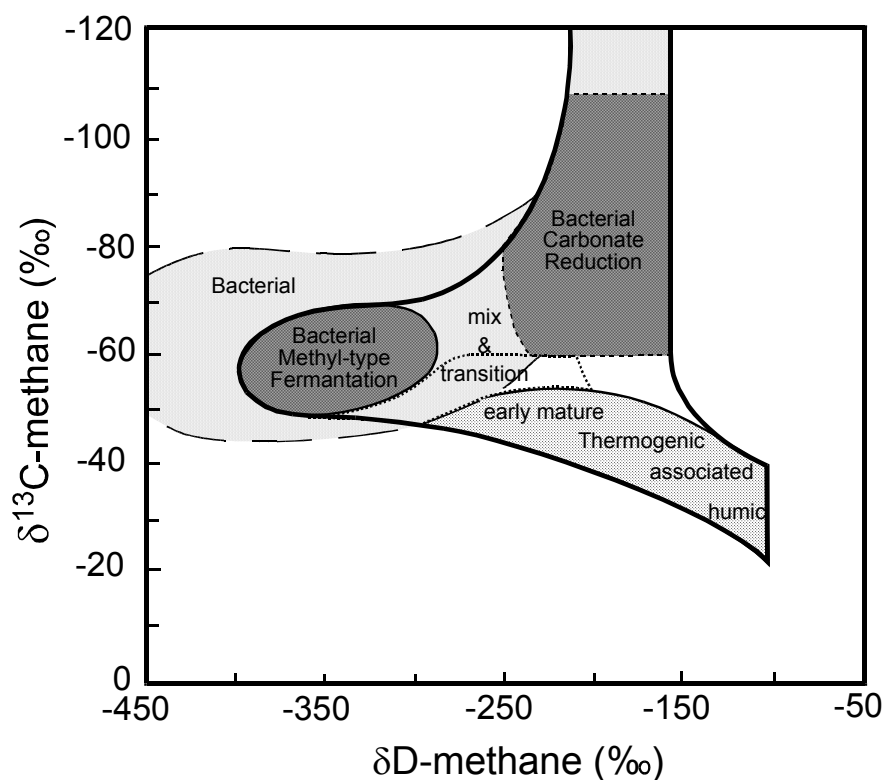


Figure 6. Carbon-deuterium diagram for classification of bacterial and thermogenic natural gas by using the combination of $\delta^{13}\text{C}$ and δD of methane information (after Whiticar, 1999).

depleted in D may only be found in fresh water environments (Woltemate et al., 1984; Whiticar et al., 1986), later studies show that similar methane depleted in D may also be generated in marine environments (Jenden and Kaplan, 1986; Burke et al., 1988). Therefore the methanogenic pathway may be sometimes independent of the depositional environment (Schoell, 1988).

Jenden and Kaplan (1986) proposed that fermentation-derived methane is primarily produced from fresh sediments of terrestrial origin and speculated that fermentation effects decrease with age (“aging effect”) by suggesting that all bacterial methane in reservoirs and older marine sediments has isotopic properties of methane derived by CO₂ reduction (e.g. Claypool and Kaplan, 1974; Schoell, 1980). Schoell (1988) improved the concept and suggested that sediment temperature may also influence the pathways of bacterial processes. At warmer sediment temperatures acetate fermentation is the predominant process whereas with lower sediment temperatures CO₂ reduction prevails (Burke et al., 1988). Acetate fermentation derived methane is generally enriched in ¹³C in comparison to methane derived from CO₂ reduction (Fig.7). However, the methane formed from fermentation is more depleted in D than methane derived from CO₂ reduction.

Some specific environments with anomalous ¹³C values of sources (e.g. interstitial CO₂ in sediments with already enriched ¹³C values) may lead enrichment of ¹³C in bacterial methane although these particular conditions do not exist with commercial quantities of bacterial gas (Nissenbaum et al., 1972). Significant increases in C₂/C₁ ratios and in ¹³C values of bacterial methane with increasing depth have been

documented (Schoell, 1977; Claypool, 1974, 1979; Mattavelli et al., 1983). The terms “early” and “late” bacterial gas of Bernard et al. (1978) is used to indicate these changes.

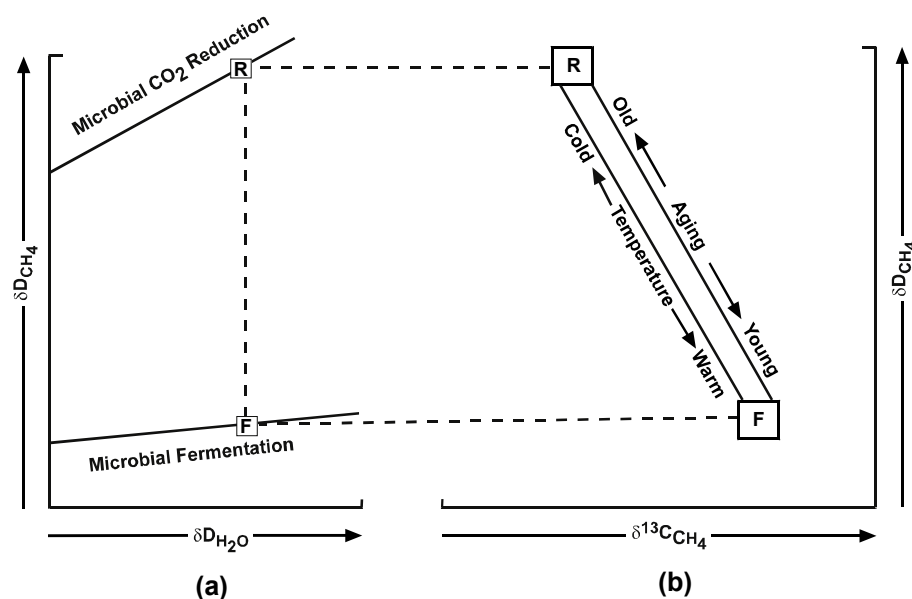


Figure 7. A general model of bacterial processes during transformation of organic matter in sedimentary environments and their control on the isotopic properties of methane (after Schoell, 1988).

The changes in the ^{13}C and the C_{2+} concentration of natural gas with depth were combined in a plot by Bernard et al. (1978) to distinguish different gas types (thermogenic versus bacterial) from each other. Bacterial methane is delineated with a field of values in $\text{C}_1 / (\text{C}_2 + \text{C}_3)$ concentrations ranging from 10^3 to 10^5 and in $\delta^{13}\text{C}$ properties varies from -60‰ to -90‰ PDB (Bernard et al., 1978) (Fig. 8).

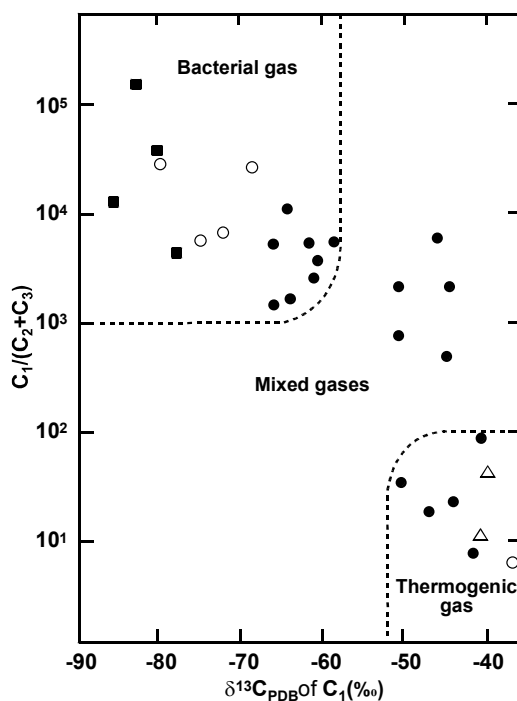


Figure 8. Bernard plot comparing gas wetness and $\delta^{13}C$ of methane for gases from various areas: solid circle: Gulf of Mexico; empty circle: Norton Sound, Alaska; solid square: western Gulf of Alaska; empty triangle: offshore southern California (after Bernard et al., 1978).

Isotopic Properties of Thermogenic Gas

Thermogenic gas has a wide range of molecular and isotopic properties, which are affected by type, amount, and maturation of organic matter (e.g. Tissot et al., 1974). Because of kinetic isotope effects, generation of thermogenic gases causes isotopic fractionation leading to a gas depleted in ^{13}C , and leaves the residue enriched in ^{13}C . Therefore, during thermal maturation, later formed gas will be enriched in ^{13}C , although still depleted with respect to the residual kerogen (Clayton, 1991). Consequently, with

increasing maturation of the source, the most mature gas will be the most enriched in ^{13}C .

Thermogenic gas has geochemical properties, which gradually change via the effects of thermal maturation history of the source material. Immature thermogenic gas is typically depleted in ^{13}C and dry to very dry ($<5\% \text{ C}_{2+}$) (e.g. Rice et al., 1989; Hunt, 1996). With increasing maturity, mature thermogenic gas is enriched in ^{13}C and the gas is wetter ($5\% < \text{C}_{2+} < 15\%$) (Rice et al., 1989). Overmature thermogenic gas is significantly enriched in ^{13}C and dry ($<5\% \text{ C}_{2+}$) (e.g. Stahl, 1977; Schoell, 1983; Whiticar, 1994).

The isotopic properties for wet thermogenic gas range from -30‰ to -60‰ PDB and -120‰ to -300‰ SMOW (Hunt, 1996). Dry thermogenic gas has isotopic properties varying from -15‰ to -40‰ PDB and -70‰ to -150‰ SMOW (Hunt, 1996). Thermogenic gas from terrestrial environments (humic source) is enriched in ^{13}C relative to the gas from marine environments (sapropelic source) (Stahl, 1975 Fuex, 1977).

There are two different approaches used to distinguish thermogenic gases: One is empirically derived cross-plots of molecular and isotopic properties. Another is isotopic partition function to calculate isotopic differences between pairs of compounds as a function of temperature.

The empirical approach has been used by evaluating gas samples of known origin and maturity, and cross-plotting various basic ratios (methane/ethane ratio, $\delta^{13}\text{C}$ versus δD of methane, etc.) to define fields that are diagnostic of each gas source (e.g.

Stahl, 1975; Bernard et al., 1978; Schoell, 1980, 1983). The partition function methods, based on calculation of equilibrium differences in $\delta^{13}\text{C}$ between hydrocarbons as function of temperature, have been used to identify thermal maturity and to carry out source rock correlations (e.g. Galimov et al., 1972; Galimov and Ivlev, 1973; Stahl, 1973; James, 1983).

James (1983) constructed a diagram by plotting the differences between the isotopic compositions of individual gases (methane, ethane, propane etc.) versus source Level of Organic Metamorphism (LOM) (Fig. 9). The primary concept behind the approach is that the difference of carbon isotopic properties between the normal alkane components of a thermogenic gas depends on the maturity at which the gas was generated (James, 1983). However, the actual ^{13}C values depend on both the isotopic properties of the source and its maturity. $\delta^{13}\text{C}$ differences between normal alkane components of a gas decrease continuously with increasing maturity (James, 1983) (Fig. 9).

Fuex (1977) and Stahl (1977) proposed an empirical differentiation of thermogenic gas based on C_{2+} composition and carbon isotopic properties of methane. Thermogenic gas associated with oil generation has $\delta^{13}\text{C}$ values in -40‰ to -58‰ PDB range, and significant quantities of C_{2+} components ($>5\%$) (Fuex, 1977). The wet thermogenic gas may be derived from a mature oil source rock or from crude oil itself (Stahl, 1975; Fuex, 1977). Deep dry thermogenic gas from either terrestrial humic or marine sapropelic organic matter is characteristically dry ($<5\%$ C_{2+}) and has methane enriched in ^{13}C ranging from -25‰ to -40‰ PDB (Stahl, 1977). The dry thermogenic

gas may be derived from overmature oil source rocks or from thermal cracking of crude oil at overmaturity (Fuex, 1977).

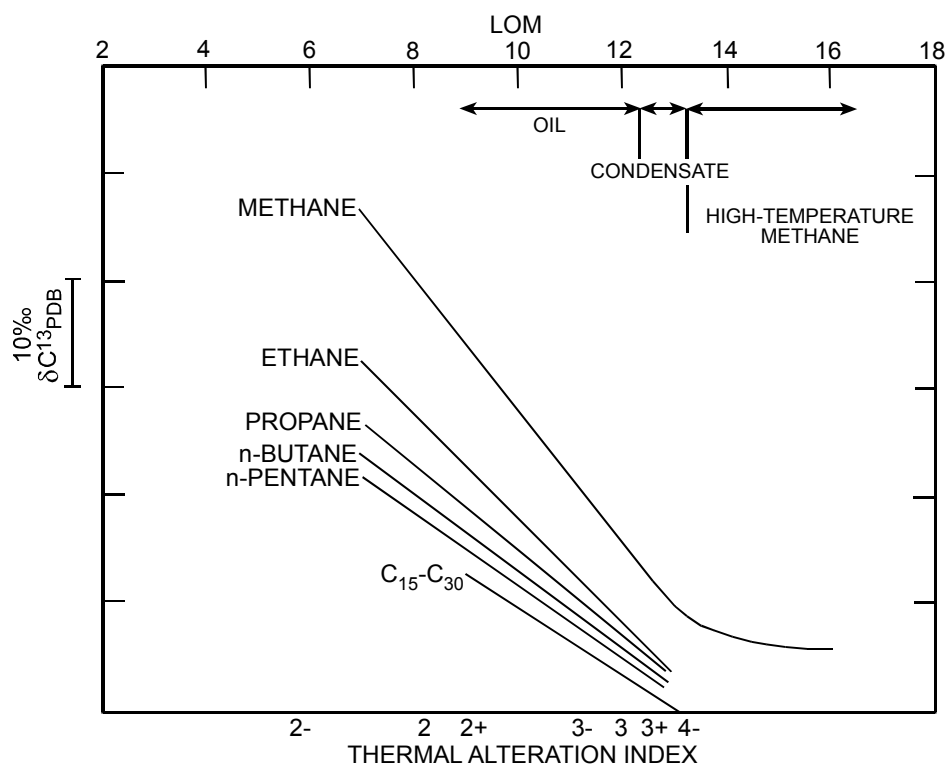


Figure 9. Thermal maturation diagram showing calculated carbon isotopic separations between gas components plotted against source rock LOM (after James, 1983).

Schoell (1980, 1983) also followed the classification mentioned above, and proposed another empirical discrimination of associated and nonassociated gases because of fractionation of hydrogen isotopes (Fig. 5). Schoell (1983) used the terms of associated and nonassociated thermogenic gas different than the standard petroleum

geologic usage, which has no genetic connotation. Schoell (1983) defined “associated thermogenic gas” as wet thermogenic gas generated from thermal cracking of kerogen or crude oil. Schoell (1983) believes that a gas from a gas cap may migrate off its primary reservoir and it may become a nonassociated gas in standard usage but the gas has still isotopic properties of an associated thermogenic gas in genetic terms.

Methane of the thermogenic gas associated with crude oil (T_o in Fig. 5) or associated with condensate (T_c in Fig. 5) is depleted in D with respect to methane of dry nonassociated gas (Schoell, 1983). The first methane of thermogenic gas associated with crude oil formed from cracking reactions in petroleum has been suggested as approximately -50‰ to -60‰ PDB and -245‰ to 340‰ SMOW (Schoell, 1983). Methane of thermogenic gas associated with condensates is enriched than -40‰ PDB indicating higher source maturities relative to that of oil associated thermogenic gas (Schoell, 1983).

In methane of dry nonassociated gases D increases with increasing maturity of organic matter of the source rock. Hydrogen isotope fractionation is the same for humic and liptinitic organic matter (Schoell, 1980). ^{13}C concentration fractionates differently when methane is formed from humic ($TT_{(h)}$ in Fig. 5) or sapropelic ($TT_{(m)}$ in Fig. 5) organic matter (Schoell, 1983).

Bernard et al. (1978) suggested a genetic diagram by correlating $C_1/(C_2+C_3)$ ratios with the ^{13}C concentration of the methane to classify natural gas types (Fig. 10). The diagram basically depends on samples suites of sediment gases, seepage, and vent sites. These samples show a large range in their relative amounts of C_{2+} hydrocarbons,

which are used to distinguish bacterial gas from thermogenic gas, particularly denoting source material (Type II and III kerogen). Molecular ratios $C_1/(C_2+C_3)$ less than 50 are typical for thermogenic hydrocarbon gases with the $\delta^{13}C$ values between -35‰ to -50‰ PDB. Thermogenic gas mainly derived from Type II kerogen show enrichment in molecular ratios up to around 10^3 , whereas thermogenic gas mainly generated from Type III kerogen show enrichment in $\delta^{13}C$ (Fig. 10).

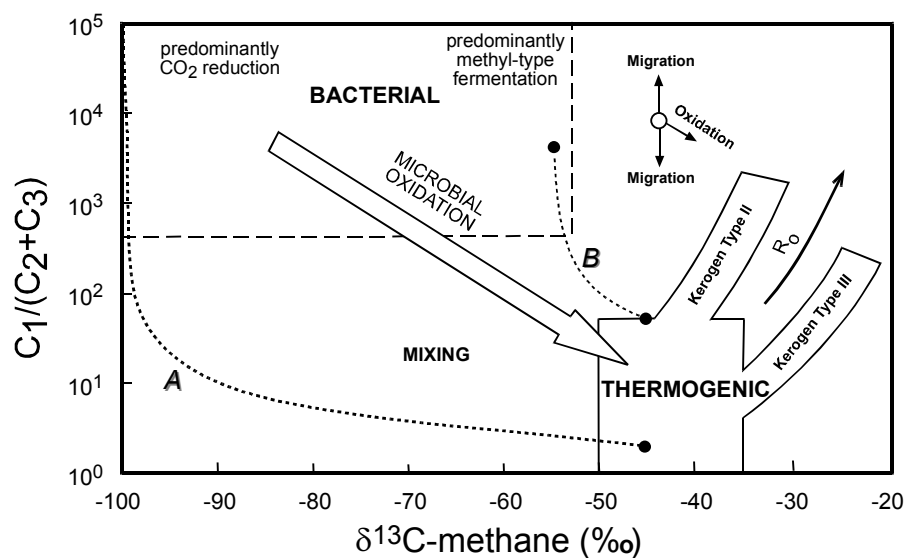


Figure 10. Natural gas interpretative (“Bernard”) diagram combining molecular and isotopic properties. Lines A and B are calculated mixing lines for possible bacterial and thermogenic gas mixtures (after Bernard et al., 1978).

Chung et al. (1988) developed an equation, which is based on the generation of gaseous hydrocarbons by thermal cracking of isotopically homogenous parent materials. This equation allows plotting the $\delta^{13}C$ of individual gases (methane, ethane, propane

etc.) as a function of the inverse carbon number of the gas molecule. This plot is called “natural gas plot” (Fig. 11). The natural gas plot has been used to interpret the natural gas origins, effects of thermal maturation and secondary effects.

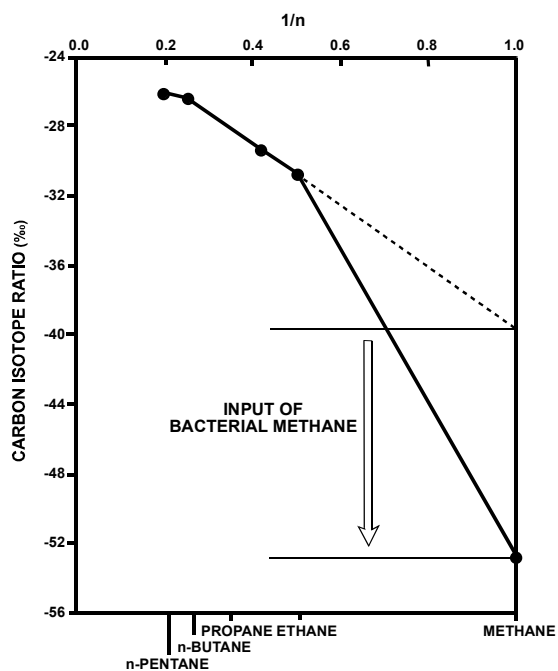


Figure 11. Natural gas plot of gaseous hydrocarbons showing calculation of amount of bacterial methane mixed in a gas sample from the Gulf of Mexico (after Chung et al., 1988).

Clayton (1991) describes a method of estimating source type and maturity of a gas based on a Rayleigh fractionation model using a kinetic approach. The author modeled the $\delta^{13}\text{C}$ of a hydrocarbon gas as a function of $\delta^{13}\text{C}$ of the gas precursor in kerogen, the extent of gas generation and a kinetic isotope fractionation factor. Using

these parameters, summary diagrams have been constructed which allow differentiation of the kerogen sources from each other and from bacterial gas and cracked oil, and recognition of gases of mixed origin. Change in $\delta^{13}\text{C}$ of the gaseous hydrocarbons between sources and with maturity is shown in Fig. 12. $\delta^{13}\text{C}$ of methane is used as a

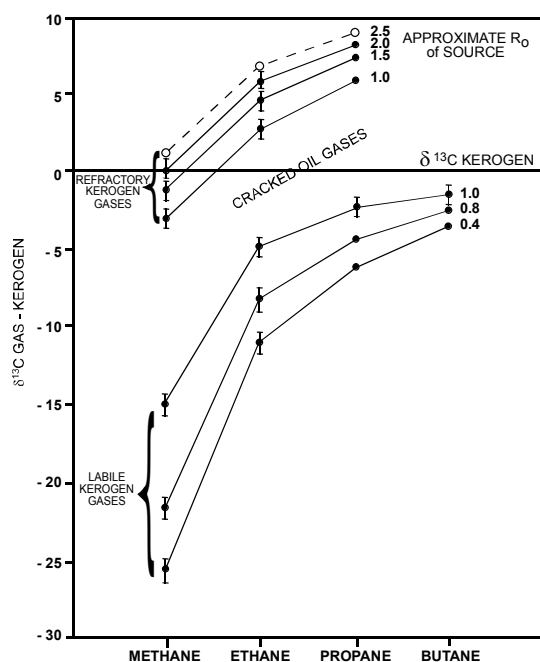


Figure 12. Modelled maturity variations in $\delta^{13}\text{C}$ of methane through butane, relative to $\delta^{13}\text{C}$ of total source kerogen (after Clayton, 1991).

guide to maturity. Pure gases plot parallel to the trends on the plot. However any mixing causes deviations from these trends and leads to crosscutting relationships. For example, addition of bacterial gas will cause a steepening of the methane-ethane line but a good fit

for ethane-propane and propane-butane lines since bacterial gas contains negligible percentages of the C₂₊ gases.

Isotopic Properties of Secondary Gas Types

The emphasis on the geochemical analyses of natural gas has been up to now, on unaltered gases. Although in many cases geochemical analyses may help in determining the characteristic of a primary gas, some secondary (post-generative) processes may alter their initial geochemical characteristics. It is common for a natural gas to represent a mixture of gases from different source rocks. In addition, the original molecular and isotopic properties of a natural gas may suffer alteration, as biodegradation or migration fractionation (e.g. Thompson and Kennicutt, 1990). Once one can recognize the influence of secondary effects on a gas and can avoid misinterpretation of it, it is possible to outline characteristics of the gas by using geochemical fingerprinting.

Mixing

A mixture of more than one gas type in a natural gas sample is a common phenomenon. This may be a bacterial gas within a thermogenic gas pool, inducing a mixed situation. Molecular and isotopic properties of a natural gas help to recognize that the gas is a mixture and to determine possible end-members of the mixture and their relative contributions (e.g. Schoell, 1983; Chung et al., 1988; Whiticar, 1994; Prinzhofer and Huc, 1995).

For a natural gas sample consisting of a mixture of two different gases, the $\delta^{13}\text{C}$ and δD of methane will plot on the mixed field of genetic classification diagram of Schoell (1983) (Fig. 5). The particular advantage of the $\delta^{13}\text{C}$ versus δD diagram is that mixing processes result in linear changes between compositions of respective end-members (Fig. 13). Both isotopic properties change in strict proportion to the mixing ratios, and thus mixing of various proportions of two gases give rise to a linear change in their isotopic properties. Additionally, mixing of gases cause also a linear relationship on the $\delta^{13}\text{C}$ versus C_{2+} diagrams (Schoell, 1983) (Fig. 13).

Mixtures of bacterial and thermogenic gas may be recognized by using $\delta^{13}\text{C}$ of methane and $\text{C}_1/(\text{C}_2+\text{C}_3)$ molecular concentration of the gas on the Bernard et al. (1978) plot (Fig. 10). Two trajectory lines, A and B, have been calculated to define mixing for possible bacterial and thermogenic gas with end-member isotopic properties ($\delta^{13}\text{C}$ of methane) and molecular $\text{C}_1/(\text{C}_2+\text{C}_3)$ compositions of -100‰ PDB, 10^5 ; -45‰ PDB, 2 (A) and -55‰ PDB, 5000; -45‰ PDB, 50 (B), respectively.

The relationship between $\delta^{13}\text{C}$ of methane and $\delta^{13}\text{C}$ of ethane data pair has also been widely used to define the mixed gas properties (Schoell, 1983; Berner, 1989). For cogenetic methane-ethane pairs in thermogenic gas, it has been observed that generally ethane is enriched in ^{13}C between 5‰ PDB and 10‰ PDB relative to methane (Silverman, 1971; Deines, 1980). If bacterial methane is added to a thermogenic methane, the $\delta^{13}\text{C}$ value of the methane changes accordingly, and the $\delta^{13}\text{C}$ value of the ethane remains constant (arrow Ms in Fig. 14) (Schoell, 1983). Mixing in $\delta^{13}\text{C}$ of

methane versus $\delta^{13}\text{C}$ of ethane diagrams results in a bent mixing pathway if gases with different C_1 and C_{2+} concentrations are mixed (Fig. 13) (Schoell, 1983).

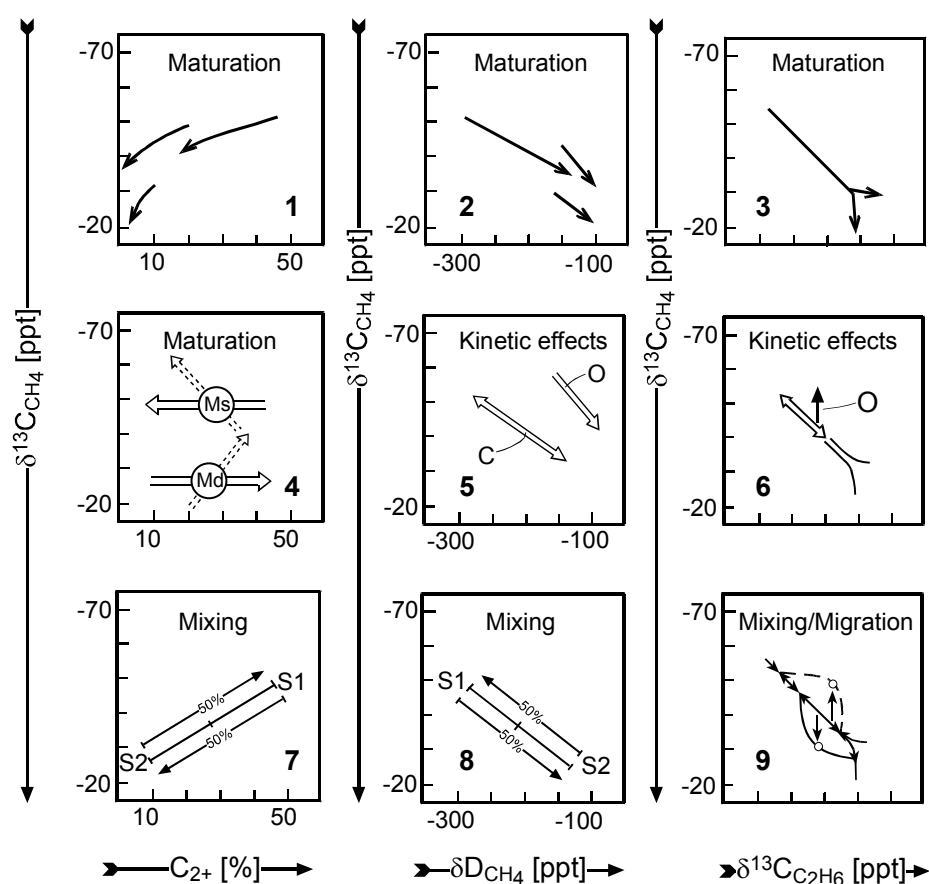


Figure 13. Diagrams showing various processes and resulting compositional variations in natural gas. C: chromatographic effect; O: oxidation effect; S1-S2: end members of mixed gases. Note various possibilities owing to migration. Dashed arrows indicate mixing owing to migration. Horizontal arrows result from a change of the C_{2+} concentrations only. Mixing in $\delta^{13}\text{C}$ -methane/ $\delta^{13}\text{C}$ -ethane diagrams may result in bent mixing pathways if gases with different C_1 and C_{2+} concentrations are mixed (after Schoell, 1983).

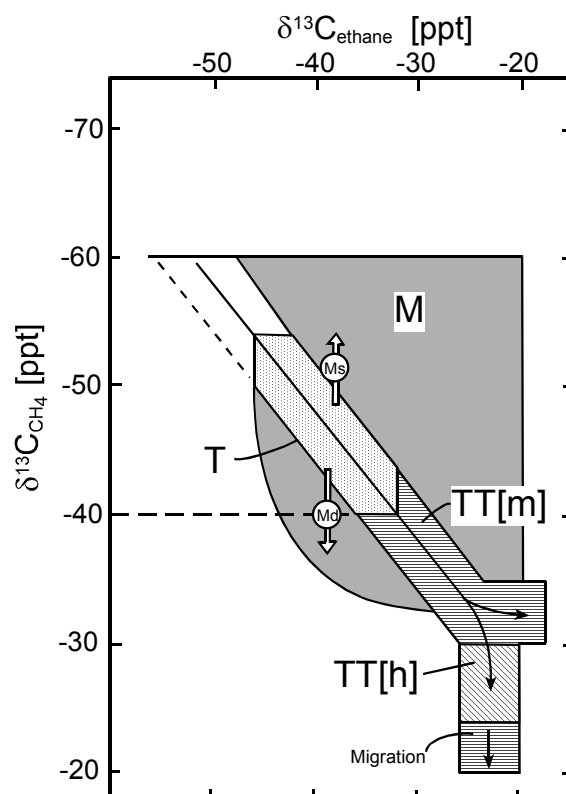


Figure 14. Carbon isotopic properties in ethane related to carbon isotopic properties in methane. Compositional changes because of mixing of gases depend on methane and ethane concentrations. Arrow Md would result if pure isotopically positive CH_4 were to mix with a gas. Admixture of bacterial methane results in change of $\delta^{13}\text{C}$ of methane only (arrow Ms) (after Schoell, 1983). Abbreviations are same as Figure 5.

Prinzhofer and Pernaton (1997) suggested using a diagram displaying ethane/methane ratios versus $\delta^{13}\text{C}$ of methane to test the mixing effects of gases. In this particular plot, they proposed that a mixing trend between two end-members must be close to a straight line (Fig. 15). In addition, Prinzhofer et al. (2000) stated that a straight line is expected to characterize a mixture between two end-members when plotting any

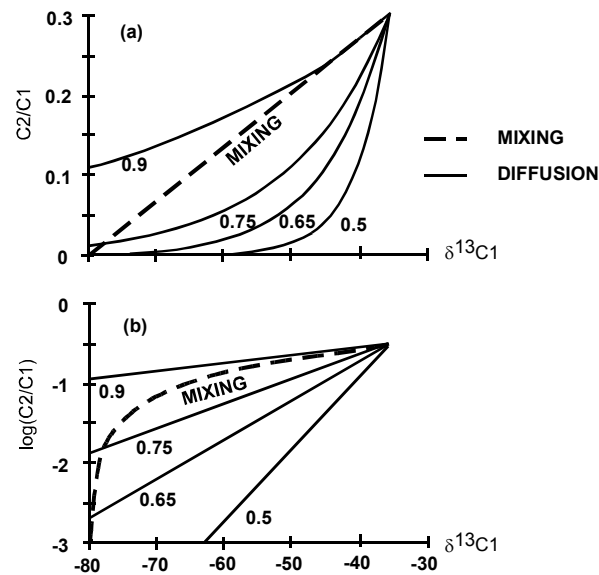


Figure 15. Model calculation of mixing and diffusion trends in a diagram C_2/C_1 versus $\delta^{13}C_1$, with linear (a) and logarithmic (b) scales. The two mixing end members have $\delta^{13}C$ of -80‰ PDB and -35‰ PDB, and C_2/C_1 ratios of 0 and 0.3 respectively. (after Prinzhofer and Pernaton, 1997).

two molecular ratios with a common denominator such as $\delta^{13}C$ of methane, ethane or propane. However, they showed that choosing the isotopic properties of C_{2+} gases allows better straight line trend corresponding a clear mixing between a principal bacterial end-member and a thermogenic one (Fig. 16).

Chung et al. (1988) have presented an equation and natural gas plots based on that equation to estimate the relative amount of bacterial methane commingled with thermogenic methane in a mixed gas (Fig. 11). By extrapolating the carbon isotopic properties of ethane, propane and butane on the natural gas plot, they have found the carbon isotopic properties of pure thermogenic methane in the mixture. In order to

estimate the proportion of bacterial methane that is contributed to the mixture they made an assumption for carbon isotopic properties of relatively pure bacterial methane and then calculated the percentage of the bacterial methane based on the assumed value of carbon isotopic properties.

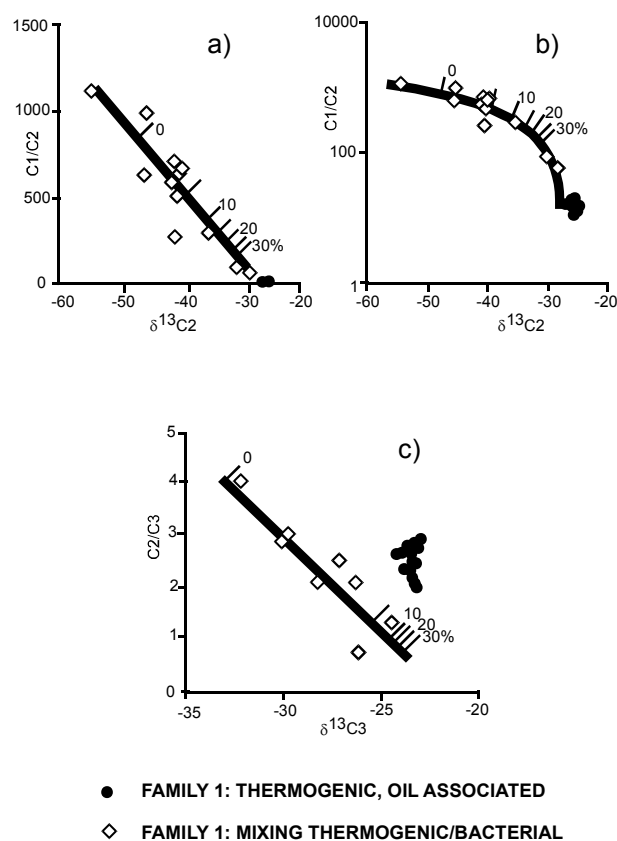


Figure 16. Gas from the two families of the Macuspana Basin plotted on different mixing diagrams: (a) C_1/C_2 versus $\delta^{13}C_2$ on a linear scale; (b) C_1/C_2 versus $\delta^{13}C_2$ on a semi-logarithmic scale; (c) C_2/C_3 versus $\delta^{13}C_3$ on a linear scale (after Prinzhofer et al., 2000).

Microbial Oxidation

Microbial oxidation (biodegradation) of gaseous hydrocarbons in relatively recent sediments and shallow aquifers has been known to occur (Coleman et al., 1981; James and Burns, 1984). The process of biodegradation is similar to microbial methane formation. But the result is the opposite in that the residual hydrocarbons become enriched in ^{13}C . When hydrocarbons are mineralized to CO_2 , due to kinetic isotope effects, ^{12}C -bearing molecules react faster than ^{13}C -bearing molecules. Therefore, the products of microbial oxidation are ^{13}C -depleted CO_2 and residual methane enriched in ^{13}C (Barker and Fritz, 1981; Coleman et al., 1981; Whiticar and Faber, 1986).

Microbial oxidation of gaseous hydrocarbons may also decrease C_1/C_{2+} (Fig. 10) (Bernard et al., 1978; Faber and Stahl, 1984). Microbes may preferentially oxidize the normal butane in the gas and may lead to higher relative abundance of the isobutane molecule (Winters and Williams, 1969). James and Burns (1984) stated that bacteria preferentially attack and remove wet gas components of a natural gas and biodegradation occur with little or no methane oxidation.

Microbial oxidation may severely alter the carbon isotopic properties of the gas by causing selective enrichment of ^{13}C in propane without affecting ethane (James and Burns, 1984). Consequently, even though the carbon isotopic properties of hydrocarbon gas components in normal, unaltered gases generally follow a smooth progression from methane to normal butane, the carbon isotopic properties of hydrocarbon gas components in a biodegraded gas illustrates a jagged pattern, particularly with distinct enrichment in propane (James and Burns, 1984) (Fig. 17).

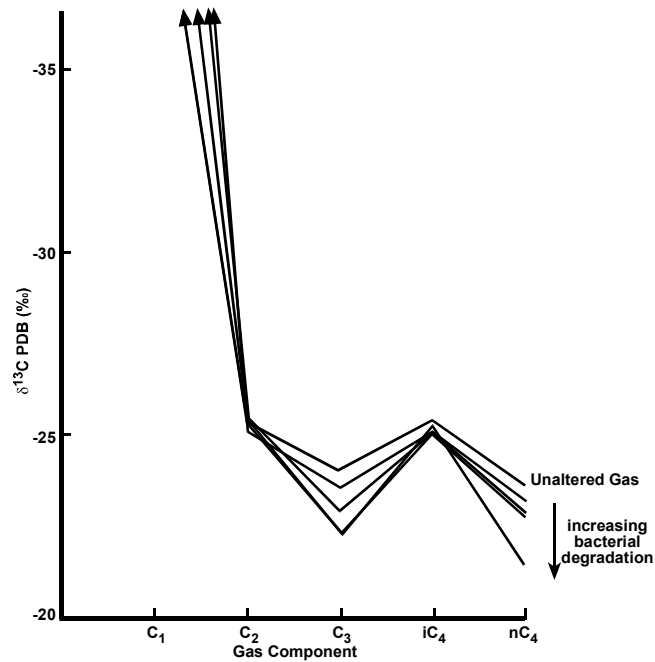


Figure 17. Diagram showing the effects of bacterial alteration on gases from Lena Field (after James, 1990).

Migration

Migration is the process of physical movement of gas from its source to a reservoir. Mass balance calculations suggest that up to 10% of a gas generated in a particular reservoir may undergo vertical or lateral migration (Barker, 1979). A criterion to determine which gases are indigenous (not migrated) is the geochemical correlation of maturity parameters of the gas and the environment at which the natural gas has been found (Schoell, 1983). There is no evidence that hydrocarbons undergo isotopic fractionation during migration. Although some arguments for isotopic fractionation have been suggested in earlier (Colombo et al., 1969; Stahl et al., 1977) investigations by

Coleman et al. (1977) and Fuex (1980) convincingly demonstrated no evidence of isotopic fractionation during gas migration.

Isotopic changes in gas during migration expected when the gas becomes mixed with another gas during migration (Schoell, 1983). But this is not, in a strict sense, migration fractionation because here the physical process of migration is not viewed as a mechanism of isotope fractionation. In contrast, molecular fractionation or redistribution of hydrocarbons during migration is significant in most situations (Thompson, 1979; Leythaeuser et al., 1984). Migrated gases are thought to behave “chromatographically” with higher diffusion coefficients associated with increasing aromaticity and decreasing carbon number (Thompson, 1979; Leythaeuser and Schwarzkopf, 1986).

Coleman et al. (1977) also demonstrated the diffusion effects on molecular composition of the gases and stated that migrated gases may be completely stripped of C₂₊ hydrocarbons, whereas the ¹³C concentration in the methane remained unchanged. Therefore, migration should result as a change parallel to the C₂₊ axis or along mixing lines on δ¹³C of methane versus C₂₊ plot (Fig. 18) (Schoell, 1983).

Schoell (1983) suggested that methane plays an important role in migration, and depending on depth, migration of methane has two effects: (1) deep migration (Md in Fig. 18) and (2) shallow migration (Ms in Fig. 18). During the deep migration, deep dry methane, which has been formed in overmature zones below oil formation zone, could migrate and act as carrier for C₂₊ hydrocarbons (Sokolov et al., 1964). Such gases may increase compositionally in wetness (horizontal arrow Md in Fig. 18). Shallow migration may result in depletion of the C₂₊ hydrocarbons. Shallow migration may result in dry

CHAPTER III

THE GULF OF MEXICO CONTINENTAL SLOPE

The Gulf of Mexico continental slope is a complex structural basin, approximately 1500 km in diameter and filled with 10 to 15 km of sedimentary rocks ranging in age from Late Triassic to Holocene (Salvador, 1991). The basin was strongly affected by massive influx of siliciclastic turbidite sediments, mobilization of large salt masses and active growth faulting during the Tertiary (Coleman et al., 1986). The Gulf of Mexico Salt Basin is one of the most petroliferous basins in the world. With depletion of onshore and shallow water reserves, deepwater Gulf of Mexico is now a significant province for petroleum exploration. Geological studies have provided improved insight to the regional geology of the Gulf slope, and upper abyssal plain (e.g. McBride et al., 1998; Weimer et al., 1998; Salvador, 1991).

The Gulf slope is a region of gently sloping seafloor that extends from the shelf edge, in ~200 m water depth, to the downdip limit of the Gulf of Mexico Salt Basin, at a depth of ~2800 m (Coleman et al., 1986) (Fig. 19). The slope occupies more than 500,000 sq km of prominent escarpments, intraslope basins, knolls, ridge and valley topography, and submarine channels (Martin and Bouma, 1978). The factors that have controlled the present day morphology on the Gulf slope are mainly salt diapirism and differential sedimentation (Coleman et al., 1986).

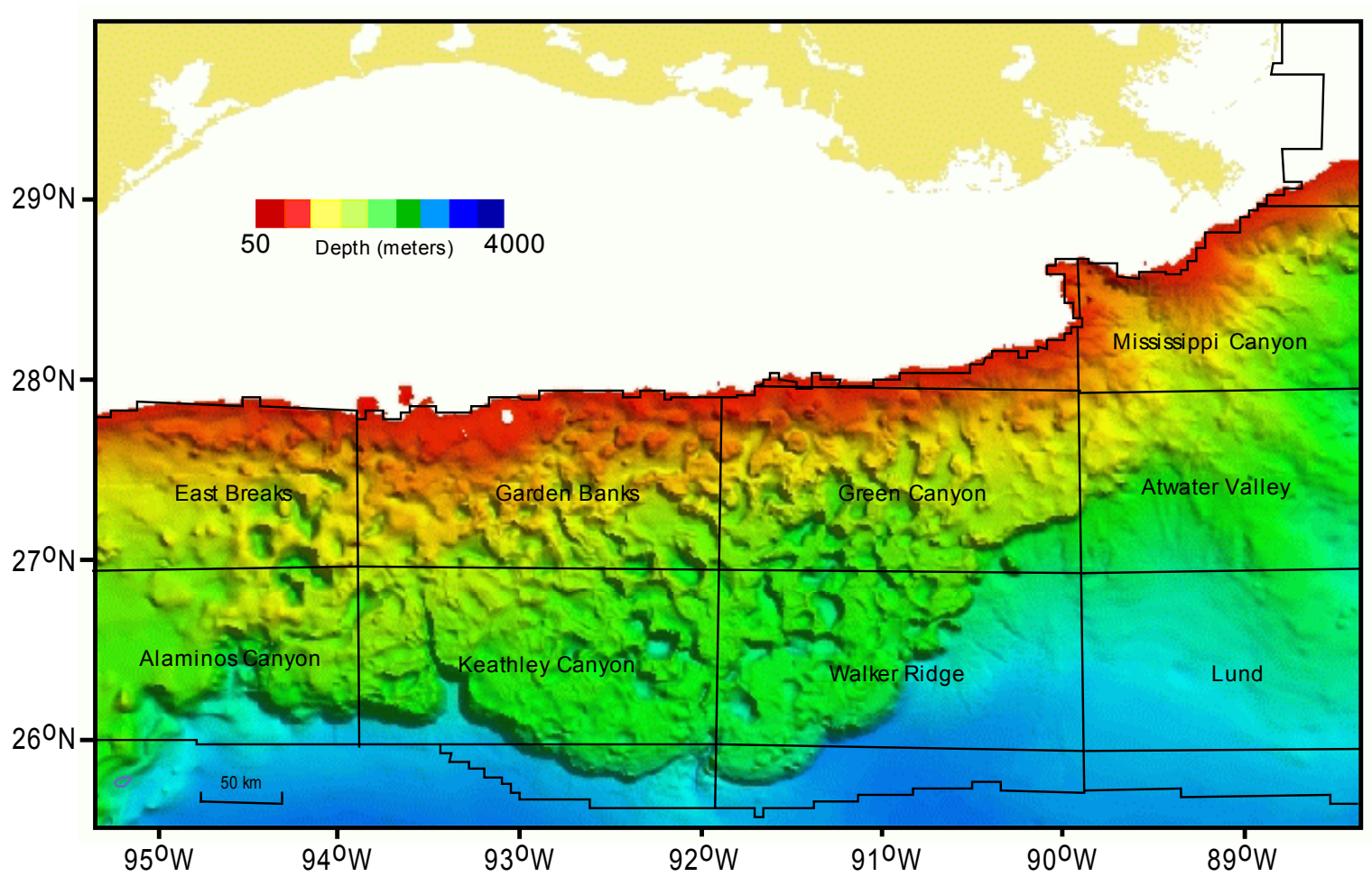


Figure 19. Bathymetric map of the Gulf of Mexico continental slope (after Liu and Bryant, 1999).

The Gulf slope (Texas-Louisiana slope) represents a bathymetrically complex and geologically dynamic salt basin in the Gulf of Mexico Salt Basin and comprises 120,000 sq km area of rise and basin seafloor. The average gradient of the slope is <1 degree. Slopes may be >20 degrees around some knolls and minibasins (Coleman et al., 1986). The extreme topographic relief of the slope is related to salt diapirism and salt withdrawal beneath the basins (Fig. 19). Intraslope basins are commonly surrounded by salt ridges and contain thick sections of Tertiary sediment (Bouma et al., 1978).

At present, the Gulf slope is affected by large sheet-like salt thrusts that extend from the shelf edge across the slope to the Sigsbee Escarpment, near the edge of the abyssal plain (Worral and Snelson, 1989). The Mississippi Canyon and Fan indicate the eastern boundary of the Gulf slope. The Mississippi Canyon is a submarine channel formed by slumping during the Late Pleistocene and has been partially filled during Holocene sea level rise (Coleman et al., 1986). The Mississippi Fan is a complex of overlapping fan lobes that were deposited during low sea level stands during Pleistocene (Moore et al., 1978).

The Mississippi Fan Foldbelt is a zone of geologic transition trending northeast-southwest (~350 km) along the lower Gulf slope. The Mississippi Fan Foldbelt represents the downdip limit of the Gulf of Mexico Salt Basin (e.g. Rowan, 1997). The Mississippi Fan Foldbelt is cored by autochthonous salt, and includes and Upper Jurassic through Lower Cretaceous section (Kennicutt et al., 1992; Wagner et al., 1994; Wenger et al., 1994; Sassen et al., 2001d). The Sigsbee Escarpment is an obvious feature at the base of the slope. The Sigsbee Escarpment is the lobate frontal edge of the Gulf salt

thrust province and is underlain by a complex system of salt ridges and overthrust tongues (Martin, 1984). The abyssal plain is to the south of Mississippi Fan Foldbelt and Sigsbee Escarpment. The abyssal plain is underlain by undeformed salt free sediments and has not been affected by either allochthonous or autochthonous salt (e.g. Wenger et al., 1994; Rowan, 1997).

Stratigraphic Framework

The stratigraphic setting of the Gulf of Mexico Salt Basin is largely the result of Mesozoic-Cenozoic sedimentation, which rapidly filled the basin during and since the Triassic (e.g. Perkins and Martin, 1985; Salvador, 1987). Cenozoic transgressive and regressive terrigenous sediments, underlain by Middle Jurassic to Late Cretaceous red beds, evaporites and carbonate rocks, are main components of the thick sedimentary section of the Gulf slope (McBride et al., 1998) (Fig. 20).

The basement of the Gulf slope is represented by thin transitional crust, which is located at depth 12-16 km below mudline. The crust is thought to be composed of Paleozoic metamorphic and igneous rocks (Buffler, 1991). Mesozoic syn-rift and post-rift strata contain non-marine siliciclastics and are overlain by evaporites, marine carbonates and shales (e.g. McFarlan and Mennes, 1991). Cenozoic strata include thick, siliciclastic wedges, which prograde along the northern margins of the basin, and allochthonous salt thrust and withdrawal features (e.g. Worrall and Snelson, 1989).

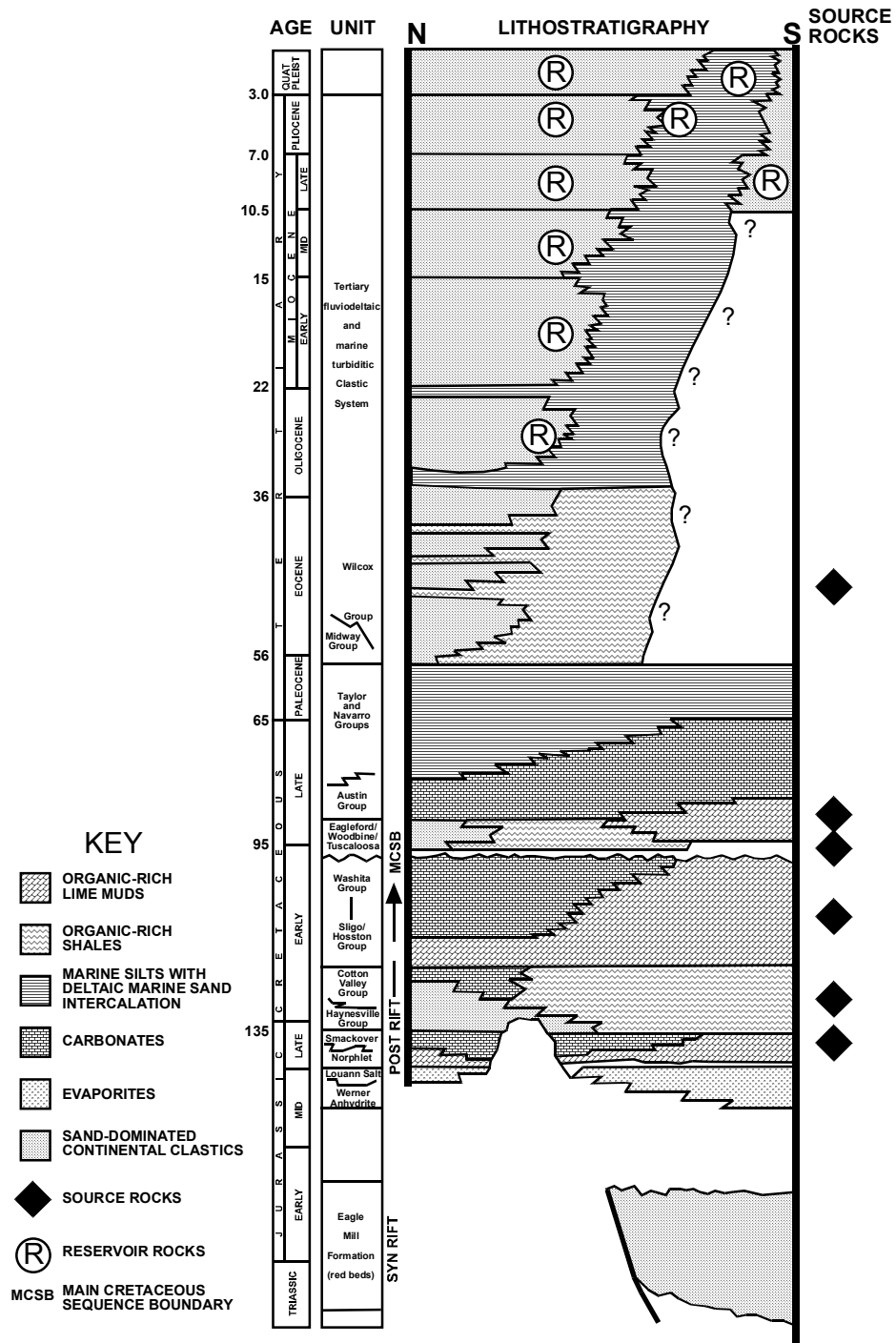


Figure 20. Generalized stratigraphic columnar section of the Gulf slope with probable source rocks and reservoirs highlighted (compiled after McBride et al., 1998 and Curtis, 1987).

Numerous regional unconformities and depositional hiatuses subdivide the Mesozoic and Cenozoic strata (e.g. Curtis, 1987; McBride et al., 1998).

Upper Triassic–Lower Jurassic red beds and volcanics (Eagle Mills Formation) filled rift basins and smaller grabens (e.g. Curtis, 1987). Following deposition of syn-rift Upper Triassic–Lower Jurassic sediments, during the Callovian, extensive and thick deposits of Louann salt (>4 km locally) and the underlying Werner anhydrite accumulated throughout the basin (Salvador, 1987). The Louann salt played an important role at later stages of basin evolution when it was deformed into salt domes and sub-horizontal thrust sheets piercing the Mesozoic-Cenozoic depositional system (Weimer et al., 1998).

During the Late Jurassic–Early Cretaceous, the basin was rimmed by broad and stable carbonate shelves, banks, and ramps (Curtis, 1987). Pelagic carbonate ooze and shale were deposited in the deeper portions of the basin. The Louann salt is overlain by an Upper Jurassic (Oxfordian) sandstone (Norphlet Formation) and a limestone (Smackover Formation). Upper Jurassic (Kimmeridgian) evaporites and red beds, which are followed by deltaic and marine shelf sandstones, shales and carbonates (Haynesville Group), overlie the Oxfordian deposits. Kimmeridgian units are succeeded by a thick sequence of deltaic and non-marine to near-shore deposits that extends into Earliest Cretaceous (Cotton Valley Group). The total thickness of Upper Jurassic rocks reaches ~3 km (e.g. Curtis, 1987; McBride et al., 1998).

Lower Cretaceous (Hauterivian through Lower Cenomanian) rocks overlap older rocks unconformably, forming a transgressive sequence over the Early Cretaceous

unconformity and hiatus (Curtis, 1987). The oldest Lower Cretaceous rocks throughout the province are terrigenous clastics (Hosston Group). These rocks are overlain by a system of mainly shelf carbonate and terrigenous clastics with intercalation of some evaporites and reef buildups (Sligo through Washita groups). The maximum thickness of known Lower Cretaceous slope and rise sediments is about ~4 km.

Following the widespread Middle Cretaceous unconformity (MCSB = Middle Cretaceous Sequence Boundary) (Buffler, 1991), which separates rocks of Lower Cretaceous from those of Upper Cretaceous (Late Cenomanian through Maastrichtian transgressive series), siliciclastic sediments began to dominate the stratigraphy. The oldest Upper Cretaceous unit (Woodbine-Eagleford-Tuscaloosa groups) is a terrigenous clastic, fluvio-deltaic and near-shore marine sequence that extends across the Early Cretaceous shelf edge, expanding in thickness across a series of growth faults (Curtis, 1987). Rocks of the conformable Austin Group are generally chalky (Austin and Selma chinks) and marly, whereas the overlying Taylor and Navarro Groups are marine terrigenous clastics. Downdip from the Lower Cretaceous shelf edge, the Upper Cretaceous rocks are slope shales, except for Tuscaloosa turbidities and Woodbine slump blocks (e.g. Curtis, 1987; McBride et al., 1998).

The Cenozoic sediments are largely terrigenous clastics, which were transported by the Rio Grande and Mississippi River drainage system from the Sevier and Laramide orogenies (Mann, 1987). Regressive basin-filling sequences comprise the sedimentary prism. These sequences consist of fluvial-inner deltaic massive sand facies, delta plain interbedded sand and shale facies, and marine prodelta-outer shelf to continental slope

shale facies, which may contain turbidite, submarine channel, and fan sands. Transgressive marine shales separate the regressive sequences.

Deltaic depocenters began prograding into the northwestern and northern portions of the basin during the Cenozoic (McBride et al., 1998). The depocenters are progressively younger to the east and towards the basin. Thick regressive sequences, deposited during Late Paleocene-Early Eocene (Wilcox Group), Middle to Late Oligocene (Frio Group), Miocene and Plio-Pleistocene times, represent major progradational pulses that constitute regressive phases (Curtis, 1987). Such changes resulted from variations in relative rates of sediment supply and subsidence, and sea-level change (Curtis, 1987). Growth faults developed at the progradational limit of each regressive unit, and extended upward in the section as deposition continued. Thus the growth faults, like the regressive sequences with which they are associated, are progressively younger towards the basin. The aggregate thickness of Cenozoic strata is about 10 km and locally exceeds 15 km.

Structural Setting

The Gulf of Mexico Salt Basin formed as a consequence of rifting, and subsequent crustal stretching and thinning during the Late Triassic-Early Jurassic (e.g. Pilger, 1981; McBride et al., 1998). The complex structural setting of the Gulf slope is the result of interplay salt deformation driven by rapid sedimentation rates. Mesozoic subsidence was deepest within the central portion of the basin because of thermal effects

(Pilger, 1981), and Cenozoic subsidence was deepest along the northern margin of the basin because of sediment loading. Humphris (1978) first suggested that large allochthonous salt masses are common features of the Gulf of Mexico Salt Basin. The entire slope is underlain by allochthonous and autochthonous salt that extends to the edge of Sigsbee Escarpment. Several tectono-stratigraphic models based on salt-tectonics and associated fault systems have been proposed to outline the structure of the Gulf of Mexico Salt Basin (e.g. Diegel et al., 1995; Weimer et al., 1998).

Diegel et al. (1995) defined a tectono-stratigraphic province map of the Gulf of Mexico Salt Basin mainly based on salt tectonics and consequent sedimentary basins (Fig. 21). They described eight structural non-genetic provinces: (1) a contractional foldbelt province at the toe of slope, (2) a tabular salt-minibasin province on the slope, (3) a Plio-Pleistocene detachment province on the outer shelf, (4) a salt dome-minibasin province, (5) an Oligocene-Miocene detachment province onshore and on the shelf, (6) an Oligocene Vicksburg detachment province onshore Texas, (7) an Upper Eocene detachment province, and (8) the Wilcox growth fault province of Paleocene-Eocene age. The Gulf slope is characterized by salt thrusts and minibasins where rapid deposition causes salt withdrawal (e.g. Worrall and Snelson, 1989; Weimer et al., 1998).

Salt systems affect the stratigraphic evolution of minibasins (Weimer et al., 1998). Salt systems determine the shifting locations and shape of minibasins through time. Each type of salt system is characterized by distinctive styles of salt bodies, folds, and faults. The evolution of each type of system determines whether there is adequate underlying salt to provide accommodation for turbidite sand deposits.

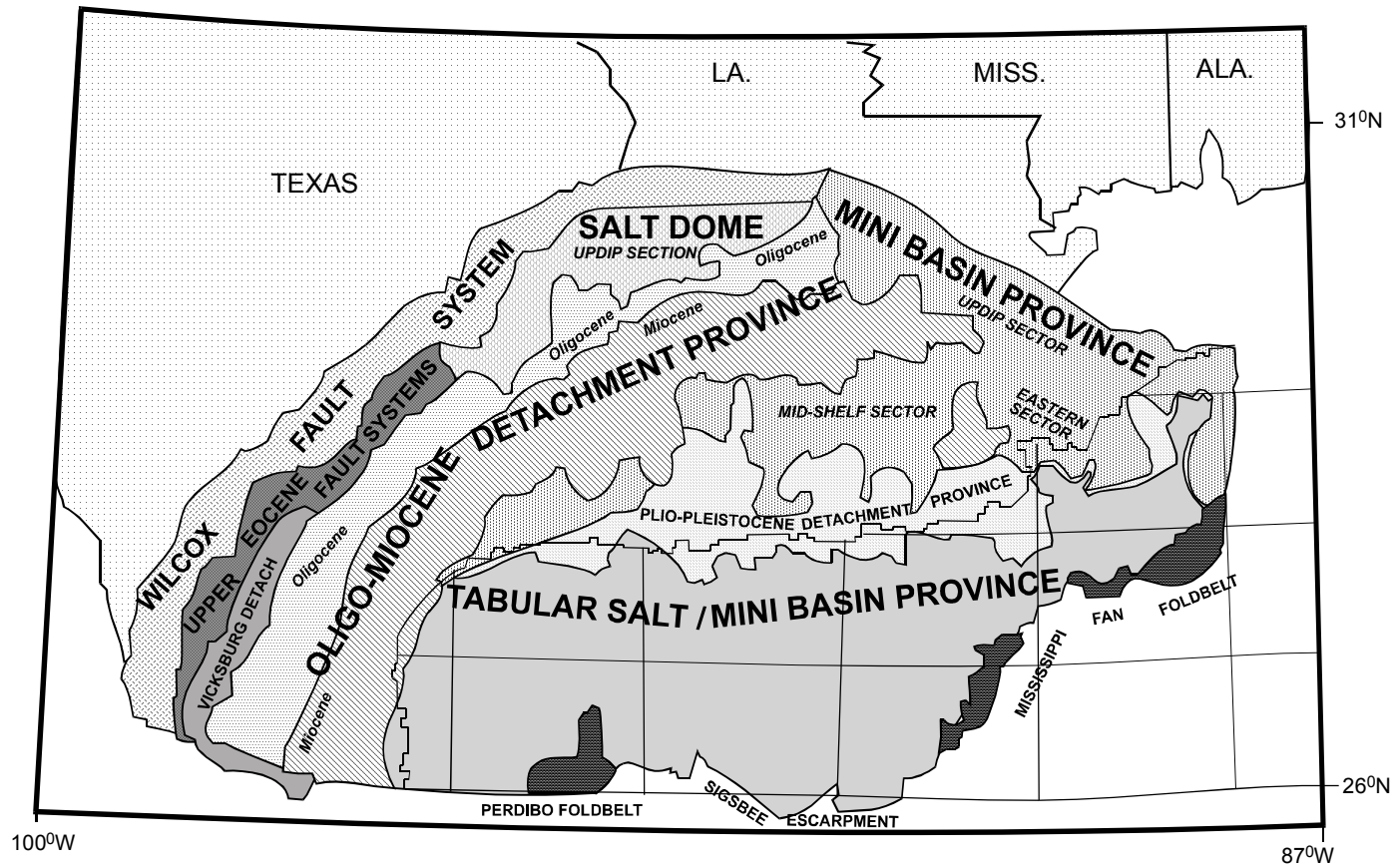


Figure 21. Tectono-stratigraphic provinces of the Gulf of Mexico Salt Basin (after Diegel et al., 1995).

Rowan et al. (1999) defined a “salt system” as a genetically and kinematically linked group of salt layers, diapirs, and welds with associated subsalt and suprasalt sediments. Rowan et al. (1999) emphasized that salt systems in the Gulf of Mexico form a complex network of interacting components. Rowan et al. (1999) classified the end-members of fault styles within this network. Fault families and fault welds are associated to different salt systems. Autochthonous salt system driven by gravity gliding and gravity spreading mechanisms are characterized by evacuation process as salt moves to upper allochthonous levels and by basinward movement of the entire overburden. Allochthonous salt system forms salt-tongue systems, salt-stock systems, and salt-nappe systems (Rowan, 1997).

Salt-tongue systems consist of isolated or combined sub-horizontal salt sheets that evolve with stepped counterregional or roho withdrawal styles (Diegel et al., 1995; Schuster, 1995). Salt-stock systems comprise bulb-shaped salt stocks that may coalesce to form canopies (Jackson and Talbot, 1989) during either stock growth or stock collapse (Rowan, 1995, 1997). Salt nappes progressively advance upward and basinward over large distance (tens to hundreds of kms) far from their feeders over geologically significant periods of time (Worrall and Snelson, 1989).

Most models for emplacement of allochthonous salt suggest that salt movement is upward and basinward from deeper sources along north-dipping (counterregional) feeder systems (e.g. Worrall and Snelson, 1989; Schuster, 1995; Diegel et al., 1995). An example of a counterregional system given by Schuster (1995) shows distinct layers of allochthonous salt with minor relief along the weld (or equivalent base of salt) (Rowan,

1995). Counterregional systems may include abundant listric growth faults that extend into the welds or salt sheets that may accommodate significant extension. These systems dominate at the outer continental shelf.

Another model for allochthonous salt emplacement explains salt stocks that gradually spread outward in all directions to form overhanging flanks (salt stock canopy systems) (e.g. McGuinness and Hossack, 1993; Rowan et al., 1994). The overhanging salt stocks eventually collapse and become sedimentary minibasins. The evacuated salt moves up and laterally to form sheets, tongues, and other secondary salt basins. Overhanging stocks may merge to form salt-stock canopies (Jackson and Talbot, 1989), either before collapse or during loading and associated salt flow. The main fault systems have an arcuate shape in plan view and are situated over lateral margins of minibasins (Rowan, 1995). These systems are more typical of the upper slope.

Seismic data obtained during petroleum exploration suggest that faults are ubiquitous in the Gulf of Mexico Salt Basin (Rowan et al., 1999). Most faults are related to deformation of the Jurassic Louann salt in the Cenozoic. Although extensional faults predominate in the basin, growth, listric, and thrust fault systems are widely developed on crest and flanks of individual salt domes and salt soles after withdrawal of allochthonous salt bodies (e.g. Cook and D'Onfro, 1991; Rowan, 1995; Schuster, 1995; Rowan et al., 1999). This diversity reflects the linked nature of gravity-driven deformation as the sedimentary overburden spreads under its own weight and slides basinward on salt detachments (e.g. Jackson and Galloway, 1984; Worrall and Snelson, 1989; Diegel et al., 1995).

Rowan et al. (1999) have proposed another classification for salt related fault systems in the Gulf of Mexico Salt Basin. This classification is geometric. The system groups faults into fault families and defines the end-members of fault styles within the network. The classification includes a number of extensional fault families divided into symmetric grabens and asymmetric arrays having a dominant dip direction. Asymmetric fault families are more common and larger than symmetric fault families in the Gulf of Mexico Salt Basin. They also define two types of contractional fault families, strike-slip fault family as lateral, and several types of fault welds.

Intraslope basins (Bouma et al., 1978) or minibasins (e.g. Koch et al., 1998) vary in size, shape, and depth, and are widely distributed in the Gulf slope. They are characterized by relatively smooth interior plains and steep walls. The basins have a circular or elliptical shape in map view (Pratson and Ryan, 1994). The term minibasin will be used exclusively. Minibasins are flanked by salt walls. Many of them are flooded by autochthonous or allochthonous salt. Typically, minibasins contain sediment accumulations >6 km. Koch et al. (1998) developed the classification for minibasins using stratal and allochthonous salt geometries. They distinguished five basin types: (1) ramp, (2) welded, (3) welded listric, (4) primary, (5) salt-floored (Fig. 22).

Basins differ with respect to migration, and trapping of hydrocarbons. Ramp basins are the most effective and salt-floored basins are the least Koch et al. (1998). As basin fill changes through geologic time, each of the basins has differing capability to

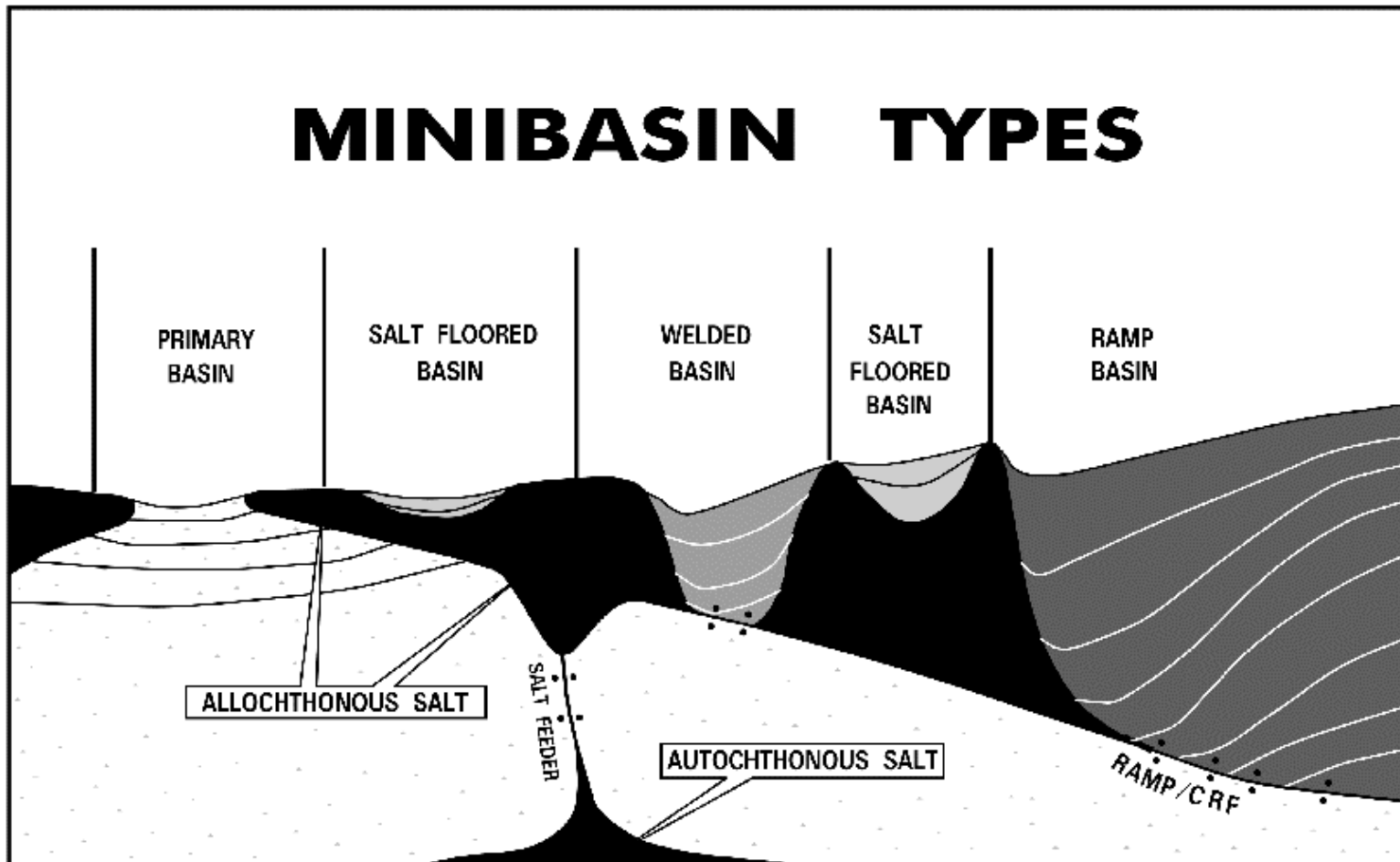


Figure 22. Types of minibasins in the Gulf slope (after Koch et al., 1998).

receive and distribute the hydrocarbons. They receive hydrocarbons by a complex plumbing system from sources at greater depths below the basins. Ramp basins have attractive plumbing and enhanced trapping focus (Koch et al., 1998). Salt-floored basins have least access to underlying sources. Strata in the salt-floored basins are separated from hydrocarbon migration pathways. The lower part of the sedimentary section in minibasins is composed of sand-prone ponded successive basin-fill facies (turbidite sands). The upper part of the sedimentary section consists of a shale-prone slope-bypass succession of facies (Prather et al., 1998).

Geologic Evolution

The Gulf of Mexico Salt Basin was formed by Mesozoic breakup of the supercontinent Pangea as North America separated from South America and Africa (Salvador, 1987) (Fig. 23). Two main rifting episodes occurred in Late Triassic and Middle Jurassic producing a series of onshore and offshore rift basins (Weimer et al., 1998). During Late Triassic-Early Jurassic, the occurrence of initial rifting led to the formation of the nascent basin filled by non-marine and volcanic sediments. The widening and subsiding basin was first flooded during the Middle Jurassic. Flooding alternated with evaporation to produce widespread evaporites, thicker than 4 km in the Gulf of Mexico Salt Basin. Louann (Callovian) salt associated with the second

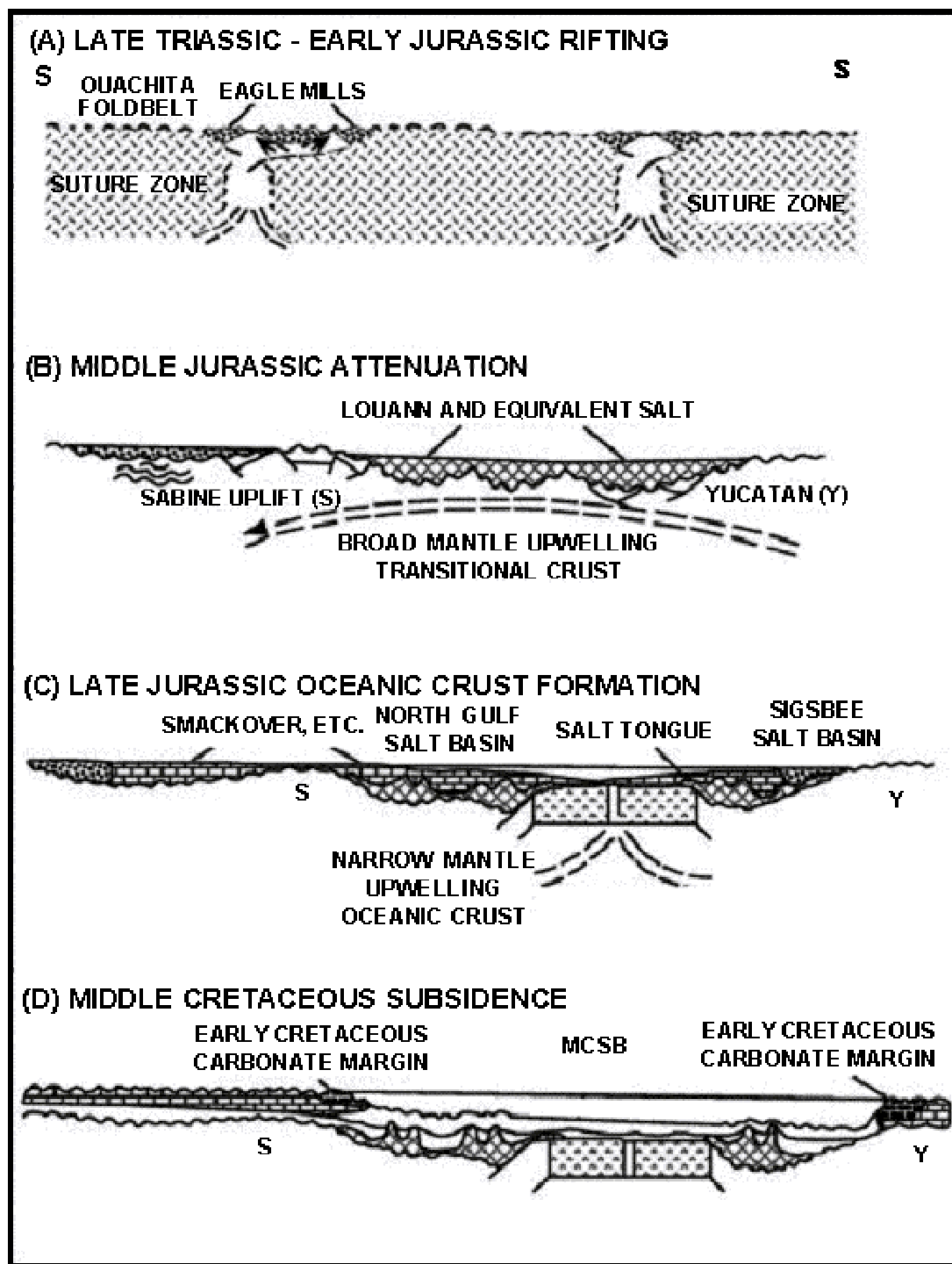


Figure 23. Schematic cross sections illustrating the early evolution of the Gulf of Mexico Salt Basin (after Buffler, 1991).

period of rifting (Worrall and Snelson, 1989). Then a brief episode of seafloor spreading occurred in the Late Jurassic (Buffler and Sawyer, 1985) (Fig. 23).

The thick salt layer was separated into northern Louann and southern Campeche salt provinces by new oceanic crust in the central part of the basin (Salvador, 1987; Humphris, 1978). Widening of the basin allowed to deposition of marine sediments. Deep-water sediments were deposited on the newly formed oceanic crust while shallow marine sediments were deposited on the broad shelf environments of adjacent transitional crust (Buffler and Sawyer, 1985).

Through the Early Cretaceous, basin subsidence because of cooling of the lithosphere was accompanied by the development of carbonate platforms surrounding the basin (Fig. 23). At that time, the Gulf of Mexico Salt Basin was a deep-water basin surrounded by the steep carbonate platforms of Florida and the Yucatan and underlain by thick salt deposits (Worrall and Snelson, 1989) (Fig. 23). The Late Cretaceous was a time of widespread marine chalk, marl and shale sedimentation.

Major changes took place in sedimentation rates and in depositional patterns of the Gulf of Mexico Salt Basin by the Late Cretaceous-Early Cenozoic in response to the Laramide orogeny, and thrust sheet emplacement in the western Cordillera. During the Cenozoic, the basin was fed by sediments through complex alluvial systems. Only terrigenous sediments were deposited in the Gulf of Mexico Salt Basin during the Tertiary (Worrall and Snelson, 1989).

The sedimentary depocenters shifted from west to east throughout the Cenozoic so that the sediments were transported into the Louisiana area of the north-central Gulf

of Mexico Salt Basin. The Pleistocene depocenters is located near the present shelf edge off central Louisiana (Worrall and Snelson, 1989). The rapid siliciclastic sediment loading mobilized and deformed underlying Louann salt. The formation and withdrawal of salt occurred progressively basinward through time in response to basinward migration of the major Cenozoic sedimentary depocenters (McBride et al., 1998).

The deformation and displacement of salt deposits strongly influenced the Cenozoic structure of the Gulf of Mexico Salt Basin causing the development of growth faulting. The Gulf slope, in particular, is affected by the large salt thrusts penetrated by salt withdrawal basins where thick and relatively undeformed sediments accumulated (Worrall and Snelson, 1989). The stratigraphically and structurally complex Cenozoic sediments are responsible for most of the hydrocarbon accumulations in the Gulf of Mexico Salt Basin.

Petroleum Systems

A petroleum system is defined by Magoon and Dow (1994) as a natural system that encompasses active source rocks, all genetically related oil and gas accumulations, and all geologic elements and processes that are essential for hydrocarbon trapping and accumulation. The essential elements comprise a petroleum source rock, reservoir rock, seal rock and overburden rock. Processes include source rock maturation, trap formation, and the generation-migration-accumulation of petroleum. These essential elements and

processes must be linked in time and space so that source rock kerogen is successfully trapped in a hydrocarbon accumulation.



Multiple Mesozoic-Cenozoic source intervals have been recognized as the source of petroleum in reservoirs of different ages in the Gulf of Mexico Salt Basin (Wenger et al., 1994) (Fig. 24). Potential source rocks vary in age (Upper Jurassic to Lower Tertiary) and in kerogen types (Type II and Type III) (Wenger et al., 1990, 1994). Oxfordian, Tithonian, Lower Cretaceous, and Eocene source rocks are believed to be responsible for the majority of oil and gas accumulations in the Gulf slope (Sassen 1990a, b; Wenger et al., 1990, 1994; Kennicutt et al., 1992; Wagner et al., 1994). Most oil is likely from Upper Jurassic sources. The other sources are fairly significant as well. Based on oil typing, Oxfordian, Tithonian, and Lower Cretaceous source rocks are considered to be Type II kerogens. The Eocene source rocks may be either Type II or Type III kerogens (e.g. Wagner et al., 1994; Wenger et al., 1994)

Upper Jurassic petroleum system is the major source of oil and gas found in reservoirs of the Gulf slope (Sassen, 1988, 1990a; Sassen and Moore, 1988; Wenger et al., 1990, 1994) (Fig. 24). Oils derived from Oxfordian carbonate source rocks (Smackover Formation) are common across the rim of the Gulf of Mexico Salt Basin (Fig. 24) (Kennicutt et al., 1992; Wenger et al., 1994; Sassen et al., 2001d). Smackover Formation is a carbonate source rock with significant regional variation in organic facies (Sassen, 1988, 1990a). Sassen (1989) described Type I oil characterized by origin from a source rock with algal kerogen preserved in a persistently



Northern Gulf of Mexico Oil Types

Source Age and Oil types



Lower Tertiary (centered on the Eocene)

- Tertiary Marine and Intermediate  1
- Tertiary Terrestrial  2



Upper Cretaceous (centered on the Turonian)

- Marine, no Tertiary influence  3
- Calcareous-moderate sulfur, no Tertiary influence  4


Lower Cretaceous (centered on the Aptian)

- Carbonate-elevated salinity  5
- Calcareous-moderate sulfur  4

Uppermost Jurassic (centered on the Tithonian)

- Marine-high/moderate sulfur  6
- Calcareous-U.Jr or L.Cr (?)  7

Upper Jurassic (centered on the Oxfordian)

- Carbonate-elevated salinity  8

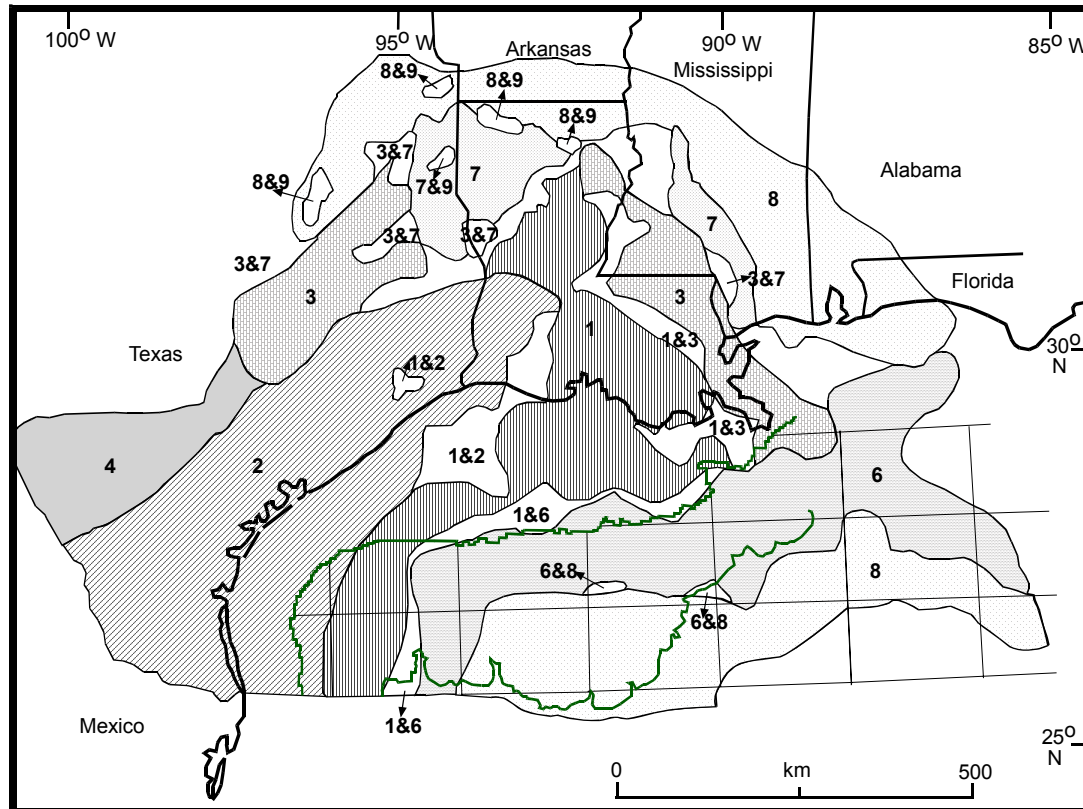


Figure 24. A regional map of the Gulf of Mexico Salt Basin showing petroleum systems (after Wenger et al, 1994).

anoxic carbonate depositional environment. The Smackover Type II oils differ because the source rock was affected by limited influx of clay rich sediment and higher plant organic matter to a carbonate source rock. Kennicutt et al. (1992) suggest that the biomarkers of upper slope oils are analogues in some respects to the higher sulfur Type II oils of Sassen (1989).

Oils derived from Tithonian source rocks are very common on the upper Gulf slope (Wenger et al., 1994) (Fig. 24). Tithonian source rocks are organic rich calcareous shales that typically contain Type II kerogens (Wenger et al., 1994). Oils derived from Tithonian source rocks are high sulfur in character.

Lower Cretaceous source rocks are carbonates and calcareous shales. Lower Cretaceous oils are with moderate sulfur content (Wenger et al., 1994). Thermal modeling of the upper Gulf slope, based on data from Mississippi Canyon block, indicates that Lower Cretaceous is the only thermally mature source rock for oil generation within Early Cenomanian-Early Tertiary interval (Wagner et al., 1994).

Eocene oil types (marine, intermediate and terrestrial) have been tied to Wilcox Group source rocks and are consistent with paleofacies distributions for the Eocene deltaic systems (Sassen and Chinn, 1990; Wenger et al., 1990; 1994). Eocene oils and gases are prevalent on the Gulf of Mexico shelf and extend onshore (Wenger et al., 1994) (Fig. 24). Eocene oils and gases are fairly significant on the upper slope (Wenger et al., 1994). The kerogens in the Eocene source interval have been interpreted as both Type II (Wenger et al., 1994) and Type III (Kennicutt et al., 1992).

Reservoir rocks are mainly of Miocene and Plio-Pleistocene siliciclastic turbidites in the petroleum systems of the Gulf slope (Cook and D'Onfro, 1991; Holman and Robertson, 1994; Weimer et al., 1998). Reservoir rocks are generally sand-sized, mildly overpressured, unconsolidated, and uncemented (Weimer et al., 1998). Reservoirs are highly permeable and porous (Weimer et al., 1998). The siliciclastic turbidites were deposited in intraslope basins affected by active salt tectonics during Cenozoic (Weimer et al., 1994, 1998; Rowan and Weimer, 1998).

The petroleum systems of the Gulf slope are affected considerably by the presence of salt. Source interval maturation in the Gulf of Mexico Salt Basin may be linked to the movement of salt (McBride et al., 1998). High thermal conductivity of allochthonous salt retards the thermal maturation of underlying source rocks by transferring heat upward from deeper strata keeping it anomalously cool (Nelson et al., 2000).

The Gulf slope (Plio-Pleistocene Detachment Province and Tabular Salt-Minibasin Province of Diegel et al., 1995) (Fig. 21) is dominated by Upper Jurassic petroleum system. The generation-migration-accumulation of hydrocarbons in the petroleum systems of the Gulf slope began during Late Cretaceous and continues to the present (McBride et al., 1998). Because the petroleum systems were significantly affected by the evolution of allochthonous salt that is widely distributed in the basin, the critical moment of peak oil generation for each of the potential source rocks varies as a function of overlying allochthonous salt evolution (McBride et al., 1998).

The Oxfordian source interval enters the early oil window during the Eocene (~40 Ma) (Nelson et al., 2000). The Oxfordian enters the peak oil window during the Middle Miocene (~12.5 Ma). At present, the Oxfordian source interval is mainly in the late oil window with pockets lying in the wet and dry gas windows (Nelson et al., 2000). The main petroleum system of the slope, Tithonian source interval, enters the early oil window during the Eocene (~40 Ma) and reaches the peak oil window during the Middle Miocene (~15.5 Ma). Currently, the Tithonian source interval rests in the wet and dry gas windows (Nelson et al., 2000). The Eocene source interval enters the early oil window during the middle Miocene (~15.5 Ma) and reaches the peak oil window during the late Miocene (~8.8 Ma). Presently, the Eocene source interval is in the wet and dry gas windows (Nelson et al., 2000).

Petroleum migration pathways in the basin are believed to be predominantly vertical along low permeable strata, by buoyancy, overpressures and faulting (Nunn and Sassen, 1986; Curtis, 1989; England et al., 1991; Sassen et al., 1993a; Waples, 1994). Allochthonous salt, which is impermeable, forms major barriers to vertical migration and deflect migration pathways laterally (McBride et al., 1998). Two elements drive hydrocarbon migration: (1) deep-cutting faults and diapiric salt connecting source to reservoir, and (2) differential compaction of the source rock section (e.g. Sassen, 1990a, b; Wagner et al., 1999). The majority of the traps, leading accumulation of hydrocarbons, were formed during the Pliocene-Pleistocene in the Gulf of Mexico Salt Basin (McBride et al., 1998).

Essential elements of the petroleum systems in the Gulf slope include source rocks of Oxfordian Smackover Formation, Tithonian shales, Lower Cretaceous calcareous rocks, and Eocene Wilcox Group; siliciclastic turbidite reservoirs of Miocene and Plio-Pleistocene, allochthonous salt as migration barriers, and Cenozoic thick overburden strata (e.g. Sassen, 1990b; Wenger et al., 1994; McBride et al., 1998).

Gas Occurrence and Associated Features

Gas in the Gulf slope has both bacterial (biogenic) and thermogenic sources. Methane is the principal constituent (up to 100%) of bacterial gas that is formed by anaerobic microorganisms at low temperature and shallow depth in sediments (Rice and Claypool, 1981; Whelan et al., 1986). Rivers supply both organic material and sediment to the Gulf slope, resulting in significant source rocks for bacterial gas at shallow depths (Anderson and Bryant, 1989). In contrast, thermogenic gas is characterized by relatively high amount of C₂₊ hydrocarbons formed by thermal degradation and cracking of organic matter at higher temperatures and greater depths (Schoell, 1988). Therefore, the presence of thermogenic gas within a few hundred meters below the seafloor indicates that the gas migrated to the seafloor along conduits such as faults. The occurrence of thermogenic gas in shallow sediments associated with faults, mud volcanoes, and diapirs supports the suggestion that salt and fault related structures served as conduits for migration of thermogenic gas from deep subsurface petroleum system.

Gas is present in relative large seep features (e.g. seafloor areas of 250 to 500 m in diameter) of the Gulf slope at subsurface depth of less or more than 100 m (Anderson and Bryant, 1990). The majority of gas seeps contain free gas, gas hydrate, oil, brine and water at the seafloor. Most hydrocarbons are eventually dispersed or lost to the seafloor because of poor trapping efficiency on the slope (Sassen, 1998). The total volume of hydrocarbons escaping from seeps to the water column is estimated as $2.5-6.9 \times 10^5$ bbl/yr for the slope region (Mitchell et al., 1999).

The Gulf slope has been well documented as a natural laboratory where a strong relationship between the regional distributions of hydrocarbon seeps and the distribution of subsurface accumulations of oil and gas may be compared (e.g. Kennicutt et al., 1988; Sassen et al., 1994; Sassen, 1998). Authigenic carbonate minerals, mud volcanoes and shale diapirs, gas hydrates, and chemosynthetic communities are the main features associated with gas occurrence and massive hydrocarbon seepage in the Gulf slope (Hovland and Judd, 1988; Sassen et al., 1994, 2001b; Roberts and Carney, 1997).

Authigenic Minerals

Carbonate mounds of variable dimensions, with as much as 10 m of vertical relief, occur at the seafloor and carbonate nodules in unconsolidated sediments, are the common features occurring over the entire depth range of the Gulf slope (Roberts et al., 1990; Roberts, 1995). The major carbonate minerals are high magnesium calcite, aragonite and dolomite (Roberts and Carney, 1997). Authigenic carbonate rock significantly influences sea-bottom topography over salt diapirs and near faults. Carbon

isotopic properties of carbonate samples from hydrocarbon seeps demonstrate an origin precipitates as a consequence from microbial hydrocarbon oxidation because the carbonate carbon is strongly depleted in ^{13}C (Roberts et al., 1990).

Barite is a minor authigenic mineral indirectly related to hydrocarbon seepage, especially in associated with brines. Barite chimneys of 5-8 cm in diameter and barite crusts 3-10 cm thick are found at several sites in the Gulf slope (Fu et al., 1994; Fu and Aharon, 1997). The barite is proposed to be precipitate by mixing of seawater and fluids advecting with hydrocarbons from the deep subsurface petroleum system (Fu and Aharon, 1997).

Mud Volcanoes and Shale Diapirs

Submarine mud volcanoes and seafloor piercing shale diapir have been found on continental shelves and slopes around the world (Hovland and Judd, 1988; Milkov, 2000). A mud volcano indicates an eruption or surface extrusion of fluid mud or clay, with deposits accumulating around the vents (Hedberg, 1974). Mud volcanoes show a conical or volcano-like shape and are associated with salt and shale diapirs, fractures, and folds. Mud volcanoes vary in diameter from 20 cm to 600 m, and show relief from several cm to more than 35 m on the Gulf slope (Neurauter and Roberts, 1994; Kohl and Roberts, 1995). Sediment in craters and mud flows of mud volcanoes range in age from Middle Miocene to Pleistocene (Kohl and Roberts, 1995). Mud volcanoes are major sources of natural oil slicks observed at the sea surface in the Gulf of Mexico (Roberts and Carney, 1997).

Gas Hydrate

The Gulf slope gas hydrate province is one of the best studied in the world. Natural gas hydrate is a mineral in which hydrocarbon and non-hydrocarbon gases are held by hydrogen bonding within rigid cages of water molecules (Sassen and MacDonald, 1997; Sassen et al., 1999a). Natural gas hydrate may form in marine and terrestrial environments where sufficiently low-temperature and high-pressure occur with abundant gas and water are satisfied (Sloan, 1998).

In the Gulf slope, gas hydrate has been discovered at >50 sites at water depth ranging from 440 m to >2400 m by shallow coring, deep ocean drilling, and research submersible operations (Pflaum et al., 1986; Sassen et al., 1999b). Both bacterial and thermogenic gas hydrates have been found (Brooks et al., 1986). Gas hydrate sometimes outcrops on the seafloor (MacDonald et al., 1994). Gas hydrate affects geochemical processes in chemosynthetic communities, and hydrate bound methane is altered by microbial oxidation (Sassen et al., 1998). This may expand the potential boundaries of life in extreme environments (Sassen et al., 1998).

Chemosynthetic Communities

Cold seep complex chemosynthetic communities associated with hydrocarbon seeps have been discovered at many locations in the Gulf slope (e.g. Kennicutt et al., 1985; MacDonald et al., 1989). They are primarily associated with sediments containing free hydrocarbon gases, gas hydrate, microbially oxidized oil and authigenic minerals (Kennicutt et al., 1988; Sassen et al., 1994, 1999b). Methane-rich fluid from either

bacterial or thermogenic sources is necessary, but production of hydrogen sulfide by bacterial sulfate reduction also plays a key role in chemosynthetic communities (Sibuet and Olu, 1998).

In the Gulf slope, the number of known chemosynthetic communities exceeds 40, ranging in water depth from a few hundred meters to 3000 m (MacDonald et al., 1989). The chemosynthetic communities at hydrocarbon seeps include bacterial mats, tube worms, seep mussels, and epibenthic and infaunal clams (Kennicutt et al., 1988; Brooks et al., 1989; MacDonald et al., 1990). Community development is believed to be closely linked to the geological and geochemical processes of seepage (MacDonald et al., 1989; Sassen et al., 1994; Carney et al., 1999).

Bacterial mats are mainly composed of the giant bacterium *Beggiatoa*, which occur at many seep sites at the interface between reducing sediment and the oxygenated water column (Sassen et al., 1993b). The *Beggiatoa* species oxidize hydrogen sulfide derived from sulfate reduction following hydrocarbon oxidation in anoxic conditions. The mats serve as a biologic barrier to retard movement of fluids in and out of sediment (Sassen et al., 1993b).

CHAPTER IV

STUDY AREA, SAMPLES, ANALYTICAL METHODS, AND DATA

Natural gas accumulations and gas geochemistry are worth studying particularly because gas is increasing in economic importance. Insights to the molecular and isotopic properties of natural gas accumulations along the Gulf slope are helpful in understanding the origin of the gas, source rock maturation, how migration conduits evolve during geologic time and how such a complex system, including many differences in hydrocarbon properties between nearby fields, is created in the basin. In this study, geochemical assessment of gaseous hydrocarbons is carried out on the molecular and isotopic data of natural gas samples from reservoirs and vent sites of the Gulf slope.

Study Area

The Gulf slope is a natural laboratory where the relationship between oil and gas accumulations and hydrocarbon seeps may be studied. The Green Canyon (GC) and Viosca Knoll (VK) areas contain many oil and gas reservoirs associated with prolific seepage. The areas lie in the large belt across the Gulf slope that includes seafloor gas and oil seeps, gas hydrates, chemosynthetic communities, authigenic carbonates and subsurface oil and gas fields (Roberts and Aharon, 1994; Sassen et al., 1994, 2001a; MacDonald et al., 1996) (Fig. 25).

Three representative oil and gas fields and associated seep and vent sites within the GC and VK areas were selected for this study. These are Jolliet Field, Genesis Field and Petronius Field. Jolliet Field (GC 184) is in the western part of the GC protraction area, Genesis Field (GC 160/161) is situated in the eastern part of GC area and Petronius Field (VK 786) is in the eastern most VK protraction area. These areas offer

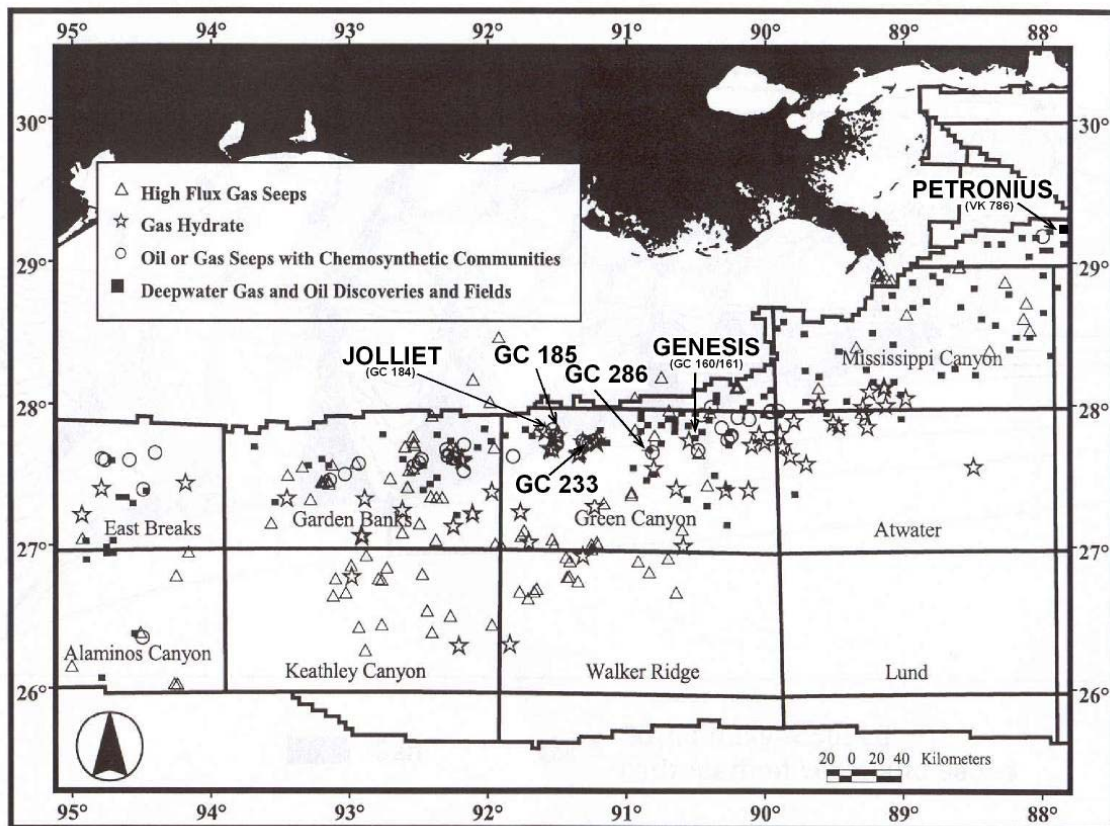


Figure 25. Map of the Gulf slope illustrating study area (selected subsurface gas accumulations and associated vent sites) in context of other subsurface hydrocarbon discoveries, seeps with chemosynthetic communities and gas hydrate occurrences (after Sassen et al., 2001c, 2002).

an opportunity where geology and hydrocarbon geochemistry may be synthesized to characterize the source of the gas, and to correlate the gas to each other, and to associated seep and vent sites (Fig. 25).

Jolliet Field

Jolliet Field is an oil and gas accumulation in eastern GC 184. A connection between an oil/gas accumulation in the subsurface and seep features from depth to the seafloor has been documented (Kennicutt et al., 1988; Sassen et al., 2001a). Water depth increases from ~250-300 m in the northwestern portion of the area to ~800 m to the south (Milkov and Sassen, 2000). Thermogenic gas hydrate, associated chemosynthetic communities, and authigenic carbonate rocks are the important seep related features within this area (Sassen et al., 2001a). Oil and gas are trapped in Pliocene-Pleistocene turbidite reservoir sands at burial depths in the ~1.7 to 3.1 km range (Cook and D'Onfro, 1991).

Jolliet Field is associated with a deep salt withdrawal basin that provides hydrocarbon charge (Fig. 26). Cook and D'Onfro (1991) studied the structural evolution of Jolliet Field. Rapid subsidence and filling of a salt withdrawal basin to the east in GC 185 occurred during the late Pleistocene-Holocene (Cook and D'Onfro, 1991). Oil and gas of Jolliet Field are produced from structural traps sealed and compartmentalized by normal faults that attained their present configuration in the Late Pleistocene-Holocene (Cook and D'Onfro, 1991).

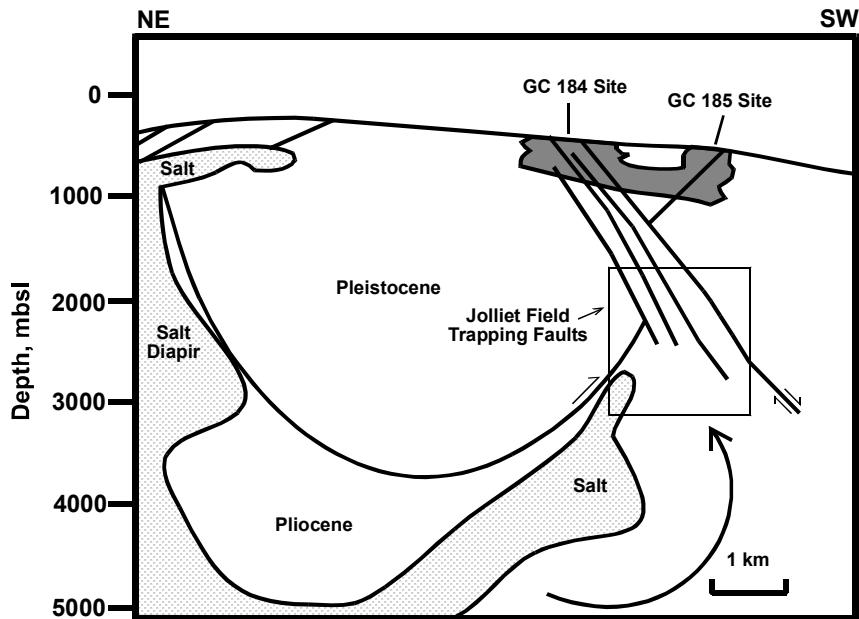


Figure 26. Diagrammatic cross section (northeast-southwest) through Jolliet Field on GC 184 and GC 185 sites (after Milkov and Sassen, 2000).

Biomarkers, carbon isotopic properties and geochemical correlation of oil and gas from Green Canyon study area suggest that there is a link to deeply buried, mature Upper Jurassic source facies (e.g. Kennicutt et al., 1988; Sassen et al., 2001a). Vertical migration of fluids is related to actively moving salt and faults, resulting in venting on the seafloor. Shallow reservoirs of Jolliet Field contain oil altered by biodegradation (Kennicutt et al., 1988; Sassen et al., 1993a, 1998) whereas deeper reservoirs contain oil that is not extensively altered by non-thermal alteration processes (Thompson and Kennicutt, 1990). The absence of major reservoir gas alteration in Jolliet Field is consistent with geologically recent migration and accumulation of oil and gas, and

ongoing charge to Jolliet Field of disassociated gas from the subsurface hydrocarbon system (Sassen et al., 2001a, c).

The GC 185 site near Jolliet Field is a fault related seep feature on the upper Gulf slope in ~540 m water depth. The site (27°45.7'N and 91°30.5'W) is a seep mound that receives hydrocarbon gas along a fault that is antithetic to the growth faults that trap the oil and gas of Jolliet Field on GC 184 (Fig. 26). The geology of the GC 185 salt withdrawal basin favors migration along active fault conduits. The major growth faults on the eastern edge of Jolliet Field that intersects the seafloor on GC 184 are active sites of hydrocarbon venting (Brooks et al., 1984, 1986).

Significant venting of thermogenic gas to the water column occurs in the GC 185 at the Bush Hill site (Sassen and MacDonald, 1997). This site is characterized by gas hydrate mounds outcrop that on the seafloor. Sediments capping hydrate mounds contain bacterially oxidized crude oil, free gas, dispersed gas hydrate nodules, and authigenic carbonate minerals depleted in ^{13}C (MacDonald et al., 1994; Sassen et al., 1994). The site is known as “Bush Hill” because of its complex chemosynthetic communities including bacterial mats (*Beggiatoa*), methanotrophic mussels and clusters of tube worms (MacDonald et al., 1989). The molecular and carbon isotopic properties of the vent gas collected at Bush Hill site are sufficiently similar to reservoir gas of Jolliet Field in order to correlate them (Sassen et al., 1998; Sassen et al., 2001a, b).

The GC 233 site is an anoxic brine pool at a water depth of ~640 m (Sassen et al., 1999b). The brine pool arises from fluid flow along a salt-related fault (Reilly et al., 1996). The brine pool is rimmed by methanotrophic mussels, whereas tube worms and

other chemosynthetic fauna are present in low abundance (Sassen et al., 1999b). Dissolved methane of bacterial origin saturates the brine itself, and free gas vents from the brine pool to the water column. The hydrocarbon geochemistry of the brine pool is dissimilar to that of the GC 185 site in that bacterial methane dominates (MacDonald et al., 1990)

Genesis Field

Genesis Field is an oil and gas field located eastward of Jolliet Field at depth beneath GC blocks 205, 160 and 161 in the Green Canyon protraction area. The field is a complexly faulted salt-cored anticlinal trap (Sassen et al., 2002) (Fig. 27). Water depths over the area range from 762-855 m. Production of oil and gas from the field is mainly from three turbidite sand units with true vertical depth ranging from ~3509-4184 m subsea (Rafalowski et al., 1996).

Deep subsurface reservoir sands of Genesis Field are Late Pliocene to Early Pleistocene. It is believed that oil and gas of Genesis Field originated from prolific Mesozoic source rocks, which became generative in the recent geologic past (Sassen et al., 1994), like most other hydrocarbons in reservoirs of the central Gulf slope (Wenger et al., 1994). Compositional data from gas and oil samples of Genesis Field suggest that there is reservoir compartmentalization, a complex migration history and effects of non-thermal alteration processes such as biodegradation, water washing and evaporite fractionation (Beeunas et al., 1999).

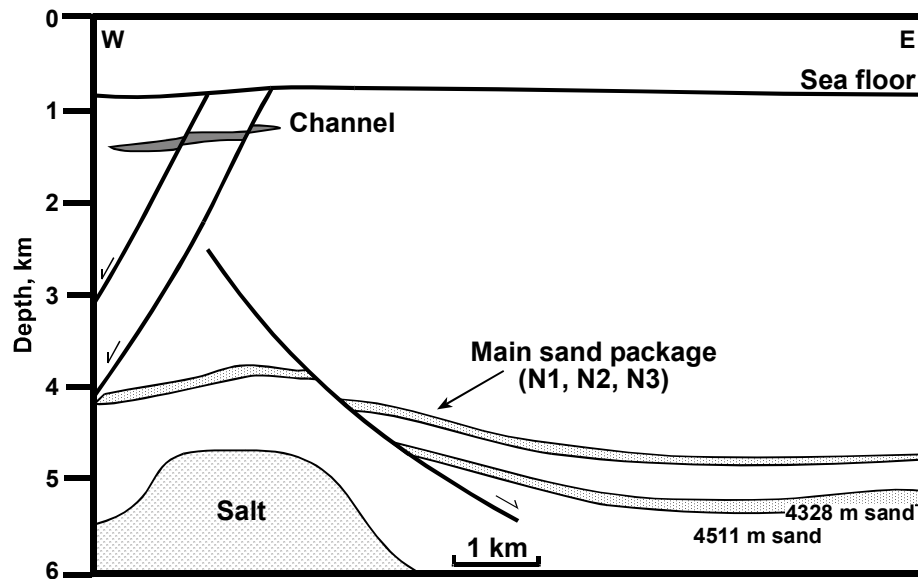


Figure 27. Schematic west-east cross section of Genesis Field showing the structure is a salt-cored anticline (after Sassen et al., 2002).

Gas and oil in Genesis Field most probably charged the trap by a combination of vertical migration upsalt followed by lateral migration along sand carrier beds (Sassen et al., 2002). Piston cores on the sea floor on GC 205 contained thermogenic gas hydrate, free gas, and biodegraded oil along an active fault scarp (Brooks et al., 1986). The main salt-cored growth fault is most probably a migration conduit to the sea floor on GC 205 site (Sassen et al., 2002).

The GC 286 site located southwest portion of Genesis Field is a newly discovered gas and oil seep sites. A mud volcano, which is significant feature for high flux venting of hydrocarbon gases to the water column (Milkov, 2000), is located on the GC 286 site (27°40.4'N and 90°49.7'W) at ~839 m water depth (Sassen et al., 2002).

Gas was observed to vent to the water column at GC 286 from the rim of a mud volcano crater ~7-10 m in diameter and ~7 m in depth (Sassen et al., 2002). Sediment near the mud volcano consisted of gassy oil-stained hemipelagic mud, hydrogen sulfide, small nodules of gas hydrates, and nodules of oil-stained authigenic carbonate rock.

Although Genesis Field is northeast of the GC 286 site, and is not directly related to the mud volcano site, the molecular and isotopic properties of vent gas from the mud volcano at GC 286 are correlated to gas from deep subsurface reservoirs of Genesis Field (Sassen et al., 2002). The oil of Genesis Field shows evidence of episodic alteration by biodegradation in reservoir (Beeunas et al., 1999) whereas isotopic properties of gas from Genesis Field reservoirs is consistent with a lack of significant effects from biodegradation (Sassen et al., 2002).

The lack of obvious alteration effects in gas properties of Genesis Field is consistent with a late charge of gas from the subsurface petroleum system. It is believed that late gas migration occurred at or near present burial depth, flushing the reservoir system of any previously biodegraded hydrocarbon gas (Sassen et al., 2002).

Petronius Field

Petronius Field is an oil and gas accumulation at 535 m water depth on Viosca Knoll block 786 on the upper Gulf slope. Sassen et al. (2001c) suggest that hydrocarbons of Petronius Field were generated from a mature Upper Jurassic shale source. Reservoir rocks of Petronius Field are Miocene deepwater sands. Reservoirs are mildly overpressured, undercompacted and uncemented with high permeability and porosity

(Wagner et al., 1999). Marine shales capable of high sealing capacity mainly represent the seal rocks of the area (Fig. 28). Traps may be combined structural and stratigraphic elements. Petronius Field had a simple filling history, mainly resulting from oil charge directly from the source rock as it attained oil-window thermal maturity (Sassen et al., 2001c). Lateral migration along Miocene sand conduits charged the stratigraphic traps (Sassen et al., 2001c). Key growth faults, often associated with salt movement, tap the deeper section and provide vertical migration conduits to charge the lateral carrier sands (Sassen et al., 2001c).

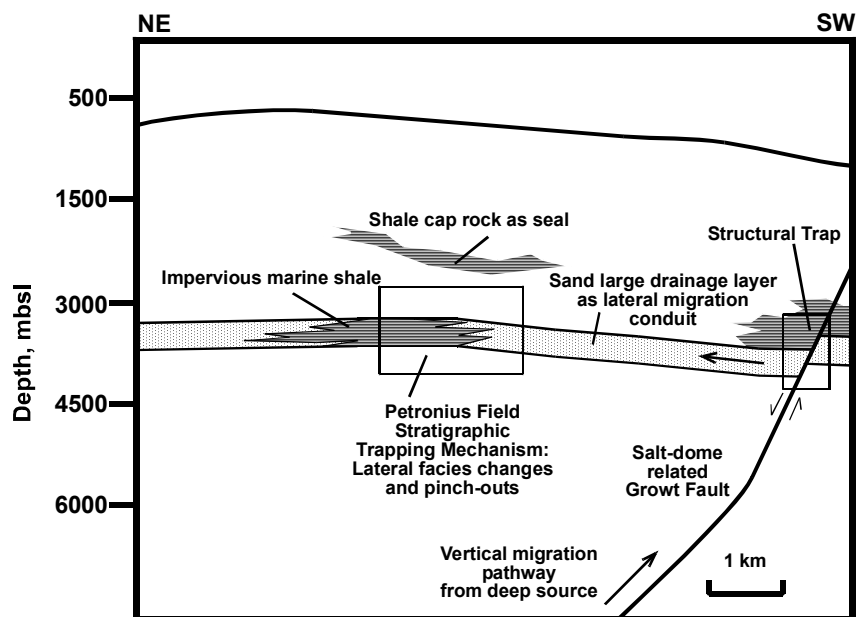


Figure 28. Schematic cross-section of Petronius Field showing probable trap mechanisms.

Non-thermal alteration processes such as biodegradation and gas washing affect the oil reservoir in Petronius Field (Sassen et al., 2001c). However, isotopic properties of gas from the field show mild thermal maturity history associated with only minor non-thermal alteration effects such as biodegradation.

Samples

In this study, reservoir gas and vent gas samples from the Gulf slope, which were collected by Geological Environmental Research Group (GERG) of Texas A&M University and by Cornell University, will be used. Reservoir gas samples were collected in stainless steel pressure vessels on the platforms at each field (Sassen et al., 2001a). Sixteen (16) samples from Jolliet Field (GC 184), three (3) samples from Genesis Field (GC 160/161) and three (3) samples from Petronius Field (VK 786) (Sassen et al., 2001a, c, 2002) will be used for interpretation of reservoir gas.

Vent gas samples were collected using a research submersible. During the 1995 and 1997 dives of the Johnson Sea-Link (JSL) research submersible, the main hydrocarbon pools related to gas venting and abundant gas hydrates within chemosynthetic communities were sampled (Sassen et al., 1999b). Free gas naturally venting into the water column was sampled (Sassen et al., 1999b). The mechanical arm of the submersible was used to hold gas-tight Lexan tubes (30 cm in length and 7.5 cm inside diameter) over gas bubble trains until the ambient seawater in the tube was displaced (Sassen et al., 1999b). Upon recovery to the sea surface, large aliquots of the

gas sample (~240 ml) were transferred from the sampling vessel to pre-evacuated aluminum vacuum containers using a 60 ml gas-tight syringe and held at -20°C until analysis. Four (4) samples from GC 185 vent site, two (2) samples from GC 233 and one (1) sample from GC 286 vent site (Sassen et al., 1999b, 2001a, 2002) will be used for interpretation of vent gas.

Analytical Methods and Data

This study encompasses interpretation of molecular and isotopic data of reservoir and vent gases, which were analyzed at GERG, Isotech Incorporated, Coastal Science Laboratories and Houston Area Research Council (HARC). Analyses are basically the same for samples of reservoir and vent gases (Sassen et al., 1999b). Analyses of the samples focused on $\text{C}_1\text{-C}_5$ gas chromatography, measurement of $\delta^{13}\text{C}$ and δD of methane, and measurements of $\delta^{13}\text{C}$ on the $\text{C}_2\text{-C}_5$ hydrocarbons (Sassen et al., 1999b, 2001a).

Precision of $\text{C}_1\text{-C}_5$ gas chromatography is $\pm 5\%$. $\text{C}_1\text{-C}_5$ hydrocarbon gases were separated mainly using a Hewlett Packard 5890 gas chromatograph using an activated alumina column temperature programmed from 100°C to 160°C at $32^{\circ}\text{C}/\text{min}$ (Sassen et al., 1999b). Known volumes of authentic hydrocarbon standards were used to identify and quantitate peak responses. Concentration of each hydrocarbon is expressed in ppm by sediment volume and normalized as percent of total $\text{C}_1\text{-C}_5$ hydrocarbons (Sassen et al., 1999b). Analyses of $\delta^{13}\text{C}$ of $\text{C}_1\text{-C}_5$ hydrocarbon gases were performed mainly by

using a Varian 3400 gas chromatograph with a Finnigan MAT 252 IRMS. Analyses of methane δD were performed by using an upgraded Micromass 602 Mass Spectrometer (Sassen et al., 1999b).

The $\delta^{13}C$ values are reported as parts per thousand (‰) relative to the Peedee belemnite (PDB) standard (precision is $\pm 0.2\%$); the δD values are reported as parts per thousands (‰) relative to the Standard Mean Ocean Water (SMOW) (precision is $\pm 5\%$) (Sassen et al., 1999b).

CHAPTER V

MIXING OF BACTERIAL AND THERMOGENIC GAS

Many geochemical studies regarding oil and gas accumulations and their associated hydrocarbon seeps have been carried out to characterize oil and gases using molecular and isotopic properties, to interpret the source on the basis of geologic history, to correlate oil and gas accumulations with their seep and vent sites, and to explain the distribution of hydrocarbon accumulations along the Gulf slope (e.g. Brooks et al., 1986, Kennicutt et al., 1988, 1992, 1993; Sassen et al., 1999b, 2001b). An association between active salt movement, faults, oil and gas seeps, and natural gas and oil fields is well established (e.g. Kennicutt et al., 1988; Sassen, 1998, Sassen et al., 1999b, 2001a).

Natural gas occurs in all sedimentary environments and is produced by a variety of biological and thermal processes. As discussed in Chapter II, understanding gas source, thermal maturity, alteration, and mixing is important. All of the processes discussed may affect the molecular and isotopic properties of natural gas sampled from the Gulf slope. However, the mixing processes and their effects are a major objective of this study.

Mixing of bacterial and thermogenic methane is common in shallow reservoirs and natural seeps in the Gulf of Mexico shelf (e.g. Rice, 1980; James, 1990; Rice and Threlkeld, 1990; Walters, 1990). In deep subsurface petroleum system of the Gulf slope, mixing of bacterial and thermogenic methane and their relative abundances has not been

studied in detail. However, more recent studies have discovered slope environment reservoir sands and associated vent sites charged with gases of mixed source (Wagner and Sofer, 1996; Sassen et al., 2001c, 2002). Understanding the mechanisms by which bacterial methane and thermogenic methane are mixed is an important goal of this study.

Gas types are genetically described based on the geochemical tools discussed in Chapter II. Thermal maturity histories are estimated. Secondary alteration affects, particularly biodegradation, are outlined in this study.

The increased use of relatively new methods of molecular and isotopic analysis of C₁-C₅ gas molecules allows development of new models to understand the processes affecting hydrocarbons gas before, after or during mixing (e.g. Chung et al., 1988; Clayton, 1991). Models contribute to better understanding source, maturity, mixing, and alteration as well as hydrocarbon migration pathways. In order to geochemically model the mixing processes of natural gas along the Gulf slope, insight to the deep subsurface petroleum system are required.

The geochemical fingerprinting techniques used in this research are based on molecular and isotopic properties of hydrocarbon gas samples. The molecular composition of C₁-C₅ hydrocarbons, carbon and hydrogen isotopic properties of methane, and carbon isotopic properties of C₂-C₅ hydrocarbons are utilized to provide a genetic classification of gas type in gas and oil reservoirs of Jolliet (GC 184), Genesis (GC 160/161) and Petronius (VK 786) fields.

The molecular and isotopic properties of vent gas from a hydrate mound at GC 185 site near Jolliet Field, from a brine pool at GC 233 site, and from a mud volcano at

GC 286 site near Genesis Field, where data are available, are compared to gases from associated deep subsurface reservoirs.

Molecular composition and isotopic properties of gas samples are used to recognize whether the gas is a mixture, to determine possible end-members of the mixture and to determine relative contributions. Using the methane/ethane (C_1/C_2) molecular ratio was a basic approach to understand mixing effects. Carbon isotopic properties of different hydrocarbons but particularly ratios between higher homologues (such as ethane and propane) were used to delineate mixing effects. Because methane is the only hydrocarbon gas formed through bacterial processes, and therefore in order to get rid of the influence of bacterial gas for assessing the role of other processes involved in the composition of hydrocarbon gases, particularly the contribution of thermogenic gas in the mixing process, the C_2 to C_5 range, where available, were used as the most reliable data.

Chung et al. (1988) introduced a model for interpretation of natural gas origins, determination of relative thermal maturity and solving the problems on the mixing of various hydrocarbons of different origins. Chung et al. (1988) proposed to plot the $\delta^{13}C$ values of individual alkanes versus the inverse of the carbon number (i.e. $\delta^{13}C$ of propane versus $1/3$) and suggested that the plot should result in a straight line for unaltered gas components generated from the same source. The slopes of such lines reflect relative gas maturities, and the y-intercepts provide an estimate of the isotopic properties of the original source methane.

The method of Chung et al. (1988) is used to model the bacterial and thermogenic gas mixtures in each field (Jolliet, Genesis, Petronius) and in associated vent sites (GC 185, GC 233, and GC 286) in the study area. The carbon isotope properties of ethane, propane, butane, and pentane on the natural gas plot are extrapolated using regression analysis. The objective is to predict the original carbon isotopic properties of thermogenic methane. Assuming a representative range of carbon isotopic properties for end-member bacterial methane appropriate for the study area, the percentage of bacterial methane mixed with thermogenic methane is calculated for each gas sample in the study area. Estimating on the amount of bacterial methane expands knowledge of the potential distribution of bacterial gas across the Gulf slope. Information on mixing of bacterial and thermogenic methane facilitates improved understanding of hydrocarbon gas charge to reservoirs, and to gas vents. This information also may improve our understanding of the depth and volume of bacterial methane sources in the deep section of the Gulf slope.

Jolliet Field

Jolliet Field (GC 184) is an oil and gas accumulation on the upper Gulf slope (Sassen et al., 2001a). The molecular and isotopic properties of C₁-C₅ hydrocarbons from gas of oil reservoirs of Jolliet Field are shown in Tables 2 and 3 (data from Sassen et al., 2001a). Methane is the main component (mean =87.7%), and relative abundance

Table 2. Molecular properties of reservoir gas in Jolliet Field (data from Sassen et al., 2001a).

Sample Location (well)	Sample (sand)	Depth (m)	% C ₁	% C ₂	% C ₃	% <i>i</i> -C ₄	% <i>n</i> -C ₄	% <i>i</i> -C ₅	% <i>n</i> -C ₅	gas wetness (vol%)	methane/ethane
A8	Reservoir gas	2084	90.5	6.0	2.3	0.3	0.6	0.2	0.1	9.5	15.1
A3ST	Reservoir gas	3076	90.2	6.5	2.3	0.3	0.5	0.1	0.1	9.8	13.9
A14ST	Reservoir gas	2104	86.2	8.3	3.8	0.5	0.9	0.2	0.2	13.9	10.4
A13	Reservoir gas	2091	87.1	7.5	3.5	0.5	0.9	0.2	0.2	12.8	11.6
A3DST	Reservoir gas	2182	87.8	7.1	3.3	0.5	0.9	0.2	0.2	12.2	12.4
A19ST	Reservoir gas	2293	87.0	7.7	3.4	0.5	0.9	0.2	0.2	12.9	11.3
A18	Reservoir gas	2280	87.4	6.9	3.5	0.6	1.1	0.3	0.3	12.7	12.7
A14DST	Reservoir gas	1900	91.4	5.1	2.4	0.4	0.6	0.1	0.1	8.7	17.9
A2DST	Reservoir gas	2167	87.3	7.4	3.4	0.5	0.9	0.2	0.2	12.6	11.8
A9	Reservoir gas	2128	88.1	7.3	3.1	0.5	0.8	0.2	0.1	12.0	12.1
A1	Reservoir gas	2713	84.6	8.9	4.1	0.7	1.2	0.3	0.3	15.5	9.5
A15D	Reservoir gas	1855	89.8	5.5	2.8	0.5	0.9	0.3	0.2	10.2	16.3
A7	Reservoir gas	2610	85.7	8.4	3.7	0.6	1.0	0.3	0.3	14.3	10.2
A6	Reservoir gas	1740	86.6	7.3	3.8	0.6	1.1	0.3	0.3	13.4	11.9
A11	Reservoir gas	2310	87.3	7.4	3.7	0.5	0.7	0.2	0.2	12.7	11.8
A9DST	Reservoir gas	2035	86.5	7.8	3.6	0.6	1.0	0.3	0.2	13.5	11.1
MEAN			87.7	7.2	3.3	0.5	0.9	0.2	0.2	12.3	12.2

Table 3. Isotopic properties of reservoir gas in Jolliet Field (data from Sassen et al., 2001a).

Sample Location (well)	Sample (sand)	Depth (m)	$\delta^{13}\text{C C}_1$	$\delta\text{D C}_1$	$\delta^{13}\text{C C}_2$	$\delta^{13}\text{C C}_3$	$\delta^{13}\text{C }i\text{-C}_4$	$\delta^{13}\text{C }n\text{-C}_4$
A8	Reservoir gas	2084	-45.8	-196	-29.5	-26.8	-27.5	-25.7
A3ST	Reservoir gas	3076	-44.9	-191	-29.2	-26.7	-27.3	-25.6
A14ST	Reservoir gas	2104	-46.9	-200	-30.2	-27.2	-27.8	-25.9
A13	Reservoir gas	2091	-47.0	-199	-29.9	-27.1	-27.7	-25.8
A3DST	Reservoir gas	2182	-46.5	-199	-29.7	-27.0	-27.6	-25.7
A19ST	Reservoir gas	2293	-46.1	-199	-29.5	-26.9	-27.7	-25.7
A18	Reservoir gas	2280	-48.7	-206	-30.0	-27.1	-27.8	-25.8
A14DST	Reservoir gas	1900	-48.1	-200	-30.0	-27.0	-27.7	-25.7
A2DST	Reservoir gas	2167	-48.7	-204	-30.1	-27.1	-27.7	-25.8
A9	Reservoir gas	2128	-47.1	-201	-29.7	-27.0	-27.6	-25.7
A1	Reservoir gas	2713	-45.9	-197	-29.6	-26.9	-27.7	-25.7
A15D	Reservoir gas	1855	-48.1	-199	-29.9	-27.0	-27.7	-25.6
A7	Reservoir gas	2610	-45.1	-194	-29.4	-26.8	-27.6	-25.6
A6	Reservoir gas	1740	-47.2	-206	-30.0	-27.3	-27.8	-25.9
A11	Reservoir gas	2310	-47.0	-200	-29.8	-27.0	-27.4	-25.8
A9DST	Reservoir gas	2035	-46.9	-200	-29.8	-27.1	-27.7	-25.8
MEAN			-46.9	-200	-29.8	-27.0	-27.6	-25.7

of higher hydrocarbons generally decreases with increasing carbon number (Fig. 29). The mean relative abundance of C₂₊ hydrocarbons is in the order of ethane (7.2%), propane (3.3%), isobutane (0.5%), normal butane (0.9%), isopentane (0.2%), and normal pentane (0.2%) (Table 2). The mean methane/ethane ratio is ~12.2 and the mean gas wetness of the reservoir gas samples of Jolliet Field is 12.3 (Table 2).

The methane has mean $\delta^{13}\text{C}$ of -46.9‰ and mean δD of -200‰ (Table 3). The mean $\delta^{13}\text{C}$ values of ethane (-29.8‰), propane (-27.0‰), isobutane (-27.6‰), and normal butane (-25.7‰) show only small variation ($<1\text{‰}$) between samples (Fig. 30). Isotopic composition of the gas in Jolliet Field is uniform.

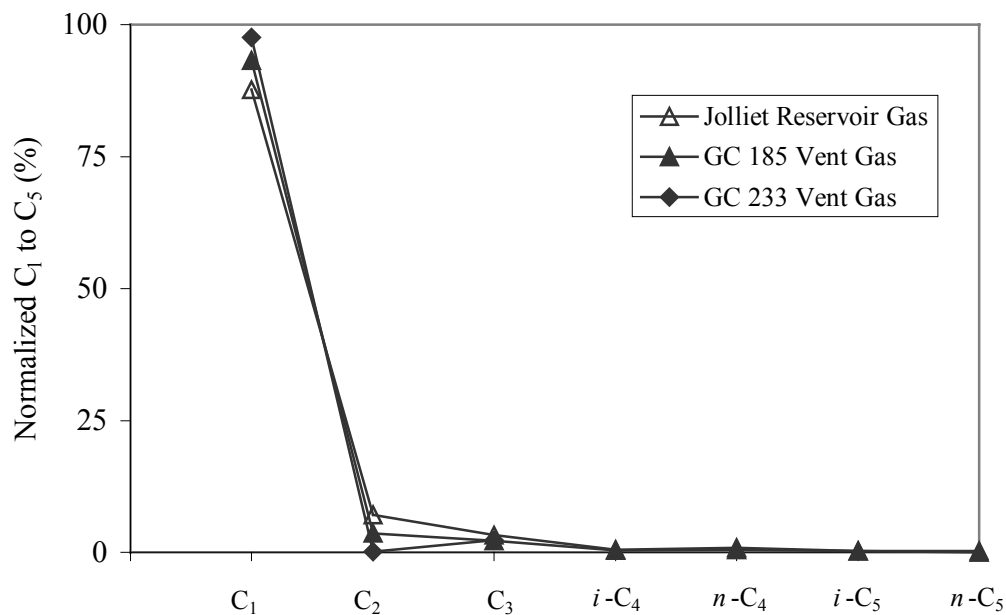


Figure 29. Mean C₁-C₅ molecular composition of reservoir gas from Jolliet Field and vent gas from GC 185 and GC 233 sites.

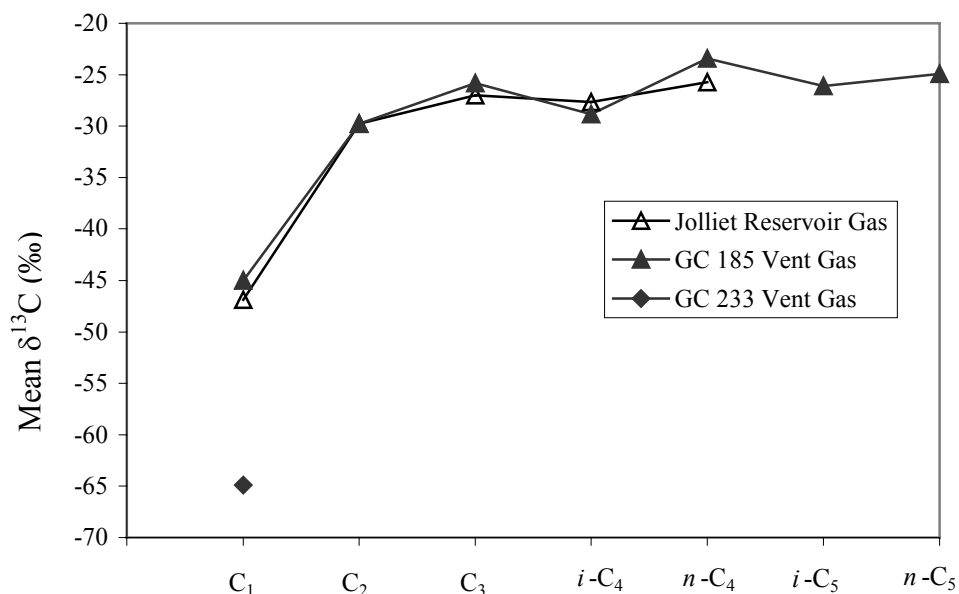


Figure 30. Mean $\delta^{13}\text{C}$ composition of C₁-C₅ hydrocarbons from reservoir gas of Joliet Field and vent gas from GC 185 and GC 233 sites.

Based on the molecular composition and isotopic properties of hydrocarbon gas, Joliet Field reservoir gas is of thermogenic origin. $\delta^{13}\text{C}$ and δD properties of methane from reservoirs of Joliet Field are overlaid on a plot proposed by Schoell (1983) (Fig. 31). Schoell (1983) plot relates the source and maturity of natural gas. Many of the gas samples from reservoirs of Joliet Field fall with the oil associated thermogenic gas field consistent with a thermogenic origin. Three samples are located on the line dividing the fields representing mixed and thermogenic sources of methane. Thus we can interpret the reservoir gas from Joliet Field as relatively unaltered thermogenic gas from subsurface reservoirs containing crude oil. Additionally, the low methane/ethane ratio of ~ 12.2 is consistent with an oil reservoir.

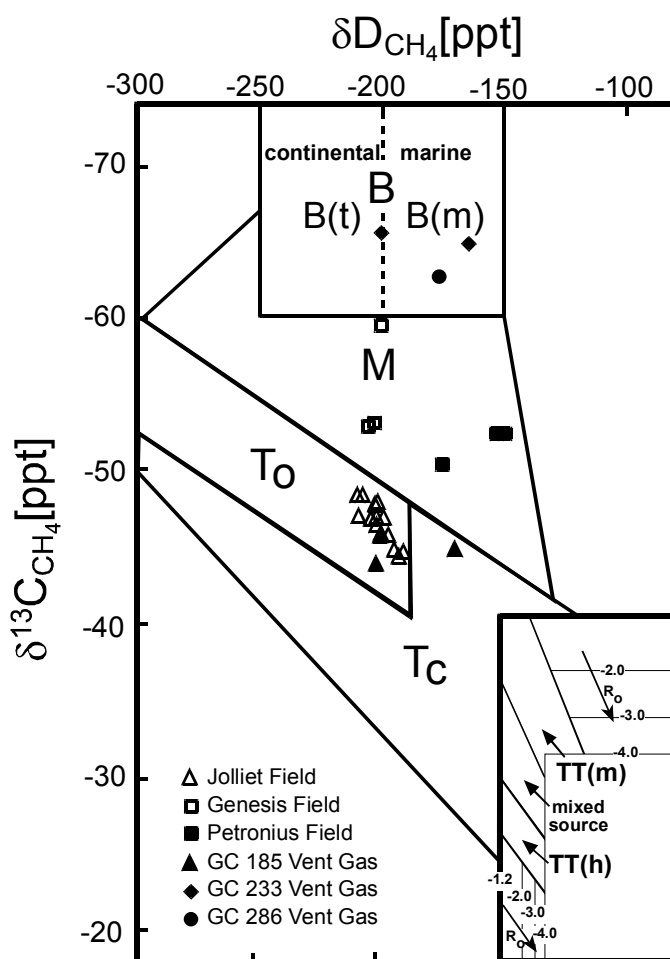


Figure 31. $\delta^{13}C$ versus δD composition of methane of reservoir and vent gas from the Gulf slope overlaid on genetic classification scheme proposed by Schoell (1983). Abbreviations are same as Figure 5.

Biodegradation alters the carbon isotopic properties of gas by selective enrichment of ^{13}C in hydrocarbons such as propane without greatly affecting ethane (James and Burns, 1984). Even though the carbon isotopic composition of hydrocarbon gas components in normal, unaltered gas generally follow a smooth progression from methane to normal butane, the carbon isotopic properties of biodegraded gas are

characterized by a jagged pattern, particularly with distinct enrichment in ^{13}C of propane. Relatively smooth pattern in carbon isotopic properties of Jolliet Field reservoir gas is observed (Fig. 30). The pattern does not show any meaningful selective enrichment in ^{13}C of propane. Because δD is particularly sensitive to biodegradation effects (Coleman et al., 1981), the narrow range of methane δD ($\sim 16\text{‰}$) is not consistent with significant biodegradation effects (Sassen et al., 2001a). The small variations in the isotopic properties of C_{2+} reservoir gases also support this suggestion.

Biodegradation of natural gas usually accompanies biodegradation of crude oil in reservoirs. Shallow oil reservoirs at Jolliet Field contain oil altered by biodegradation, which is shown by preferential depletion of *n*-alkanes and increased sulfur content (Kennicutt et al., 1988; Sassen et al., 1993a). Chromatograms of oil from deep reservoirs of Jolliet Field illustrate some basic geochemical characteristics of oils that are not altered by biodegradation or by other non-thermal processes (Thompson and Kennicutt, 1990). Although it is difficult to explain why the isotopic properties of the gas are so uniform in Jolliet Field while oil in shallow reservoirs shows biodegradation, Sassen et al. (2001a) hypothesized that late gaseous hydrocarbons charged Jolliet Field in the recent geologic past after biodegradation effects ceased.

In order to test the mixing hypothesis of thermogenic methane from reservoirs of Jolliet Field with bacterial methane, one approach is to examine methane/ethane ratios. The reservoir gas with low methane/ethane ratio (~ 12.2) does not suggest a great predominance of bacterial methane compared to bacterial methane sites of the Gulf slope where ratios may be higher than 10,000 (Thompson, 1996). Prinzhofer and Pernaton

(1997) suggest a diagram displaying ethane/methane ratios versus $\delta^{13}\text{C}$ of methane to test a mixing hypothesis. The principle in such mixing diagrams is that a straight line is expected to define a mixture between two end members when plotting any two ratios with a common denominator. Plotting ethane/methane ratios of gaseous hydrocarbons in Jolliet Field versus $\delta^{13}\text{C}$ of methane composition provides a nearly horizontal straight line that the thermogenic gas may contain at least some bacterial methane (Fig. 32).

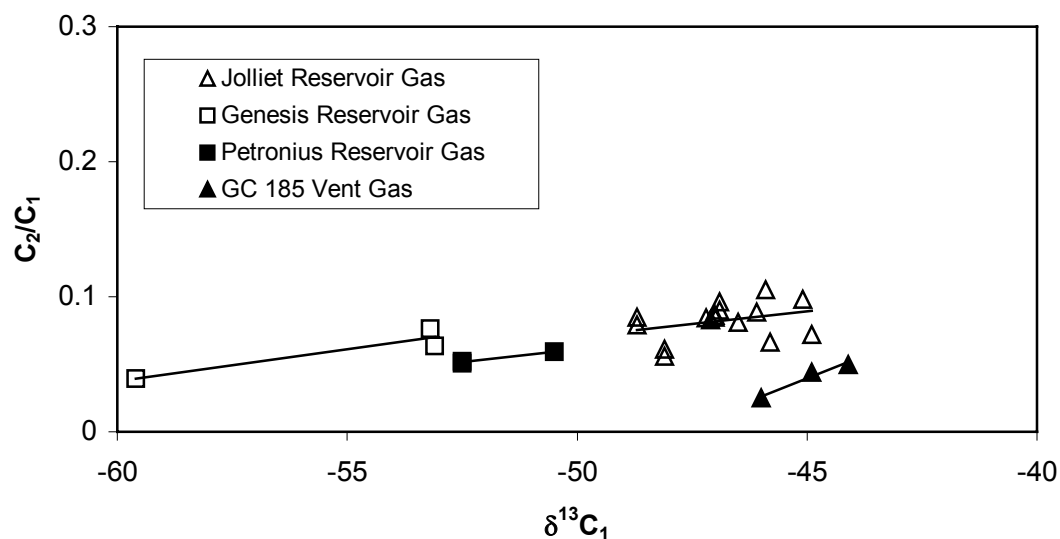


Figure 32. Gases from the Gulf slope plotted on the mixing diagram of Prinzhofer and Pernaton (1997) relating the ethane/methane molecular ratio in gas to $\delta^{13}\text{C}$ concentration in methane.

As discussed in Chapter II, Schoell (1983) provides a plot relating variations in the carbon isotopic properties of ethane and methane, based on the hypothesis that mixing of

various proportions of two gases results in a linear change of their isotopic properties. When the isotopic properties of the gas from Jolliet Field are plotted the data (Fig. 33) suggest that samples from Jolliet Field illustrate some effects of mixing because they plot along the mixing line.

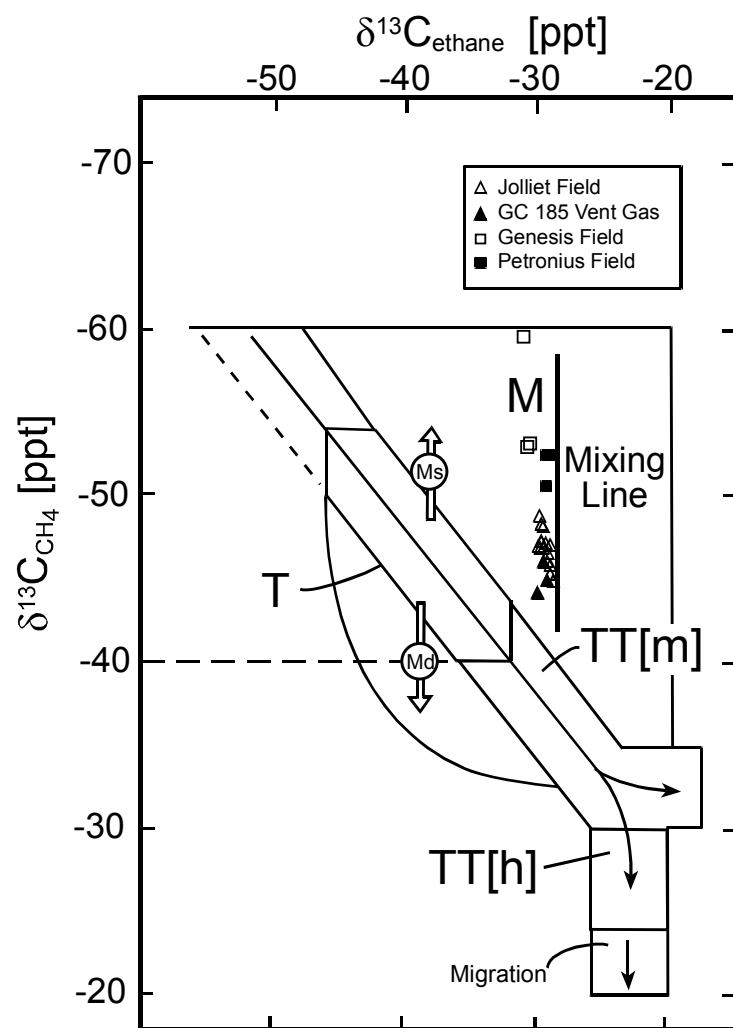


Figure 33. Overlay of the Gulf slope gases on a plot proposed by Schoell (1983) relating carbon isotopic properties in ethane and methane. Abbreviations are same as Figure 5.

The method of Chung et al. (1988) is used to model the methane mixture assuming a range of $\delta^{13}\text{C}$ for end-member bacterial methane (Fig. 34). For Jolliet Field reservoir gas samples, if we assume the $\delta^{13}\text{C}$ of pure bacterial methane end-member is -70‰ , then the total methane is $\sim 28\%$ bacterial, and if we assume the $\delta^{13}\text{C}$ of pure bacterial methane is -90‰ , then methane is $\sim 17\%$ bacterial (Fig. 34). The estimated original $\delta^{13}\text{C}$ of value of end-member thermogenic methane from Jolliet Field is -38‰ (Fig. 34). The solid line in Fig. 34 represents the $\delta^{13}\text{C}$ of mixed bacterial and thermogenic methane. The dashed line illustrates the $\delta^{13}\text{C}$ of estimated original thermogenic methane. The estimated percentage of bacterial methane in Jolliet Field is not geochemically significant. Reservoir gas from Jolliet Field is not a mixed gas. The lack of significant mixing effects suggests that reservoir gas from Jolliet Field is useful for purposes of comparison to other fields, or to vent sites where mixing may be more important.

The $\delta^{13}\text{C}$ and δD properties of methane from Jolliet Field are consistent with oil-window thermal maturity. The slope of natural gas plot of Chung et al (1988) also relates to thermal maturity. A change of the slope from steep to gentle indicates increasing thermal maturation. Therefore, less mature gas corresponds to steeper slopes on the natural gas plots. Carbon isotopic properties of ethane through butane of Jolliet Field reservoir gas shows a moderate slope consistent with intermediate maturity (Fig. 34).

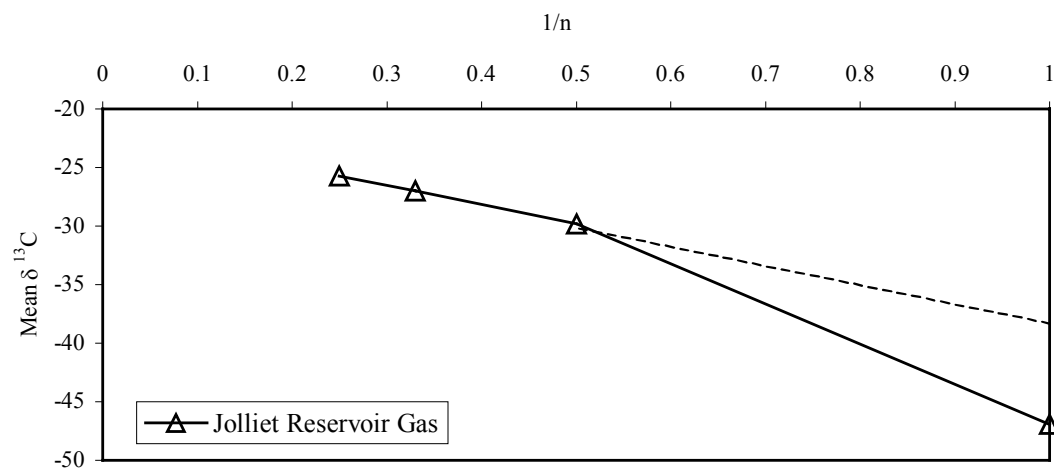


Figure 34. The method of Chung et al (1988) is used to estimate relative contributions of bacterial methane to C₁-C₄ hydrocarbon gases from reservoirs of Jolliet Field. Dashed line shows estimated original δ¹³C of thermogenic methane.

GC 185 and GC 233 Vent Sites

Jolliet Field area is an example of direct connection between oil and gas accumulation in the subsurface (Jolliet Field) and gas venting to the water column from hydrate mound at GC 185 vent site on the nearby sea floor (Sassen et al., 2001a).

The GC 185 vent site, at ~540 m water depth, has been extensively sampled by research submarine and by piston cores (Sassen et al., 1999b). Molecular and isotopic properties of C₁-C₅ hydrocarbons from vent gas at GC 185 site are shown in Tables 4 and 5 (data from Sassen et al., 2001a).

Table 4. Molecular properties of vent gas in GC 185 and GC 233 sites (data from Sassen et al., 1999b, 2001a).

Sample Location	Depth(m)	Sample	% C ₁	% C ₂	% C ₃	% <i>i</i> -C ₄	% <i>n</i> -C ₄	% <i>i</i> -C ₅	% <i>n</i> -C ₅	gas wetness (vol %)	methane/ethane
GC 185	540	Vent gas	95.9	2.4	1.2	0.1	0.3	0.3	<0.1	4.29	39.96
GC 185	540	Vent gas	90.4	4.5	3.7	0.6	0.6	0.2	<0.1	9.60	20.09
GC 185	540	Vent gas	93.5	4.1	1.5	0.3	0.5	0.3	<0.1	6.69	22.81
MEAN			93.3	3.7	2.1	0.3	0.5	0.3	<0.1	6.86	27.62
GC 233	640	Vent gas	97.8	0.1	2.1					2.20	978
GC 233	640	Vent gas	97.4	0.1	2.5					2.60	974
MEAN			97.6	0.1	2.3					2.40	976

Table 5. Isotopic properties of vent gas in GC 185 and GC 233 sites (data from Sassen et al., 1999b, 2001a).

Sample Location	Depth (m)	Sample	$\delta^{13}\text{C C}_1$	$\delta\text{D C}_1$	$\delta^{13}\text{C C}_2$	$\delta^{13}\text{C C}_3$	$\delta^{13}\text{C } i\text{-C}_4$	$\delta^{13}\text{C } n\text{-C}_4$	$\delta^{13}\text{C } i\text{-C}_5$	$\delta^{13}\text{C } n\text{-C}_5$
GC 185	540	Vent gas	-46.0	-198	-29.7	-25.0		-22.6	-26.1	-24.4
GC 185	540	Vent gas	-44.1	-200	-30.2	-26.3	-27.9	-23.3	-26.1	-25.3
GC 185	540	Vent gas	-44.9	-171	-29.4	-26.2	-29.8	-24.4		-25.1
MEAN			-45.0	-189.7	-29.8	-25.8	-28.9	-23.4	-26.1	-24.9
GC 233	640	Vent gas	-64.3	-165						
GC 233	640	Vent gas	-65.5	-200.0						
MEAN			-64.9	-182.5						

Methane is the main hydrocarbon component (mean =93.3%) in GC 185 vent gas. Relative abundance of individual C₂-C₅ hydrocarbons tends to decrease with increasing carbon number (Fig. 29). Mean relative abundance of the C₂₊ hydrocarbons is in the order of ethane (3.7%), propane (2.1%), isobutane (0.3%), normal butane (0.5%), isopentane (0.3%), and normal pentane (<0.1). The mean methane/ethane ratio is ~27.6 and the mean gas wetness of the vent gas sample is 6.9 (Table 4). Compared to reservoir gas of Jolliet Field, methane is more abundant in the vent gas of GC 185, whereas ethane, propane and butanes are less abundant in the vent gas (Fig. 29).

The mean $\delta^{13}\text{C}$ of vent methane from GC 185 site is -45‰ varying by 1.9‰ , and δD values with mean of -190‰ show little variation (Table 5). The mean $\delta^{13}\text{C}$ values of ethane (-29.8‰), propane (-25.8‰), isobutane (-28.9‰), and normal butane (-23.4‰) show small variation between samples (Fig. 30). The isotopic properties of methane and associated C₂-C₄ hydrocarbons are consistent with a thermogenic origin. The methane of vent gas from GC 185 site is slightly enriched both in ^{13}C and D relative to Jolliet Field reservoir methane. The $\delta^{13}\text{C}$ values of C₂₊ hydrocarbons are generally similar to reservoir gas, within $\sim 2\text{‰}$. The mean $\delta^{13}\text{C}$ values of ethane (-29.8‰) in vent gas (GC 185) and reservoir gas (Jolliet Field) is identical, but the mean $\delta^{13}\text{C}$ values of both propane and normal butane in vent gas are slightly enriched in ^{13}C when compared to reservoir gas. A geochemical correlation, on the basis of molecular and isotopic properties, between seep gas from GC 185 site and reservoir gas from Jolliet Field has been established earlier (Kennicutt et al., 1988; Sassen et al, 2001a). However the data of present study confirms previous work and illustrates that GC 185 vent gas sample has

more or less identical molecular and isotopic properties to that of reservoir gas from Jolliet Field.

The molecular ratio of $C_1/(C_2+C_3)$ and carbon isotope properties of methane from vent gas GC 185 site are used in order to delineate its origin. Bernard et al. (1978) proposed a genetic classification diagram combining molecular and isotopic properties of gases from vents, seeps and sediments in various areas. GC 185 vent gas plots on the thermogenic field of the diagram with its mean $C_1/(C_2+C_3)$ molecular ratio of 16.1 and mean methane $\delta^{13}C$ of -45‰ (Fig. 35). Using the isotopic criteria of Schoell (1983), relating source and maturity, the methane of GC 185 vent gas also plots as thermogenic gas. In terms of this diagram vent methane is more or less identical to Jolliet Field reservoir gas (Fig. 31). The effects of biodegradation on GC 185 vent methane are more meaningful than on Jolliet Field reservoir methane.

Relative to reservoir gas in Jolliet Field, vent methane from the GC 185 site is enriched in ^{13}C by as much as 4.6‰ and is enriched in D by as much as 35‰. Enrichment in ^{13}C and D of vent methane may be best explained by kinetic isotope effects from biodegradation. During biodegradation, ^{12}C and 1H are preferentially used from the methane reactant pool, resulting in enrichment of ^{13}C and D in the residual methane (Coleman et al., 1981). Slight enrichment in $\delta^{13}C$ values of propane of GC 185 vent gas is also consistent with biodegradation (James and Burns, 1984) (Fig. 30). In addition, the range of δD (~29‰) is larger than that of reservoir gas stating more effective biodegradation (Table 5) (Coleman et al., 1981).

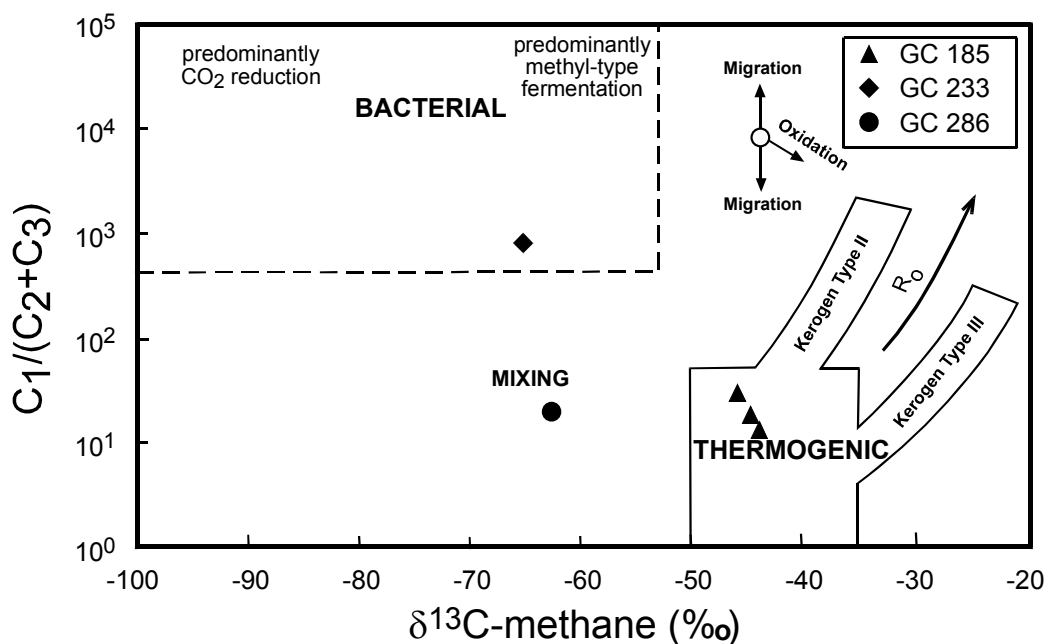


Figure 35. Overlay of gases from vent sites of the Gulf slope on a plot proposed by Bernard et al. (1978) comparing gas wetness and $\delta^{13}C$ of methane for gases in vents, seeps and sediments from various areas.

$\delta^{13}C$ and δD properties of methane of gas samples from GC 185 site do not show a geochemically significant bacterial contribution. Even though the methane/ethane ratio of ~ 27.62 is higher than that of Jolliet Field reservoir gas, it still does not represent a meaningful mixture of bacterial and thermogenic methane. However, if we use ethane/methane ratio of vent gas and relate that to the $\delta^{13}C$ of methane, the mixing diagram shows a straight line suggesting that the thermogenic vent gas may contain at least some bacterial methane (Fig. 32). Variations in carbon isotopic properties of ethane and methane are related in Fig. 33. GC 185 samples plot through the mixing line

together with gases from Jolliet Field. This may suggest a mixture of bacterial and thermogenic methane in Jolliet Field and vent gas from the GC 185 site.

Using the method of Chung et al. (1988), different methane sources may be modeled (Fig. 36). If we assume the $\delta^{13}\text{C}$ of pure bacterial methane is -70‰ , then the total methane of GC 185 vent gas is $\sim 12.6\%$ bacterial, and if we assume the $\delta^{13}\text{C}$ of pure bacterial methane is -90‰ , methane is $\sim 7.4\%$ bacterial (Fig. 36). The estimated original $\delta^{13}\text{C}$ value of thermogenic methane from GC 185 vent gas is -41.4‰ (Fig. 36). The percentage of bacterial methane contribution in the vent gas may be less than that of reservoir gas in Jolliet Field. The range of values (7.4% to 12.6%) representing the amount of bacterial methane component in vent gas from the site is not so great to classify it as mixed gas.

The ^{13}C composition of vent gas from GC 185 site, which is slightly enriched compared to reservoir gas from Jolliet Field, may represent to different thermal maturation history. The slope on the natural gas plot of C_2 to C_5 hydrocarbons, however, is nearly identical with the slope on the plot of reservoir gas from Jolliet Field (Fig. 36). It is assumed that GC 185 vent gas is in the same or similar thermal maturation range as the gas from reservoirs of Jolliet Field.

The GC 233 vent site, at ~ 640 m water depth, has been extensively sampled by research submarine and by piston cores (Sassen et al., 1999b). Molecular and isotopic properties of C_1 - C_5 hydrocarbons from vent gas at GC 233 site are shown in Tables 4 and 5 (data from Sassen et al., 1999b).

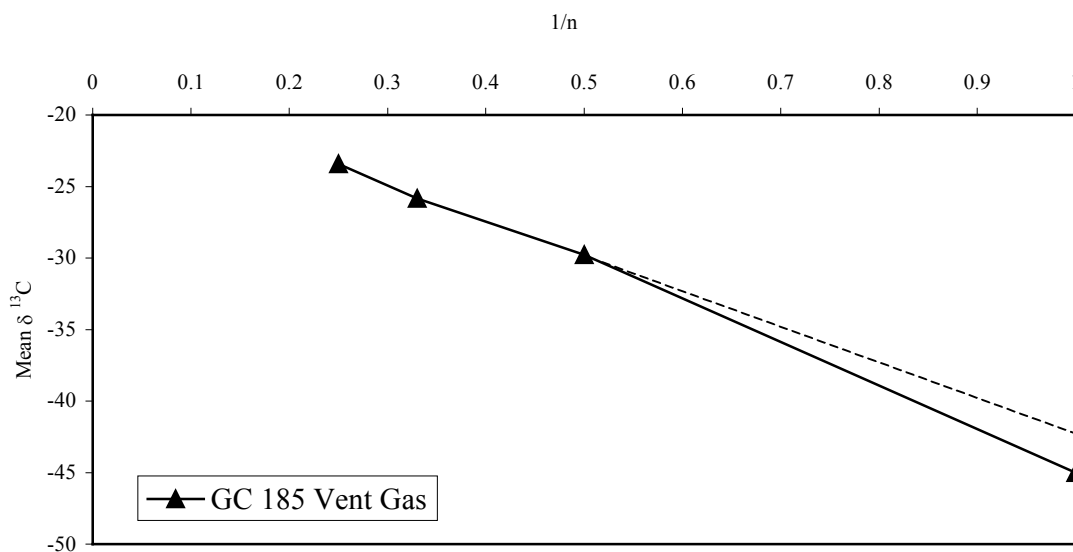


Figure 36. The method of Chung et al (1988) is used to estimate relative contributions of bacterial methane to C₁-C₄ hydrocarbon gases from GC185 Vent Site. Dashed line shows estimated original δ¹³C of thermogenic methane.

Vent gas from GC 233 site has completely different molecular and isotopic properties when compared to the reservoir gas in Jolliet Field, and to the vent gas from GC 185 site (Tables 4 and 5). Molecular composition is distinctive in that two samples of vent gas at GC 233 are essentially pure methane (97.8% and 97.4%) (Table 4). Thermogenic C₂ and C₃ are minor components, and the C₄ and C₅ hydrocarbons are absent or below detection limits (Table 4). The mean methane/ethane ratio is ~976, and the mean gas wetness of the vent samples is 2.4. Vent gas from the GC 233 site has methane with a mean δ¹³C of -64.9‰, which is depleted by as much as 20.8‰ compared to vent gas from GC 185 site and by as much as 20‰ compared to reservoir gas from Jolliet Field. The mean δD value of methane of the GC 233 vent gas is -182.5‰.

In order to distinguish the origin of vent gas at GC 233 site, the molecular ratio of $C_1/(C_2+C_3)$ and carbon isotopic properties of methane are used as in the case of GC 185 vent gas. Based on the genetic classification diagram proposed by Bernard et al. (1978), which combines molecular and isotopic properties of gases from vents, seeps and sediments in various areas, GC 233 vent gas plots on the bacterial field with a mean $C_1/(C_2+C_3)$ molecular ratio of ~ 976 and mean methane $\delta^{13}C$ of -64.9‰ (Fig. 35). Moreover, Schoell (1983)'s diagram of $\delta^{13}C$ versus δD of methane may be consistent with a marine bacterial origin for vent gas sample GC 233 (Fig. 31).

Methane from GC 233 is enriched in D (-182.5‰) relative to vent gas by 7.2‰ at GC 185 (-189.7‰) and to reservoir gas (-200‰) by 17.5‰ at Jolliet Field. Enrichment in D of methane may be an indicator of biodegradation of vent gas at the GC 233 site.

The methane/ethane ratio of ~ 976 is much larger than that of vent gas at GC 233 site or reservoir gas at Jolliet Field. The high ratio may indicate that vent gas at GC 233 is from a totally different migration conduit. It is clear that the vent gas in GC 233 site cannot be correlated to the reservoir gas in Jolliet Field or to the vent gas in GC 185 site because geochemical properties are greatly different. However, the GC 233 brine pool emphasizes the volumetric importance of bacterial methane production in the Green Canyon study area.

Genesis Field

Genesis Field (GC 160/161) is an oil and gas accumulation on the upper Gulf slope (Sassen et al., 2002). Molecular and isotopic properties of liquid hydrocarbons of Genesis Field are interpreted to indicate a complex migration history, reservoir compartmentalization, and effects of non-thermal alteration processes including water washing, biodegradation and evaporative fractionation (Beeunas et al., 1999). Whole-oil chromatograms of oil samples from Genesis Field are also interpreted to show alteration by biodegradation and are consistent with multiple episodes of migration (Sassen et al., 2002). Multiple episodes of migration are consistent with a late pulse of migration of fresh oil and gas in reservoirs where the hydrocarbons remain relatively unaltered by biodegradation

The molecular and isotopic properties of C₁-C₅ hydrocarbons from reservoir gas of the subsurface reservoirs of Genesis Field (GC 160 /161) are presented in Tables 6 and 7 (data from Sassen et al., 2002). Methane is the major component (mean =90.9%) in the reservoir gas. The C₂ (mean =5.5%) and C₃ (mean =2.3%) hydrocarbons are lesser components, and the C₄ and C₅ hydrocarbons are present as minor components (Fig. 37). The mean methane/ethane ratio is ~ 16.6 and the mean gas wetness of the reservoir gas samples of Genesis Field is 9.1% (Table 6).

Table 6. Molecular properties of reservoir gas in Genesis Field (data from Sassen et al., 2002).

Sample Location	Depth (m)	Sample	% C ₁	% C ₂	% C ₃	% <i>i</i> -C ₄	% <i>n</i> -C ₄	% <i>i</i> -C ₅	% <i>n</i> -C ₅	gas wetness (vol %)	methane/ethane
GC 160	3705	Reservoir gas	93.6	3.8	1.7	0.3	0.5	0.1	0.1	6.49	24.63
GC 161	3761	Reservoir gas	87.8	6.7	3.2	0.6	1.0	0.3	0.3	12.11	13.10
GC 161	3924	Reservoir gas	91.2	5.9	2.0	0.3	0.4	0.1	0.1	8.80	15.46
MEAN			90.9	5.5	2.3	0.4	0.6	0.2	0.2	9.13	16.62

Table 7. Isotopic properties of reservoir gas in Genesis Field (data from Sassen et al., 2002).

Sample Location	Depth (m)	Sample	$\delta^{13}\text{C C}_1$	$\delta\text{D C}_1$	$\delta^{13}\text{C C}_2$	$\delta^{13}\text{C C}_3$	$\delta^{13}\text{C } i\text{-C}_4$	$\delta^{13}\text{C } n\text{-C}_4$
GC 160	3705	Reservoir gas	-59.6	-198	-31.3	-27.8	-28.6	-26.5
GC 161	3761	Reservoir gas	-53.2	-200	-30.8	-27.9	-28.6	-26.7
GC 161	3924	Reservoir gas	-53.1	-201	-30.9	-27.9	-28.6	-26.6
MEAN			-55.3	-199.7	-31.0	-27.9	-28.6	-26.6

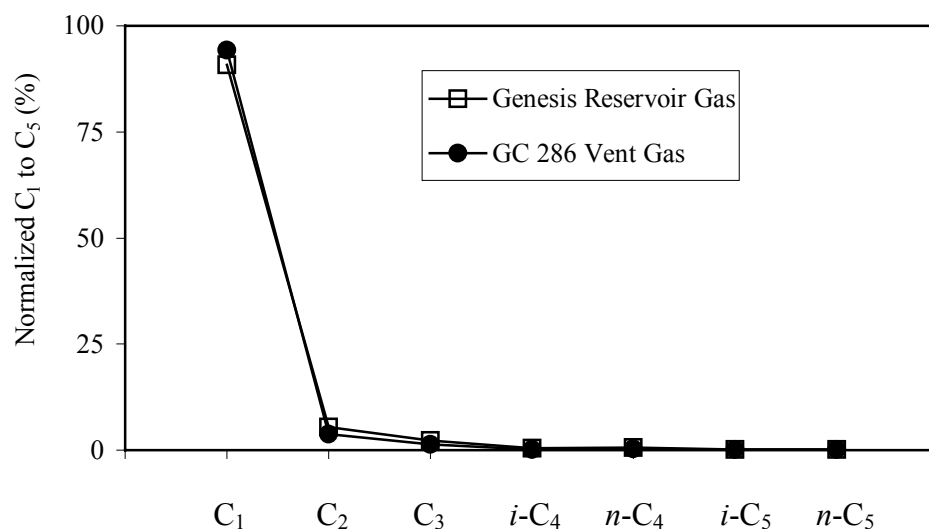


Figure 37. Mean C₁-C₅ molecular composition of reservoir gas from Genesis Field and vent gas from GC 286 Site.

The mean $\delta^{13}\text{C}$ value of the methane is -55.3‰ , and the mean δD value is -199.7‰ (Table 7). The mean $\delta^{13}\text{C}$ values of C₂ (-31‰), C₃ (-27.9‰), *i*-C₄ (-28.6‰), and *n*-C₄ (-26.6‰) indicate enrichment in ^{13}C relative to methane (Fig. 38).

The $\delta^{13}\text{C}$ values of subsurface methane from Genesis Field vary widely (by $\sim 6.4\text{‰}$) within -53.1‰ to -59.6‰ range, whereas δD is in the narrow -198‰ to -201‰ range. Carbon and hydrogen isotopic compositions of methane in the gas show significantly depleted values relative to methane of thermogenic origin. Because the gas from Genesis Field reservoirs contain significant amount of thermogenic gas components (C₂ through C₅), an end-member source of bacterial methane appears

unlikely. Using the isotopic criteria of Schoell (1983), the methane of Genesis Field plots as a mixture of thermogenic and bacterial methane based on carbon and hydrogen isotopic properties (Fig. 31).

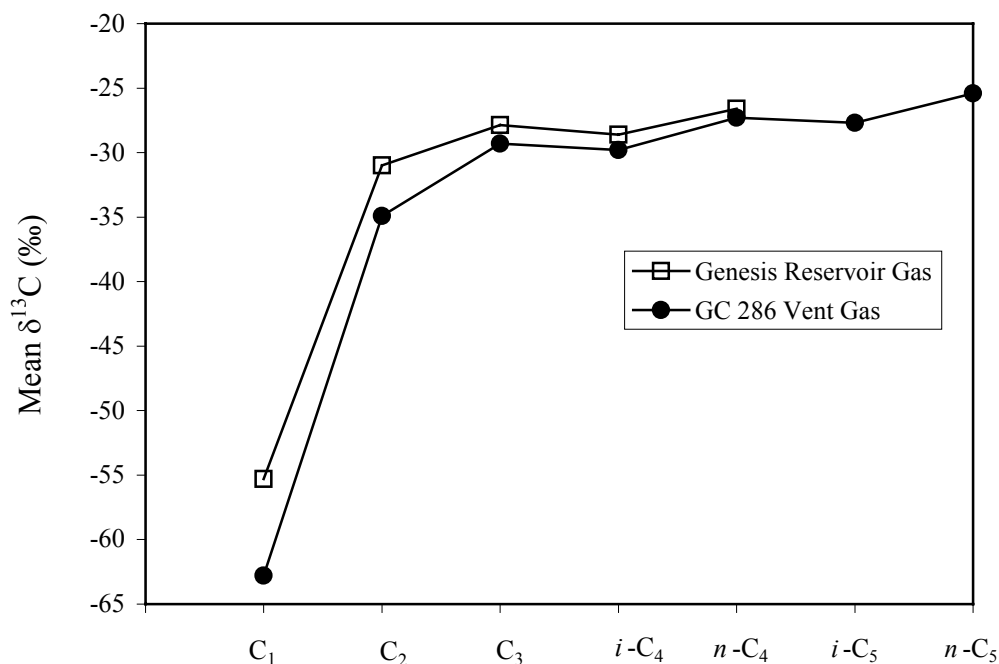


Figure 38. Mean $\delta^{13}\text{C}$ composition of $\text{C}_1\text{-C}_5$ hydrocarbons from reservoir gas of Genesis Field and vent gas from GC 286 Site.

Because the molecular and isotopic properties of natural gas are sensitive indicators of biodegradation, the C_4 hydrocarbons are used as an index of biodegradation (Winters and Williams, 1969). Microbes in reservoirs preferentially oxidize n -butane leading to higher relative abundance of the i -butane molecule. Normal butane is present

in higher relative abundance than isobutane in each gas sample from Genesis Field (Table 6). Propane may show strong enrichment in ^{13}C as a consequence of KIE from preferential microbial oxidation (James and Burns, 1984). The $\delta^{13}\text{C}$ values of propane in samples are not greatly enriched relative to ethane.

Moreover, the plot of isotopic properties of $\text{C}_1\text{-C}_4$ gas from Genesis Field approximates a straight line (Fig. 38), which is consistent with a lack of significant biodegradation effects. Because δD is particularly sensitive to biodegradation effects (Coleman et al., 1981), the narrow range of methane δD ($\sim 3\text{‰}$) is not consistent with significant biodegradation effects. While geochemical properties of hydrocarbons of oil reservoirs from Genesis Field show significant alteration effects by biodegradation, the lack of obvious alteration in gas properties of Genesis Field is best explained by a late charge of gas from subsurface petroleum system (Sassen et al., 2002).

The mean methane/ethane ratio of ~ 16.6 of gas from Genesis Field, although it is higher than that of Jolliet Field, is still low to interpret the gas as a mixture with much bacterial methane. The ratio does not suggest a great predominance of bacterial methane especially when it is compared to bacterial methane of other sites of the Gulf slope where ratios are higher than 10,000 (Thompson, 1996). Using the ethane/methane ratio versus $\delta^{13}\text{C}$ of methane relation to test the mixing hypothesis, hydrocarbons gas from reservoirs of Genesis Field plot along a straight line suggesting a gas mixing not noted in gas from Jolliet Field (Fig. 32). Carbon isotope properties of ethane and methane from Genesis Field are plot along straight trend through an ideal mixing line in Schoell's (1983) diagram (Fig. 33).

The data presented in Fig. 33 suggest that samples of gas from Genesis Field, which have the most depleted ^{13}C isotopic properties of methane and ethane, is consistent with mixture of bacterial and thermogenic methane compared to hydrocarbon gas from Jolliet Field. In order to model methane sources for Genesis Field based on the method of Chung et al. (1988), we made some assumptions. If we assume the $\delta^{13}\text{C}$ of pure bacterial methane is -70‰ , then the total methane of Genesis Field reservoir gas is $\sim 51\%$ bacterial (Fig. 39). If we assume the $\delta^{13}\text{C}$ of pure bacterial methane is -90‰ , methane is $\sim 31\%$ bacterial (Fig. 39). This fraction (31%-51%) is more significant when compared to the range of bacterial methane contribution (17%-28%) in Jolliet Field gas samples. The estimated original $\delta^{13}\text{C}$ value of thermogenic methane end-member from Genesis Field is -40.0‰ (Fig. 39).

The measured mean $\delta^{13}\text{C}$ composition of methane (-55.3‰) from Genesis Field is not so enriched as to suggest an oil-window thermal maturity for the gas. But, the corrected original $\delta^{13}\text{C}$ of thermogenic methane from the field (-40.0‰) is consistent with mature oil source rock. On the natural gas plot of Chung et al. (1988), carbon isotopic properties of ethane through butane of reservoir gas from Genesis Field have almost same slope compared to that of natural gas plot of Jolliet Field (Fig. 39). This observation indicates that gas from Genesis Field and Jolliet Field have similar thermal maturity histories.

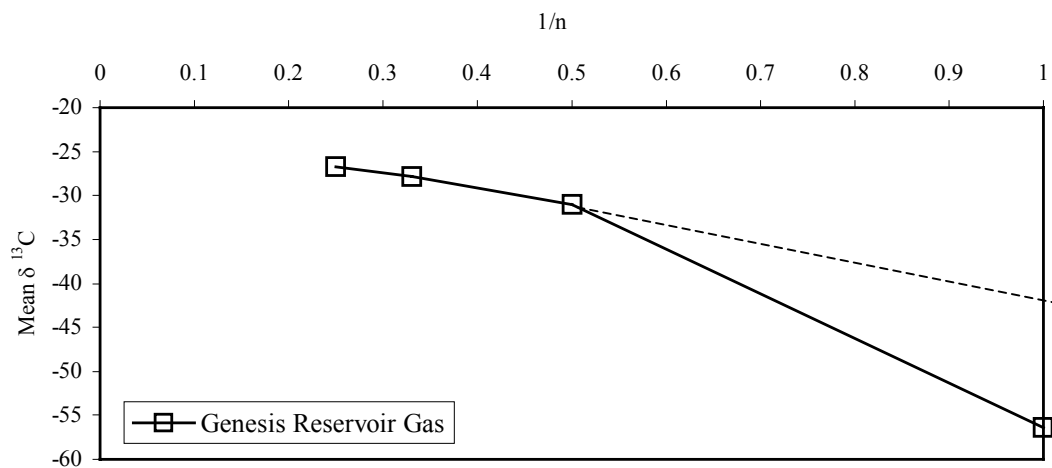


Figure 39. The method of Chung et al (1988) is used to estimate relative contributions of bacterial methane to C₁-C₄ hydrocarbon gases from reservoirs of Genesis Field. Dashed line shows estimated original δ¹³C of thermogenic methane.

GC 286 Vent Site

The GC 286 mud volcano site, at ~ 839 m water depth and at northwest of Genesis Field, was sampled by a research submersible (Sassen et al., 2002). The molecular and isotopic properties of C₁-C₅ hydrocarbons from vent gas sample of GC 286 mud volcano site are shown in Tables 8 and 9 (data from Sassen et al., 2002).

The vent gas sample from the site is mainly methane (94.2%) (Table 8). The C₂ (3.7%) and C₃ (1.3%) hydrocarbons are lesser components, and the C₄ and C₅ hydrocarbons are present as minor components (<0.3%) (Fig. 37). The methane/ethane

Table 8. Molecular properties of vent gas in GC 286 Site (data from Sassen et al., 2002).

Sample Location	Depth (m)	Sample	% C ₁	% C ₂	% C ₃	% <i>i</i> -C ₄	% <i>n</i> -C ₄	% <i>i</i> -C ₅	% <i>n</i> -C ₅	gas wetness (vol %)	methane/ethane
GC 286	839	Vent gas	94.2	3.7	1.3	0.2	0.3	0.1	0.1	5.71	25.46
MEAN			94.2	3.7	1.3	0.2	0.3	0.1	0.1	5.71	25.46

Table 9. Isotopic properties of vent gas in GC 286 Site (data from Sassen et al., 2002).

Sample Location	Depth(m)	Sample	$\delta^{13}\text{C C}_1$	$\delta\text{D C}_1$	$\delta^{13}\text{C C}_2$	$\delta^{13}\text{C C}_3$	$\delta^{13}\text{C }i\text{-C}_4$	$\delta^{13}\text{C }n\text{-C}_4$	$\delta^{13}\text{C }i\text{-C}_5$	$\delta^{13}\text{C }n\text{-C}_5$
GC 286	839	Vent gas	-62.8	-176.0	-34.9	-29.3	-29.8	-27.3	-27.7	-25.40
MEAN			-62.8	-176.0	-34.9	-29.3	-29.8	-27.3	-27.7	-25.40

ratio is ~25.5. Gas wetness of the vent gas sample of GC 286 mud volcano is 5.7% (Table 8). Compared to reservoir gas of Genesis Field, methane is more abundant in the vent gas of GC 286, whereas, ethane and propane are less abundant in the vent gas (Fig. 37).

The $\delta^{13}\text{C}$ value of the methane is -62.8‰ , and the δD value is -176‰ (Table 9). The $\delta^{13}\text{C}$ values of C_2 (-34.9‰), C_3 (-29.3‰), *i*- C_4 (-29.8‰), *n*- C_4 (-27.3‰), *i*- C_5 (-27.7‰), and *n*- C_5 (-25.4‰) indicate enrichment in ^{13}C relative to methane (Fig. 38). The isotopic properties of methane and Schoell (1983)'s genetic classification diagram relating $\delta^{13}\text{C}$ and δD properties of methane indicate that the vent gas is dominantly of bacterial origin (Fig. 31). GC 286 vent gas includes 5.7% of C_2 - C_5 thermogenic hydrocarbons. The gas wetness is too high to simply interpret the gas as a bacterial end-member. Isotopic properties of the C_2 - C_5 hydrocarbons from the vent gas appear to be exclusively from a thermogenic source in the deep subsurface petroleum system (Fig. 38). Thus, the vent methane from GC 286 is assumed to contain at least some thermogenic methane because such methane initially accompanied the higher hydrocarbon gases, and for this reason, an end-member source of bacterial methane appears unlikely. The vent methane from GC 286 may be a mixture of bacterial and thermogenic methane.

The molecular ratio of $\text{C}_1/(\text{C}_2+\text{C}_3)$ and carbon isotope composition of methane of the vent gas from the GC 286 site provides some insight to origin. GC 286 vent gas, with mean $\text{C}_1/(\text{C}_2+\text{C}_3)$ molecular ratio of 18.84 and mean methane $\delta^{13}\text{C}$ of -62.8‰ plots on the mixed gas field using the diagram of Bernard et al. (1978) (Fig. 35). Although the

low methane/ethane ratio suggests that there is no enormous predominance of bacterial methane, mixed source for that vent gas appears likely.

Genesis Field is not directly related to the GC 286 mud volcano site (Sassen et al., 2002). However, the molecular and isotopic properties of vent gas from GC 286 site and the gas from Genesis Field show some similarities. Although the methane of vent gas GC 286 is depleted (within $\sim 7.5\%$) in ^{13}C relative to Genesis Field reservoir methane, the most depleted methane from the reservoir gas approaches the $\delta^{13}\text{C}$ of methane from the vent gas site within $\sim 3.2\%$. The $\delta^{13}\text{C}$ values of C_{2+} hydrocarbons are generally similar to reservoir gas, within $\sim 4\%$. The difference in isotopic compositions of methane may be caused by varying mixture of bacterial methane and thermogenic methane.

To understand the effects of biodegradation on a gas sample, propane is used as an index of alteration. Propane may show strong enrichment in ^{13}C as a consequence of kinetic isotope effects from preferential biodegradation, as much as $\sim 9\%$ (James and Burns, 1984). The $\delta^{13}\text{C}$ value of propane in GC 286 vent gas sample is not greatly enriched in ^{13}C relative to ethane, differing by $\sim 5.6\%$. However, this value is greater than the difference in $\delta^{13}\text{C}$ values ($\sim 3\%$) of propane and ethane molecules in Genesis Field gas samples, indicating more meaningful biodegradation in GC 286 vent gas compared to Genesis Field. The other index of biodegradation is butane hydrocarbons (Winters and Williams, 1969). The *n*-butane (0.3%) is present in higher relative abundance than *i*-butane (0.2%) in GC 286 vent gas sample, suggesting a lack of significant biodegradation. Additionally, the plot of isotopic properties of $\text{C}_1\text{-C}_5$ gas

from GC 286 vent site approximates a straight line, which is not consistent with significant biodegradation (Fig. 38).

The vent methane from GC 286 site is assumed to contain some thermogenic methane because of the higher hydrocarbon gases in the vent gas, even though $\delta^{13}\text{C}$ and δD values of methane indicate a bacterial source. Although the methane/ethane ratio of ~ 25.5 is higher than that of Genesis Field, it still does not represent a significant mixture of bacterial and thermogenic methane. This is particularly true when compared to many high-flux methane seep sites of the Gulf slope where the ratios may be frequently higher than 10,000 (Thompson, 1996).

The method of Chung et al. (1988) is used to model the methane mixture assuming a range of $\delta^{13}\text{C}$ values for end-member bacterial methane (Fig. 40). If we assume the $\delta^{13}\text{C}$ of pure bacterial methane is -70‰ , then the total vent methane is $\sim 64\%$ bacterial (Fig. 40). If we assume the $\delta^{13}\text{C}$ of pure bacterial methane is -90‰ , vent methane is $\sim 32\%$ bacterial (Fig. 40). The estimated original $\delta^{13}\text{C}$ value of thermogenic methane from the vent site at GC 286 is -50.2‰ (Fig. 40). The percentage of bacterial methane, with a significant fraction of 32% to 64%, is similar to the fraction of bacterial methane in methane from reservoirs of Genesis Field.

The corrected $\delta^{13}\text{C}$ of methane in vent gas from GC 286 vent site (-50.2‰) is depleted in ^{13}C by $\sim 10.2\text{‰}$ compared to Genesis Field, possibly indicating wilder thermal maturation effects. The slope on natural gas plot of C_2 to C_5 hydrocarbons is steeper than the slope on the plot of reservoir gas from Genesis Field (Fig. 40). The steeper slope on the natural gas plots may indicate that the gas has a milder thermal

maturity history. Thus, vent gas from GC 286 vent site may be slightly less mature than the gas in reservoirs of Genesis Field. On this basis, the gas of Genesis Field may have experienced more advanced thermal cracking than the vent gas from GC 286 vent site. Different migration conduits are assumed to be involved.

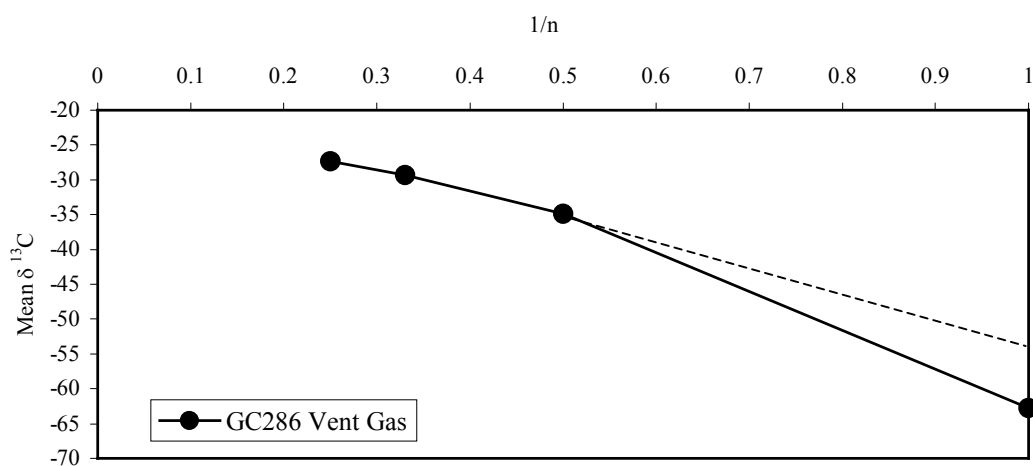


Figure 40. The method of Chung et al (1988) is used to estimate relative contributions of bacterial methane to C₁-C₄ hydrocarbon gases from GC 286 Vent Site. Dashed line shows estimated original δ¹³C of thermogenic methane.

Petronius Field

Petronius Field (VK 786) is an oil and gas accumulation at ~3.3 km on the upper Gulf slope at 535 m water depth (Sassen et al., 2001c). Geochemical properties of medium gravity crude oil show some evidence of non-thermal alteration processes such

as biodegradation. Molecular and isotopic properties of C₁-C₅ hydrocarbons from gas in reservoirs of Petronius Field are shown in Tables 10 and 11 (data from Sassen et al., 2001c). The gas of Petronius Field is dominantly methane (mean =91.2%), and higher hydrocarbons, ethane through pentane, decrease in relative abundance with increasing carbon number (Table 10). Mean relative abundance of C₂₊ hydrocarbons is in the order of ethane (4.9%), propane (2.4%), isobutane (0.4%), normal butane (0.7%), isopentane (0.2%), and normal pentane (0.2%) (Fig. 41). The mean methane/ethane ratio is ~18.5 and the mean gas wetness of the reservoir gas in Petronius Field is 8.8 (Table 10).

The mean carbon isotopic composition of methane from Petronius Field is -51.8‰, and the mean hydrogen isotope composition of methane is -160.7‰ (Table 11). The mean δ¹³C values of C₂ (-29.4‰), C₃ (-27.7‰), *i*-C₄ (-28.2‰), *n*-C₄ (-26.9‰), *i*-C₅ (-27.2‰), and *n*-C₅ (-27.2‰) indicate enrichment in ¹³C relative to methane (Fig. 42). The mean δ¹³C values of C₂-C₅ hydrocarbons show only small variation (<1‰) within the samples suggesting that the isotopic composition of the gas from Petronius Field may be nearly invariant.

The δ¹³C values of subsurface methane from Petronius Field are uniform within a narrow range of ~2‰, whereas δD values are more variable in the ~24‰ range. The carbon isotopic and hydrogen isotopic properties of methane are slightly depleted in ¹³C compared to the typical thermogenic gas samples of the Gulf slope. Even though proposing a thermogenic origin for Petronius Field gas is reasonable, it should be stated

Table 10. Molecular properties of reservoir gas in Petronius Field (data from Sassen et al., 2001c).

Sample Location	Depth (m)	Sample	% C ₁	% C ₂	% C ₃	% <i>i</i> -C ₄	% <i>n</i> -C ₄	% <i>i</i> -C ₅	% <i>n</i> -C ₅	gas wetness (vol %)	methane/ethane
VK 786	3105	Reservoir gas	91.8	4.8	2.1	0.3	0.6	0.2	0.2	8.20	19.13
VK 786	3105	Reservoir gas	92.3	4.7	1.9	0.3	0.6	0.2	0.1	7.79	19.64
VK 786	3105	Reservoir gas	89.6	5.3	3.1	0.5	1.0	0.3	0.3	10.49	16.91
MEAN			91.2	4.9	2.4	0.4	0.7	0.2	0.2	8.83	18.49

Table 11. Isotopic properties of reservoir gas in Petronius Field (data from Sassen et al., 2001c).

Sample Location	Depth (m)	Sample	$\delta^{13}\text{C C}_1$	$\delta\text{D C}_1$	$\delta^{13}\text{C C}_2$	$\delta^{13}\text{C C}_3$	$\delta^{13}\text{C }i\text{-C}_4$	$\delta^{13}\text{C }n\text{-C}_4$	$\delta^{13}\text{C }i\text{-C}_5$	$\delta^{13}\text{C }n\text{-C}_5$
VK 786	3105	Reservoir gas	-52.5	-154	-29.2	-27.2	-28.2	-26.6	-27.2	-27.2
VK 786	3105	Reservoir gas	-52.5	-152	-29.5	-27.9	-28.5	-27.0	-27.1	-27.4
VK 786	3105	Reservoir gas	-50.5	-176	-29.5	-28.0	-27.9	-27.0	-27.2	-27.1
MEAN			-51.8	-160.7	-29.4	-27.7	-28.2	-26.9	-27.2	-27.2

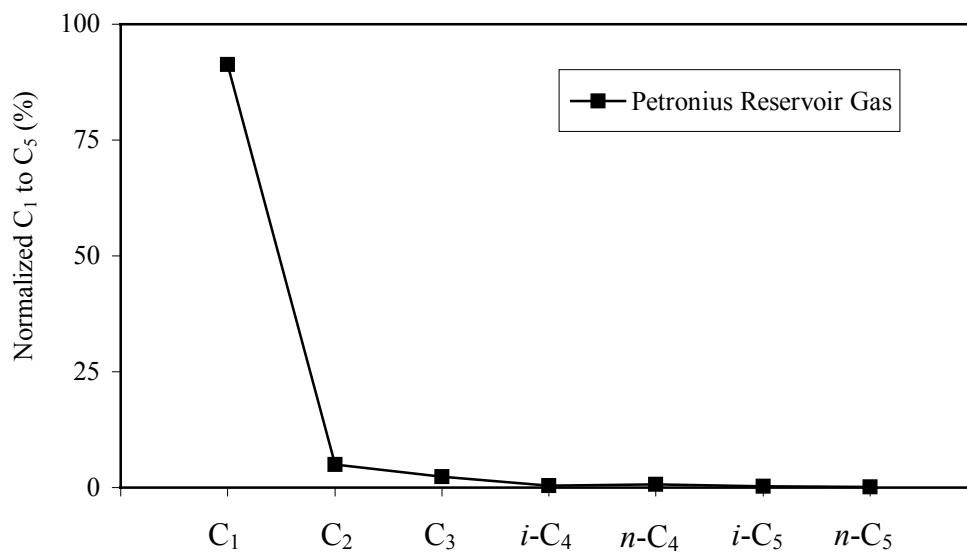


Figure 41. Mean C₁-C₅ molecular composition of reservoir gas from Petronius Field.

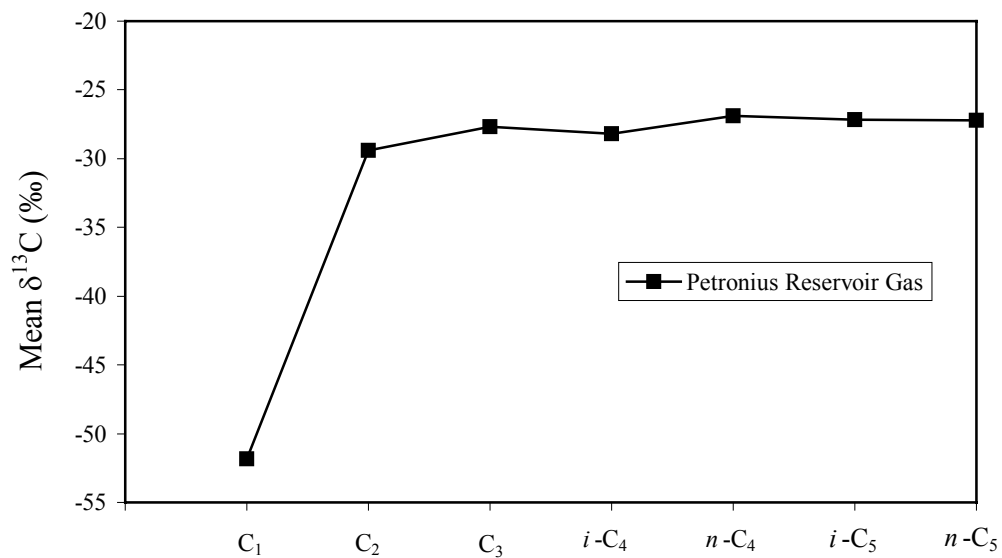


Figure 42. Mean $\delta^{13}\text{C}$ composition of C₁-C₅ hydrocarbons from reservoir gas of Petronius Field.

that the mean carbon isotopic composition of methane with -51.8‰ contains a portion of bacterial methane. Using Schoell (1983)'s source and maturity diagram, the methane plots as a mixture of bacterial and thermogenic origin supporting the assumption that the gas from Petronius Field has bacterial component to some extent (Fig. 31).

In order to test the effects of biodegradation in reservoir gas samples of Petronius Field, molecular and isotopic properties of propane and butanes are used. The $\delta^{13}\text{C}$ values of propane are not greatly enriched compared to that of ethane molecule, differing by $\sim 1.7\text{‰}$. The *n*-butane is present in higher relative abundance than *i*-butane in each gas sample from Petronius Field. This indicates that the gas is not significantly altered by biodegradation. Carbon isotopic properties of $\text{C}_1\text{-C}_5$ hydrocarbons in reservoir gas of Petronius Field show approximately a straight line indicating no obvious evidence of biodegradation (Fig. 42). The δD properties of methane in gas from Petronius Field are variable across a whole range ($\sim 24\text{‰}$) when compared to the methane from Jolliet and Genesis fields. Because δD in a methane sample is particularly sensitive to biodegradation effects (Coleman et al., 1981), this observation may suggest that the gas from Petronius is the more bacterially oxidized than in other fields.

Plotting the data of gas from reservoirs of Petronius Field in the $\delta^{13}\text{C}$ versus C_2/C_1 ratio diagram (Prinzhofer and Pernaton, 1997), it is possible to support the hypothesis of mixing with a linear trend even though mean methane/ethane ratio of the all sampled gases from this field is low (~ 18.5) (Fig. 32). The principle behind the mixing diagram is that a straight line should be observed to characterize a mixing between two end members. The molecular ratio between ethane and methane

hydrocarbons and isotopic ratio of methane of the gas from Petronius Field illustrate such a straight line that the gas is expected to represent a mixture between thermogenic and bacterial end-members.

This observation is also supported by carbon isotopic compositions of ethane and methane in the gas. Carbon isotopic properties of methane and ethane in the gas from reservoirs of Petronius Field are overlaid on the plot proposed by Schoell (1983) relating carbon isotopic properties in ethane and methane (Fig. 33). Ethane and methane carbon isotopic composition of gases, with most enriched $\delta^{13}\text{C}$ values of ethane compared to that of gases from Jolliet and Genesis fields, give a nearly vertical straight line along the mixing line proposed in the diagram.

Using the method of Chung et al. (1988), the amount of bacterial methane mixed with thermogenic gas is modeled. If we assume the $\delta^{13}\text{C}$ of pure bacterial methane is -70‰ , then the total methane of Petronius Field reservoir gas is $\sim 49\%$ bacterial (Fig. 43). If we assume the $\delta^{13}\text{C}$ of pure bacterial methane is -90‰ , methane is $\sim 31\%$ bacterial (Fig. 43). The corrected original $\delta^{13}\text{C}$ value of thermogenic methane from Petronius Field is -34.5‰ (Fig. 43). Thus, bacterial methane, which is mixed with the thermogenic methane of Petronius Field, is in significant fraction (31%-49%) similar to that of Genesis Field.

The mean $\delta^{13}\text{C}$ composition of methane (-51.8‰) from Petronius Field is not consistent with an oil-window thermal maturity for the gas. The overall carbon isotopic properties of the gas are consistent with a milder thermal maturity history compared to that of Jolliet and Genesis fields. However, the estimated original $\delta^{13}\text{C}$ of thermogenic

methane from the field (-34.5%) is coherent with mature oil source rock. On natural gas plot of Chung et al. (1988), carbon isotopic properties of ethane through butane molecules of reservoir gas from Petronius Field have gentle slopes as in the case of natural gas plots of Jolliet and Genesis fields (Fig. 43). This observation also supports that the gas from Petronius Field has more or less same maturity level with the gases from other fields.

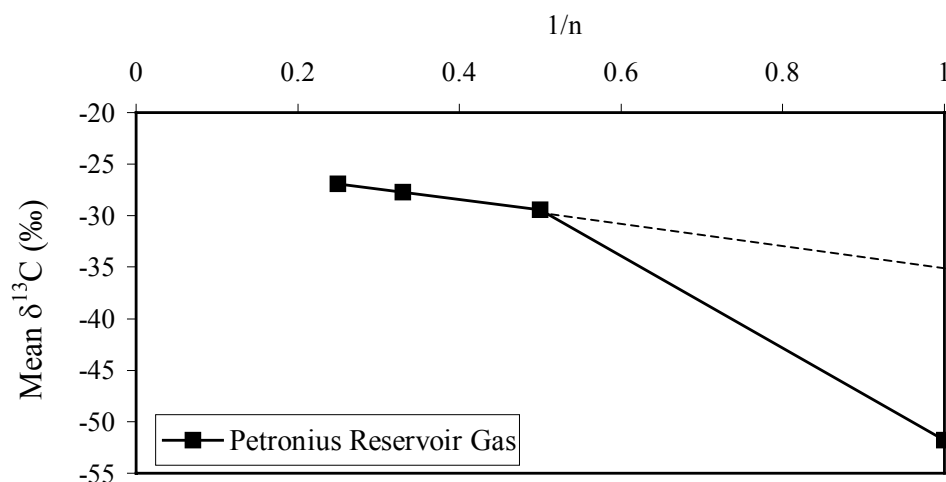


Figure 43. The method of Chung et al (1988) is used to estimate relative contributions of bacterial methane to $\text{C}_1\text{-C}_4$ hydrocarbon gases from Petronius Field. Dashed line shows estimated original $\delta^{13}\text{C}$ of thermogenic methane.

In addition to all the data presented up to now, oil-gas correlation is illustrated by using the method of Chung et al. (1988). They state that the source of gaseous hydrocarbons, whether it is an oil or kerogen, may be approximated as a molecule

having a large number of carbon atoms. The carbon isotope ratio of the source, therefore, is the y-intercept at the left side of a natural gas plot when the number of carbon atoms is a large number. The intercepts, representing the estimated $\delta^{13}\text{C}$ value of oil source, in Fig. 44 are -21.5‰ for the gas sample from Jolliet Field, -22‰ for that from Genesis Field, and -24.5‰ for Petronius Field. The values are very similar to each other, consistent with the suggestion that the gases may be sourced from oils, which are from the same or similar source at similar thermal maturity levels.

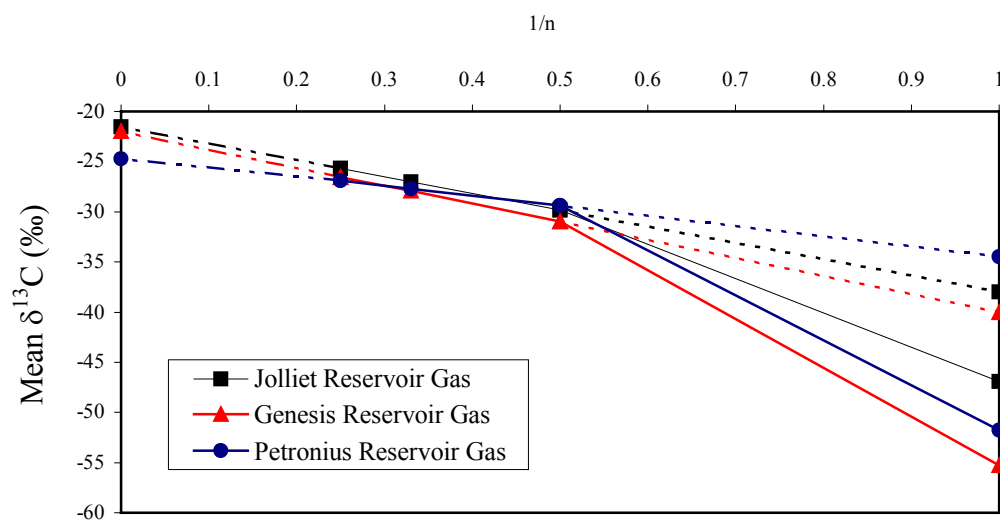


Figure 44. Natural gas plots of all fields in the study area showing the application of method of Chung et al. (1988). Dotted lines show estimated original $\delta^{13}\text{C}$ of thermogenic methane. Dashed lines show estimated $\delta^{13}\text{C}$ of oil source.

The measured $\delta^{13}\text{C}$ values of oils from Petronius and Jolliet fields are -27.6‰ and -27‰ respectively (Sassen et al., 2001a, c). It is observed that the carbon isotope ratios of oils are generally lighter than that the intercept of the natural gas plots of the gaseous hydrocarbons. Such a deviation is also noted in the method of Chung et al (1988). This may be caused by non-thermal alteration processes by which oils are affected after emplacement in reservoirs.

CHAPTER VI

DISCUSSION AND SYNTHESIS

Mixing of bacterial and thermogenic methane is common in shallow subsurface reservoirs and natural seeps in a variety of settings including the Gulf of Mexico Salt Basin (e.g. Subalpine Molasse Basin, Schoell, 1977, 1983; Gulf of California, Schoell, 1982; Po and Apulian Basins, Mattevelli et al., 1983). During the last two decades, it has been shown that mixing of bacterial and thermogenic methane in reservoirs of the Gulf of Mexico shelf, basically a gas province, is not unusual (e.g. Bernard, 1978; Rice and Threlkeld, 1990; Walters, 1990; Schoell and Beeunas, 1996; Sassen et al., 1998; Beeunas et al., 2001). Bacterial methane is trapped as dry gas fields accounting for up to 80% of the gas resource and production from reservoirs in the Gulf of Mexico shelf (Wagner and Sofer, 1996). It is not unreasonable to find mixtures of thermogenic and bacterial methane in reservoirs of the Gulf of Mexico shelf under condition such that much bacterial end-member methane accumulated in shallow reservoirs of the shelf.

Mixtures of thermogenic and bacterial methane and their relative abundances in deep subsurface petroleum system of the Gulf slope, mainly an oil province, are not yet addressed widely (Sassen et al, 2002). Insight to the mixing of the gas in the slope may improve reservoir characterization and understanding of the generation, migration, accumulation, and alteration histories of the gas. Understanding origin of bacterial

methane, relative abundance in mixtures, and conditions favorable for generation are key parameters to better realize elements in the petroleum systems of the Gulf slope.

The Gulf slope is a geochemically and geologically dynamic setting associated with extensive salt tectonics. Presence of large volumes of hydrocarbons in minibasins as well as hydrocarbon seepage, gas hydrate formation, chemosynthetic communities, and authigenic carbonate precipitation are important features observed on the slope (e.g. Kennicutt and Brooks, 1990; Roberts et al., 1990; Sassen et al, 1993a, 1999b, 2001a, b, c; Roberts and Carney, 1997; Milkov and Sassen, 2000). Hydrocarbons migrate vertically along salt and fault conduits, and laterally along sand carrier beds (Sassen et al., 1999a; 2001a). Multiple hydrocarbon charge episodes occur (Sassen et al., 2001a, c). Trapping efficiencies are poor (Sassen, 1998). Degrees of alteration of hydrocarbons are variable even in a single petroleum field.

Increasing deep-water research in slope settings show that mixtures of thermogenic and bacterial methane are observed in hydrocarbon fields and show that there may be large volume of bacterial methane (Wagner and Sofer, 1996; Sassen et al., 1998; Sassen et al., 2002). Insight to gas mixing, and origin of bacterial methane in deep individual petroleum fields in the slope will help to synthesize reservoir filling histories and the occurrence of the gas by establishing geochemically meaningful links between fields.

Geochemical assessment of hydrocarbons are summarized in Table 12 illustrating source, thermal maturity, migration style, alterations, mixing effects and the

Table 12. Summary table showing geochemical assessment of hydrocarbons from the fields (Jolliet, Genesis and Petronius fields). Data compiled from (A) Sassen et al., 2001a; (B) Sassen et al., 2002; (C) Sassen et al., 2001c.

FIELDS	JOLIET FIELD^(A)	GENESIS FIELD^(B)	PETRONIUS FIELD^(C)
Location on Upper Slope	GC 184 Green Canyon	GC 160/161 Green Canyon	VK 786 Viosca Knoll
Depth of Reservoir (m)	1855-3076	3509-4184	3343-3375
Water Depth (m)	540	762-855	535
Reservoir Temperature(T°C)	~65 at 2187.9m	~71	?
Geothermal Gradient (T°C/km)	29.7	20.2	?
Reservoir Lithology	Slope fan turbidite channel-fill sands	Slope fan turbidite channel-fill sands	turbidite sands
Reservoir Age	Plio-Pleistocene	Plio-Pleistocene	Miocene
Trapping Mechanism	Structural (growth fault)	complex Structural (fault and anticline)	Structural (growth fault) and Stratigraphic barrier
Seal Lithology	shale	shale and salt	shale
Compartmentalization	Common	Three main reservoirs	Common
HC Accumulation	Crude oil & Natural gas	Crude oil & Natural gas	Crude oil & Natural gas
Nearby Vent Sites	GC 185, GC 233	GC 286	?
Migration Pathway	long (only vertical)	long	long
Migration Style	Vertical: growth fault (rapid migration)	Vertical: growth fault Lateral: carrier sand	Vertical: growth fault Lateral: carrier sand
CRUDE OIL			
Probable Age of Source	Upper Jurassic	Upper Jurassic	Upper Jurassic
Thermal Maturity	oil-window	oil-window	oil-window
Corrected $\delta^{13}\text{C}$ of Oil	-21.5‰ PDB	-22‰ PDB	-24.5‰ PDB
Non-thermal Alterations	insignificant gas washing biodegradation	insignificant gas washing biodegradation	insignificant gas washing biodegradation
NATURAL GAS			
Gas Type	Thermogenic	Mixed	Mixed
Generation	Thermal cracking from oil	Thermal cracking from oil	Thermal cracking from oil
Mixing Effect	low-almost none	high	high
Bacterial Methane (%)	17%-28%	31%-51%	31%-49%
Biodegradation	not meaningful	almost none	almost none
Corrected $\delta^{13}\text{C}$ of Thermogenic Methane	-38‰ PDB	-40‰ PDB	-34.5‰ PDB
Thermal Maturity	mature	mature	mature

amount of bacterial methane in hydrocarbons found in Jolliet, Genesis and Petronius fields and their associated vent sites (GC 185, GC 233, and GC 286). The fields in the study area are mainly oil accumulations containing gas. Based on the molecular and isotopic data available, the gas accumulated in the fields are largely of thermogenic

origin. However, the gas may show mixing effects in variable degrees. Bacterial methane volumes in mixed gases may extend to significant amounts (up to 51%).

Thermogenic gas from reservoirs of Jolliet Field is the least mixed gas (17%-28% bacterial methane) among the studied fields. Oil accumulated in shallower reservoirs of Jolliet Field illustrates slight biodegradation (Kennicutt et al., 1988; Sassen et al., 2001a). Deep Pleistocene reservoirs contain oil that is not substantially altered by biodegradation or other non-thermal processes (Thompson and Kennicutt, 1990). The gas displays no meaningful effects of biodegradation. Late charge of hydrocarbon gas may enter Jolliet Field after an earlier filling episode and the biodegradation of oil (Sassen et al., 2001a). There may be ongoing reservoir flushing by late thermogenic gas during Late Pleistocene-Holocene (Cook and D'Onfro, 1991; Sassen et al., 2001a). It is reasonable to assume that thermogenic gas in reservoirs of Jolliet Field is the product of thermal cracking of oil before final migration to the present reservoir (Sassen et al., 2001a). The corrected $\delta^{13}\text{C}$ (-38‰ PDB) of thermogenic methane from the field is consistent with oil window phase of thermal maturity.

Rapid vertical migration of late gas charge along active fault conduits may have initiated leakage from Jolliet Field to the vent sites at the sea floor (Sassen et al., 2001a). To investigate the probable source of the episodic oil and gas charge, and the contribution of bacterial methane to thermogenic gas of Jolliet Field, insight to the properties of vent gas at GC 185 and GC 233 site is necessary. Two geochemically distinct types of vent gas are observed at GC 185 (Bush Hill) and GC 233 (Brine Pool) sites (Kennicutt et al., 1988; Sassen et al., 1994; Sassen et al., 1999b). The geochemical

properties of vent gas at GC 185 site are consistent to that of gas in reservoirs of Jolliet Field ($\delta^{13}\text{C}$ of C_{2+} hydrocarbons in 1.9‰ range) although the vent gas is biodegraded compared to the reservoir gas (Kennicutt et al., 1988; Sassen et al., 2001a). The GC 185 vent gas is of thermogenic origin with corrected methane. The GC 185 vent gas shows very limited mixing with bacterial methane of 7.4%-12.6%. Gas sample from GC 233 vent site is pure bacterial methane with mean $\delta^{13}\text{C}$ of -64.9‰ PDB. Thermogenic and bacterial end-members of methane are observed in nearby vent sites. Bacterial methane thus is available for mixing.

The gas in Pliocene-Pleistocene deep reservoirs of Genesis Field is of mixed origin with 31%-51% bacterial methane. The volume of bacterial methane is distinctly higher in mixed gas of Genesis Field compared to that of Jolliet Field. The oil of Genesis Field shows evidence of episodic alteration by biodegradation in the reservoir (Beeunas et al., 1999). Mixed gas of Genesis Field displays no meaningful effects of biodegradation. Whole-oil chromatograms are consistent with multiple episodes of hydrocarbon charge to reservoirs (Sassen et al., 2002). Biodegradation of oil earlier in the burial history is overprinted by late charge of less altered hydrocarbons more recently in the burial history. The early charge of hydrocarbons may have been followed by lateral migration of fresh gas and oil to reservoirs in which hydrocarbons remain relatively unaltered by biodegradation (Sassen et al., 2002).

Volumetrically significant late gas charge may have contributed to the evaporative fractionation also noted in the field (Beeunas et al., 1999). The best explanation of the evidences is that late gas migration may have occurred at or near

present burial depth, flushing the reservoir system of previously biodegraded hydrocarbon gas to include any previous bacterial methane (Sassen et al., 2002). The gas in Genesis Field may be generated by thermal cracking of oil before entering the reservoir (Sassen et al., 2002). The corrected original $\delta^{13}\text{C}$ of thermogenic methane in the field (-40‰ PDB) is consistent with mature oil source. More complex and probably longer migration pathways (both vertical and lateral conduits) than that of Jolliet Field has played greater role for Genesis hydrocarbons.

The $\delta^{13}\text{C}$ isotopic properties of C_{2+} hydrocarbons in GC 286 vent gas are different than that of the reservoir gas in Genesis Field, within 3.9‰ PDB. Vent gas at GC 286 is more biodegraded than the gas in Genesis Field. The vent gas from the GC 286 site, even though carbon isotopic properties of methane show a bacterial origin ($\delta^{13}\text{C}$ of -62.8‰ PDB), is explained by mixing of thermogenic and bacterial methane as in the case of Genesis Field. A significant fraction of 32% to 64% of bacterial methane in the vent gas is consistent with the bacterial component in mixed gas of Genesis Field. The corrected original $\delta^{13}\text{C}$ of thermogenic methane at GC 286 vent site is -50.2‰ PDB. The observation that bacterial and thermogenic methane are present with oil at GC 286 imply that the vertical migration conduits that charge the vent may have a deep, large drainage area (Sassen et al., 2002).

The gas in reservoirs of Petronius Field is of mixed origin with 31%-49% bacterial methane. The volume of bacterial methane in the gas of Petronius Field is very similar to that of Genesis Field. Oil in reservoirs of Petronius Field shows some evidence

of non-alteration processes such as biodegradation or gas washing (Sassen et al., 2001c). The gas in the field shows no meaningful effects of biodegradation.

It is assumed that Petronius Field had a simple filling history mainly resulting from oil charge directly from the source rock, as it is attained oil-window thermal maturity (Sassen et al., 2001c). As in the case of Genesis Field, hydrocarbons migrated by a combination of vertical (growth faults) and lateral conduits (carrier sand beds) (Sassen et al., 2002). Hydrocarbons, which are trapped by a combination of stratigraphic and structural (growth fault) components, migrated from large lateral drainage areas to the Miocene sand reservoirs of Petronius Field. The significant bacterial methane contribution in this gas, similar to that of Genesis Field, may be the result of mixing in large drainage areas during migration.

The corrected $\delta^{13}\text{C}$ (-34.5‰ PDB) of thermogenic methane from the field is consistent with oil-window thermal maturity. The gas may be the product of thermal cracking of crude oil.

The gas from reservoirs of Jolliet, Genesis, and Petronius fields on the upper Gulf slope are similar to each other based on their geochemical properties (Table 12 and Fig. 45). Hydrocarbon gases in these fields are in the moderate in terms of thermal maturity level. The carbon isotopic properties ($\delta^{13}\text{C}$) of $\text{C}_2\text{-C}_5$ hydrocarbons in reservoirs of the fields are quite similar, within a range between 1.2‰ PDB and 1.6‰ PDB (Fig. 45).

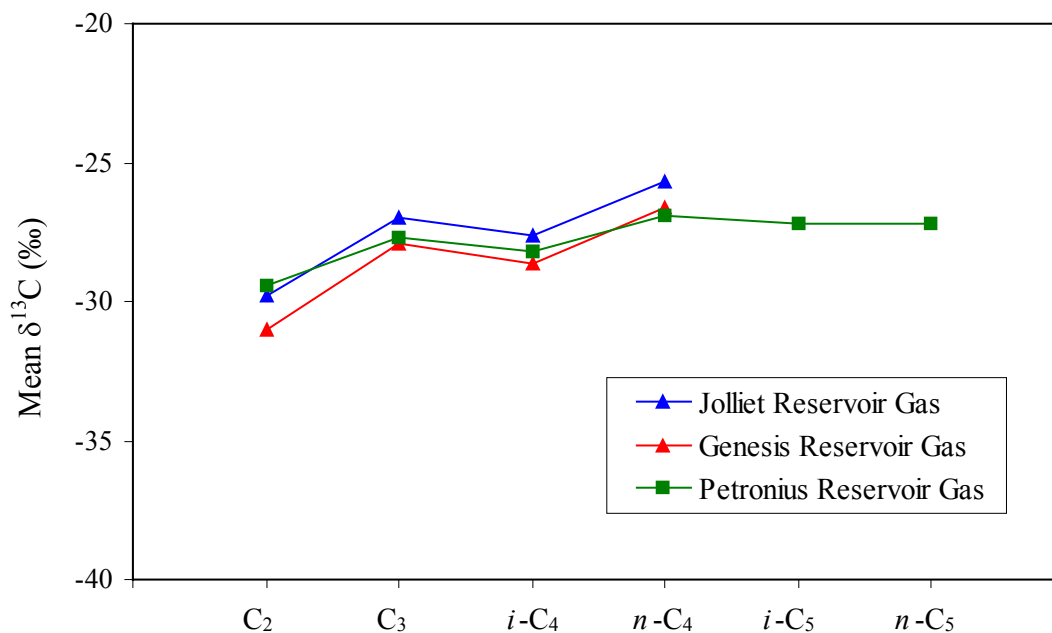


Figure 45. Diagram comparing the mean $\delta^{13}\text{C}$ of C₂-C₅ hydrocarbons from the gas in reservoirs of the study area.

The corrected $\delta^{13}\text{C}$ of original thermogenic methane in the fields are in a range between $\sim -34\text{‰}$ PDB and -40‰ PDB. The gases in the reservoirs of Joliet, Genesis, and Petronius fields may be the product of thermal cracking of crude oil before final migration to the present reservoir. Using the method of Chung et al (1988), the oil-gas correlation shows that the corrected $\delta^{13}\text{C}$ values of oil source are similar for the gas from the fields, giving a range between $\sim -22\text{‰}$ PDB and -25‰ PDB (Table 12).

Most oil in reservoirs of the upper Gulf slope is likely derived from Upper Jurassic sources (e.g. Sassen, 1988, 1990a; Wenger et al., 1994). The gas in the fields of

the study area may also be generated from an Upper Jurassic oil source similar to other fields from the upper slope.

The lack of obvious biodegradation in the gas characters particularly with respect to the oil of Jolliet, Genesis and Petronius fields may be explained by multiple episodes of late charge of relatively unaltered hydrocarbons. Overprinting of geochemical properties of early hydrocarbon by a later charge of relatively unaltered hydrocarbons is common in Upper Cenozoic reservoirs of the Gulf slope (Curiale and Bromley, 1996; Whelan et al., 2001; Sassen et al., 2002).

Petronius and Genesis fields have similar gas mixtures in reservoirs including significant amount of bacterial methane (31% to 51%). Although the gas in reservoirs of Jolliet Field seems not to have affected by mixing process (17% to 28% bacterial methane) as much as the other fields, geochemical properties of recently charged fresh gas may have mask effects on the isotopic properties of old gas in reservoirs of the field.

Molecular and isotopic properties of oil and gas from reservoirs in the fields suggest that the bacterial methane mixed with thermogenic methane before charging the reservoirs in the deep petroleum system. A number of lines of evidence suggest that the charging occurred at approximately the present depth of burial and at present reservoir temperatures. In the dynamic geological setting of slope, it is suggested that the source of the bacterial methane is logically deeper than the reservoirs of Jolliet (3076m depth), Genesis (4184m depth) and Petronius (3375m depth) fields because the drainage area of the migration conduits that charged the field extends still deeper (e.g. Sassen et al., 2001a, c, 2002). There are some evidences to explain how mixtures of thermogenic and

bacterial methane occurred and which source supplied the bacterial methane into deep reservoirs of the fields.

Since bacterial methane is known to be derived by microbial reduction of CO₂ from oxidation of various hydrocarbons at geologically shallow depths up to ~700 m (e.g. Whelan et al., 1986; Thompson, 1996; Sassen et al., 2001a), it is reasonable to find significant fractions of bacterial methane at vent sites of slope. Molecular and isotopic properties of vent gas at GC 185 (thermogenic methane end-member), GC 286 (mixed gas), and GC 233 (bacterial methane end-member) sites suggest that biodegradation of hydrocarbons at shallow depths is very effective.

Vent gas at GC 185 site is of thermogenic origin without meaningful mixing (~7%-13% bacterial methane). Insignificant mixing may be explained by rapid vertical migration. Fresh late gas charge may have initiated leakage from Jolliet Field along the active fault conduits that compartmentalized the reservoirs of the field (Cook and D'Onfro, 1991), permitting rapid vertical migration to the sea floor (e.g. GC 185 vent) (Sassen et al., 2001a). Isotopic properties of vent gas at GC 233 suggest that bacterial methane end-member may indicate the occurrence of bacterial methane at shallow depths.

Without insight to the molecular and isotopic properties of gas from deep reservoirs, it may be assumed that the bacterial methane of the vent at GC 286 is from a shallow source, and is fortuitously associated with thermogenic hydrocarbon gases from a deep source (Sassen et al., 2002). However, the molecular and isotopic properties of

gas from the vent site of GC 286 may be better explained by mixing of gases during migration within the deep subsurface petroleum system in the Green Canyon area.

Bacterial methane may be formed by microbial consumption of organic matters in shallow sediments. The mean total organic carbon of sediment samples across the Gulf slope is 0.82% (Fang et al., 1990). The organic matter is mainly Type III kerogen (Fang et al., 1990). Therefore, there may be a shallow source for microbial methane production in young sediments (Sassen et al., 2002).

Other carbon pools such as crude oil and gaseous hydrocarbons in the shallow reservoirs may cause microbial methane production by anaerobic degradation and sulfate reduction (Thompson, 1996; Sassen et al., 1999a). The generalized temperature limit of $\sim 66^{\circ}\text{C}$ (Philippi, 1977; Schoell, 1983; Machel and Foght, 2000) for the biosphere is also consistent of hydrocarbon biodegradation in shallow reservoirs. It has been observed that shallower and cooler reservoirs in their burial history may hold significant bacterial methane (e.g. Schoell, 1983; Noble and Henk, 1998; Machel and Foght, 2000). Biodegradation of hydrocarbons in shallow reservoirs of Jolliet, Genesis, and Petronius fields are observed (Sassen et al., 2001a, c, 2002). However, the bacterial methane formed by biodegradation in shallow reservoirs and at vent sites is insufficient to explain the origin of mixed gas in deep reservoirs in the study area (e.g. >4 km in reservoirs of Genesis Field).

Bacterial methane may be formed *in situ* in deep reservoirs. The deep biosphere may extend beyond the generalized temperature limit of $\sim 66^{\circ}\text{C}$ (Philippi, 1977; Schoell, 1983; Machel and Foght, 2000). However, sediments become more hostile to microbes

with increasing depth as temperature rises. The present reservoir temperatures (e.g. ~71°C in Genesis Field, Sassen et al., 2002) and geothermal gradients (e.g. ~25-30°C/km on the upper Gulf slope, Milkov and Sassen, 2001) are thought too high to permit microbial activity. There is as yet no direct evidence of living microbes and *in situ* bacterial methane formation in the deep reservoirs of the study area or elsewhere in the deep section (Sassen et al., 2002).

Bacterial methane may be formed shallow, then deeply buried and may have been gathered by the same subsurface migration system that gathered thermogenic gas and oil from a large subsurface drainage area. The most defensible explanation of deep-source methane, at present, is that during rapid deposition living microbes and bacterial methane may have been stranded in deep sediments with a meaningful carbon pool before the temperature became untenable for microbial reduction of CO₂ (Sassen et al., 2002). Low concentrations of residual or trapped bacterial methane dispersed across the large drainage areas of deep subsurface petroleum systems may have been swept by migrating fluids, and then trapped in these fields with thermogenic gas and oil (Sassen et al., 2002). Low geothermal gradients in relatively cooler minibasins along upper slope may preserve the rapidly buried bacterial source (Sassen et al., 2002).

Depocenters of young Tertiary basins are filled at high sedimentation rates. High sedimentation rates are conducive to preservation of disseminated organic matter (e.g. Schoell, 1995). Turbiditic sedimentation of thick shale-sand sequences, and early tectonic deformation allow accumulation of initially disseminated methane in gas fields. Rapid sedimentation in the depocenters may have deformed salt, activated faults,

decreased trapping efficiency by breaching the seals of downdip reservoirs, and released gas for remigration to updip reservoirs (Sassen et al., 2001a).

Even though the conclusion of the deep source of bacterial methane is not generalized to other areas of the Gulf slope, the fields on the upper slope may share a common origin by mixing during migration at geologically significant depth (>4 km). The maximum depth of bacterial methane sources cannot yet be determined. Although there is as yet no direct biologic evidence from deep petroleum system, the deep biosphere may extend beyond the generalized temperature limit of ~66°C. Insofar as the Gulf slope is an appropriate analogy, the maximum depth and the volume of bacterial methane sources in the deep section of rapidly subsiding basins may be underestimated (Sassen et al., 2002). This suggestion may be significant with respect to models of hydrocarbon charge to reservoirs, vents and seeps, to estimates of carbon pool of methane, and to models of climate change.

CHAPTER VII

CONCLUSIONS

Modeling of mixtures of bacterial and thermogenic methane and estimation of relative amount of bacterial methane in the gas mixtures may address problems of understanding the generation, migration, accumulation, and alteration histories of the gas in the study area. Modeling of gas mixtures may also be significant for understanding the probable source of bacterial methane in the deep subsurface petroleum system of the Gulf slope. This study suggests the following conclusions:

1. Assessment of molecular and isotopic properties of oil and gas in reservoirs and vent sites of three different fields across the upper Gulf slope was performed. The fields (Jolliet, Genesis and Petronius fields) have mainly oil accumulations containing natural gas in reservoirs. Although the gas accumulated in the reservoirs is of thermogenic origin, it may illustrate mixing effects in variable degrees. Bacterial methane contributions may extend to significant amounts (up to 51%). Petronius and Genesis fields have similar gas mixtures in reservoirs including significant amount of bacterial methane (31% to 51%). However, Jolliet Field have not much affected by mixing process (17% to 28% bacterial methane).

2. The gas from the reservoirs of the fields are of similar thermal maturity levels and are most probably generated from thermal cracking of Upper Jurassic crude oil which is in oil-window phase thermal maturity.

3. Geochemical properties of hydrocarbons in the reservoirs are compared to that at vent sites. Vent gas at GC 185, GC 233, and GC 286 sites are of thermogenic, bacterial, and mixed origin, respectively. Shallow reservoirs and vents are the main sites of non-thermal alteration particularly biodegradation. Molecular and isotopic properties of early hydrocarbons in the reservoirs may be different than that of relatively unaltered late charge hydrocarbons.

4. Migration pathways and large drainage areas in the dynamic geological setting of the Gulf slope may play an important role in mixing and alteration processes.

5. Molecular and isotopic properties of reservoir gas suggest that bacterial methane mixed with thermogenic methane before entering the deep reservoirs. This study presents data on reservoirs at depths $> \sim 4$ km with significant volumes of bacterial methane.

6. The present reservoir temperatures are thought too high to permit microbial activity. There is as yet no direct evidence of living microbes and *in situ* bacterial methane formation in the deep reservoirs of the study area.

7. Because high sedimentation rates are conducive to preservation of disseminated organic matter and because low geothermal gradients in minibasins along slope may provide low temperatures need for bacterial activity, the following explanation of deep source bacterial methane seems defensible. During rapid deposition, living microbes and bacterial methane were trapped in deep sediments before the temperature became untenable for microbial CO_2 reduction. Therefore, large

undiscovered reservoirs of bacterial methane at the deep subsurface the Gulf slope may be possible. The maximum depth of bacterial methane sources cannot yet be determined.

8. The amount of bacterial methane in mixed gas of other fields from the upper slope should also be estimated and should be correlated with the estimated volumes of bacterial methane in the fields of this study. The amount of bacterial methane in the mixed gas of reservoirs from middle and lower slope should be estimated for future research. Developing models that documents the estimates of the methane carbon pool based on the suggestions of this study may be helpful.

9. This study has been done in an unknown territory of the Gulf basin therefore the results are in the hypothetical level and should not be generalized to other areas of the Gulf basin.

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