

NATURAL GAS SEEPAGE IN THE GULF OF MEXICO

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Hydrocarbon compositions and $\delta^{13}\text{C}$ values for methane of fourteen natural seep gases and four underwater vents in the northwestern Gulf of Mexico are reported. The $C_1/(C_2 + C_3)$ ratios of the seep gas samples ranged from 68 to greater than 1000, whereas $\delta_{\text{PDB}}^{13}\text{C}$ values varied from -39.9 to -65.5% . Compositions suggest that eleven of the natural gas seeps are produced by microbial degradation whereas the remaining three have a significant thermocatalytically produced component. Contradictions in the inferences drawn from molecular and isotopic compositions make strict interpretation of the origins of a few of the samples impossible.

1. Introduction

Hydrocarbon gas is present in sediments in the Gulf of Mexico generally as the product of one of two major processes. The gas can originate from the microbial decomposition of organic matter in anoxic environments at temperatures below 50°C (biogenic gas), and it can be produced by thermocatalytic processes acting on organic matter at higher temperatures (petrogenic gas).

Microbial degradation produces hydrocarbon gas with $C_1/(C_2 + C_3)$ ratios * greater than 1000, i.e., almost exclusively methane [1]. These methane products usually have carbon isotope ratios, or $\delta^{13}\text{C}$ values **, lighter than -60% [2]. Petrogenic processes produce a wide spectrum of low molecular weight hydrocarbons with $C_1/(C_2 + C_3)$ ratios ranging from 0 to 50 [3], and a highly complex mixture of the higher molecular weight hydrocarbons. The isotopic composition of methane produced by petrogenic processes is normally heavier than -50% [4]. Thus, the two parameters, $C_1/(C_2 + C_3)$ ratios and $\delta^{13}\text{C}$ values of methane, should be highly diagnostic of the origin of most natural hydrocarbon gases.

* $C_1/(C_2 + C_3) = \text{CH}_4 \text{ conc.}/(\text{C}_2\text{H}_6 \text{ conc.} + \text{C}_3\text{H}_8 \text{ conc.})$.

** $\delta^{13}\text{C} = \left[\frac{^{13}\text{C}/^{12}\text{C} \text{ sample}}{^{13}\text{C}/^{12}\text{C} \text{ standard}} - 1 \right] \times 1000$, where the standard is PDB.

As gas is generated in sediments as a product of either biogenic or petrogenic processes it may accumulate, migrate upward through the sediment, and eventually seep into the overlying water column. Early work reported by Ohle [5], Pickwell [6], and McCartney and Bary [7] indicated that bubbles rising from gas seeps can be readily detected at sea by standard sonar equipment. Over the past few years more than one hundred seeps have been located along the continental shelf of the northern Gulf of Mexico [8–12]. If a large proportion of naturally occurring seepage were indicative of underlying petroleum and natural gas reservoirs, acoustical gas seep detection would provide an almost ideal method for offshore hydrocarbon exploration. However, in a preliminary study, Brooks et al. [12] reported collecting two seep gases having hydrocarbon compositions (99.98% methane) and isotopic ratios of methane ($\delta^{13}\text{C} \approx -60\%$) highly indicative of a biogenic origin. Since a better knowledge of the compositions of naturally occurring seep gases is extremely important from an oil exploration standpoint as well as for an understanding of the geochemistry of natural hydrocarbon gases, a concentrated and successful effort was made over the past year to collect additional seep gas samples. The analyses reported here suggest that some seepage has an appreciable petrogenic component.

2. Sample collection and storage

A total of 14 gas samples from seepage in the northwestern Gulf of Mexico has been collected since May 1974 as part of this study. The bubbling gas seeps were detected by 12-KHz acoustical reflection techniques and the gas samples were collected under the sea surface by snorkel divers using inverted glass jars. The seeps were located mainly over topographic highs between the 50 and 100 fathom contours on the upper Texas-Louisiana shelf (Fig. 1), so the bottom depths from which most samples emerged were shallower than would be indicated by the general contour lines in Fig. 1. At site 3, East Flower Garden Bank, gas samples were collected by scuba divers at the surface, at 15 m depth, and at 30 m depth as the bubbles emerged from the bottom. All other samples were collected within 3 m of the sea surface. The gas seepage to the surface varied in volume from sporadic, single-stream bubbles of

less than a milliliter per minute to plumes with seepage rates of over 50 liters per minute, so the amount of gas collected at a given seepage site varied from less than 10 ml to several liters. After collection the jars containing the samples were sealed while still immersed in the ocean, returned to the ship, and stored inverted with a seawater seal until analysis.

3. Methods of analysis

The molecular compositions of the seep gases were determined using a Hewlett-Packard 5710A Gas Chromatograph with a flame ionization detector in conjunction with a Hewlett-Packard 3380A Electronic Integrator. 1-cm³ samples were injected into the chromatographic stream and separated on a 1.8-m Porapak Q column thermostated at 60°C. Carbon isotope ratios were determined by combustion of aliquots of the

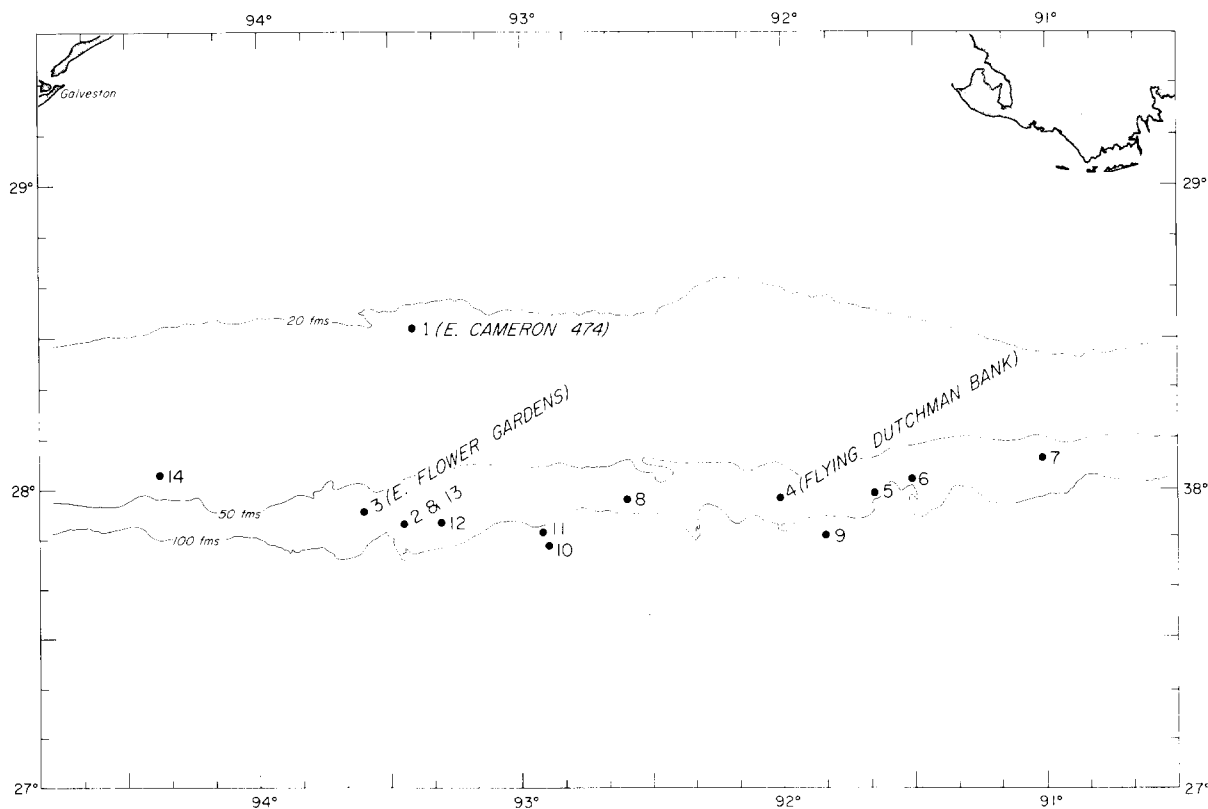


Fig. 1. Gas seepage locations.

methane samples to CO₂ at 800°C and subsequent analysis on a dual collecting Nuclide mass spectrometer [13]. A radiocarbon age for a several-liter sample collected at site 3 was determined by conversion of the methane to benzene for counting by liquid scintillation techniques [14].

4. Results and discussion

Locations, bottom depths, and molecular and isotopic compositions of the seep gases collected in this study are listed in Table 1. Data for seep samples 1 and 2 were reported earlier by Brooks et al. [12]. Also tabulated are the compositions of gas samples collected from four underwater vents. These gas vents are non-commercial by-products of offshore petroleum production operations.

It should be noted that there were considerable amounts of atmospheric gas in most samples and the

compositions reported in Table 1 are for only the hydrocarbon fraction. Most of the atmospheric fraction is the result of dissolved air diffusing into the hydrocarbon bubbles during their ascent through the water column or during storage. The carbon dioxide contents determined by infrared techniques on the samples in greatest quantity were less than 0.1%.

As illustrated in Table 1, all of the natural seep gases analyzed were composed primarily of methane with eleven of fourteen samples having C₁/(C₂ + C₃) ratios greater than 1000, two between 100 and 1000, and one less than 100. Isotopic values of methane in the samples ranged from -39.0‰ to -65.5‰ with all samples more negative than -55‰ having C₁/(C₂ + C₃) ratios greater than 1000, and the more positive δ¹³C values generally associated with larger fractions of ethane and propane. The hydrocarbon compositions, isotopic values of methane, and trends between the two parameters are similar to those reported on hydrocarbon gases found in several Deep Sea Drilling Pro-

TABLE 1

Composition of gas seepage in the OCS region of the northern Gulf of Mexico

Seep no.	Location		Depth (m)	[CH ₄] (%)	[C ₂ H ₆] * (%)	[C ₃ H ₈] * (ppm)	$\frac{[C_1]}{[C_2] + [C_3]}$	CH ₄ : δ ¹³ C * (‰)
	(°N)	(°W)						
1	28° 32.3'	93° 24.5'	40	99.98	0.02	nd	>1000	-61.0
2	27° 54.4'	93° 26.0'	50	99.98	0.02	nd	>1000	-58.0
3 **	27° 55.4'	93° 35.5'	30	99.86	0.14	12	710	-51.3
4	27° 56.5'	92° 01.8'	57	99.95	0.05	5	>1000	-50.9
5	27° 59.0'	91° 39.0'	62	98.05	0.88	5600	68	-39.9
6	28° 02.9'	91° 31.0'	44	99.92	0.08	nd	>1000	-65.5
7	28° 14.6'	91° 02.0'	55	99.79	0.20	130	470	-44.7
8	27° 57.8'	92° 36.5'	33	99.98	0.02	nd	>1000	-65.5
9	27° 50.4'	91° 50.5'	81	99.98	0.02	nd	>1000	-45.9
10	27° 49.4'	92° 53.5'	100	99.93	0.07	44	>1000	-63.3
11	27° 51.9'	92° 55.0'	75	99.95	0.05	nd	>1000	-44.8
12	27° 53.0'	93° 18.0'	48	99.99	0.002	nd	>1000	-59.1
13	27° 54.5'	93° 26.0'	48	99.97	0.03	nd	>1000	-60.4
14	28° 03.0'	94° 23.0'	70	99.96	0.04	nd	>1000	-61.0
<i>Vents</i>								
1	28° 25.5'	92° 37.8'	-	96.8	1.6	1.1%	36	-50.8
2	28° 35'	92° 28'	-	95.8	2.4	1.0%	28	-43.9
3	28° 35'	92° 28'	-	94.6	2.9	1.4%	22	-46.8
4	28° 13.4'	91° 41.1'	-	84.1	7.0	4.8%	7	-42.0

* Reproducibility of replicate determinations: for C₂ and C₃ conc. ±10% and δ¹³C ± 0.2‰.

** Methane had radiocarbon age >30,000 years.

ject (DSDP) cores by Claypool et al. [15]. For clarity, Fig. 2 shows a plot of the log of $C_1/(C_2 + C_3)$ ratios versus $\delta^{13}\text{C}$ for the samples listed in Table 1.

There appears to be a major contradiction between the inferences drawn from the molecular and isotopic compositions of several of the samples plotted in Fig. 2. $\delta^{13}\text{C}$ values between -39.9‰ and -51.3‰ for seep numbers 3, 4, 5, 7, 9, and 11 suggest a thermocatalytic origin, but the $C_1/(C_2 + C_3)$ ratios are considerably greater than expected for thermocatalytic products. There are several possible explanations for this contradiction. First, methane produced by methanogenic bacteria acting on substrates such as carbon dioxide,

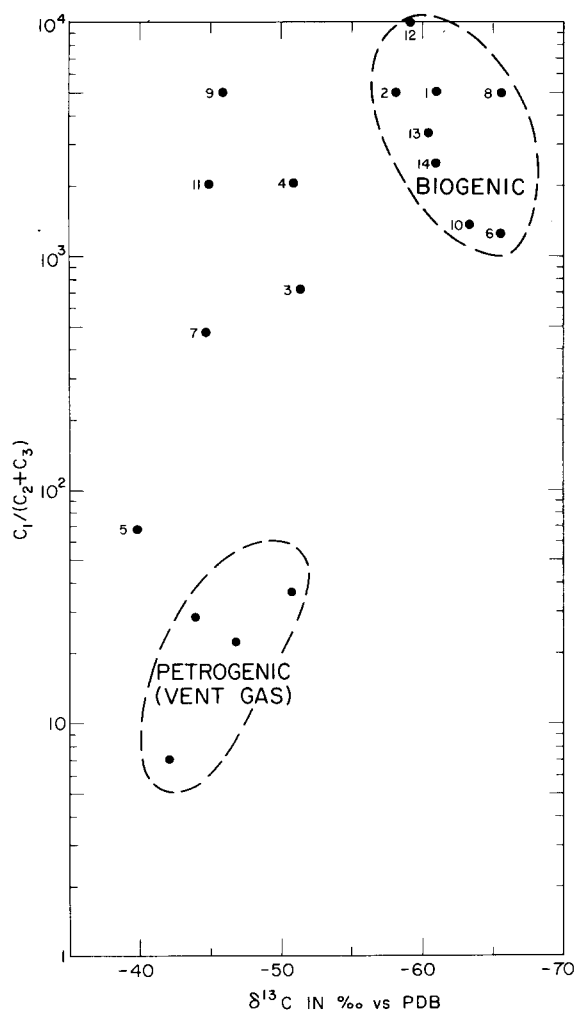


Fig. 2. Log $C_1/(C_2 + C_3)$ versus $\delta^{13}\text{C}$ for gas samples listed in Table 1.

formate, acetate and methanol may change in isotopic composition as the substrate is depleted. For example, Rosenfeld and Silverman [16] showed that during bacterial fermentation of methanol, the methane changed in isotopic composition from about a 70‰ enrichment in $^{12}\text{CH}_4$ relative to the substrate carbon at the beginning of an experiment to about a 70‰ depletion in $^{12}\text{CH}_4$ near the end of the experiment when the methanol was almost completely utilized by the bacteria. Other evidence for isotopically heavy biogenic methane is a $\delta^{13}\text{C}$ value of -45‰ for methane in Lake Kivu, reported by Deuser et al. [17]. This methane is certainly biogenic although a volcanic source of heavy CO_2 may be responsible for an anomalously heavy methane composition. Without knowledge of the isotope fractionation associated with other methane-producing microbial processes, the isotopic composition of the CO_2 and other possible substrates, or the degree of utilization of the substrate reservoir, isotopically heavy methanes produced by microbial processes cannot be eliminated as an explanation. Indeed, they may be represented by sample numbers 4, 9, and 11, with relatively heavy isotopic compositions -50.9 , -45.9 , and -44.3‰ , respectively, but with very small amounts of ethane and higher hydrocarbons.

Samples 3, 5, and 7 contain larger fractions of higher hydrocarbons than microbial degradation can produce (hydrocarbons as high as heptane were detected in sample 5), but their $C_1/(C_2 + C_3)$ ratios are still higher than the petrogenic vent gases. The vent gas samples are representative of light hydrocarbon concentrations normally associated with oil and gas reservoirs located in Texas and Louisiana, as over 95% of the wells examined in these regions have $C_1/(C_2 + C_3)$ ratios smaller than 50 [3]. As further evidence, Claypool et al. [15] report finding hydrocarbon gas in DSDP cores with $C_1/(C_2 + C_3)$ ratios between 10 and 40 over a presumed salt dome in the Gulf of Mexico. Seep 5 has isotopic and molecular compositions comparable to the petrogenic vent gases, but if gases 3 and 7 are also seeping up from petrogenic hydrocarbon sources they have been depleted in ethane and higher hydrocarbons before analysis.

One explanation of low ethane and higher hydrocarbon concentrations in gas produced by thermocatalytic processes involves a molecular fractionation of the light hydrocarbons due to differences in water solubilities. According to McAuliffe [18], the Bunsen sol-

ubility coefficients of methane, ethane, and propane in water at 20°C are 34.2, 45.1, and 31.8 ml STP/liter, respectively, with solubility decreasing for the butanes and higher alkanes. Changes in temperature and salinity affect the solubilities of the individual hydrocarbons and deviations from single-component solubilities are caused by mixtures of two or more soluble components, so solubilities for hydrocarbon gas mixtures in seawater are not accurately known. It may be predicted, however, that due to the high solubility of ethane, a gas bubble containing a mixture of the light hydrocarbons will be depleted in ethane while rising through the water column. The solubility of propane is so similar to that of methane that the concentration ratio (C_1/C_3) should remain fairly constant. These predictions have been confirmed in this study by laboratory experiments which showed that hydrocarbon mixtures similar in composition to petrogenic gas, when equilibrated with hydrocarbon-gas-free water, gave a greater C_1/C_2 ratio in the remnant bubble than in the initial gas mixture. The C_1/C_2 ratio of the gas dissolved in the solvent water was correspondingly smaller than that of the initial gas mixture. No differences in the C_1/C_3 ratio between the initial gas, the remnant gas, or the gas dissolved in the water were observed.

Whereas solubility differences resulting in the depletion of ethane could possibly explain small discrepancies in ethane concentration between the vent gases and gas seeps 3, 5, and 7, it is not likely that ethane is preferentially removed from hydrocarbon bubbles by solution to the extent observed. For example, at seep site 3, where samples were collected at 1, 15, and 30 m below the surface, no ethane concentration differences were detected between samples. It should be noted that these gas bubbles were extremely large and rose rapidly, allowing relatively little surface area to be exposed to the water. If ethane were depleted to a significant extent in small bubbles rising through the water column, petrogenic seepage from the deeper locations should be the most affected, but there is no such ethane depletion trend with bottom depth between samples 3, 5, and 7. In addition, propane is not appreciably more soluble than methane and should not be depleted by solution, so the very pronounced deficiencies in propane of the three seep samples with respect to the vent samples cannot be explained by preferential solution.

Another explanation for the relatively low ethane and propane concentrations observed in presumed ther-

mocatalytic gas seepage is that of molecular fractionation during migration through the sediments. As gases migrate upward from their source region, the sediments may act as a fractionating "chromatographic" column, retarding the higher hydrocarbons. Any subsequent gas seepage from the sediment could be deficient in the higher hydrocarbons relative to the initial composition in the reservoir. Thus, higher hydrocarbons may be removed to a greater extent than propane, which in turn may be depleted more than ethane, as observed for 3, 5, and 7. This relationship has been reported for light-hydrocarbon concentration differences between a natural-gas reservoir and gases dissolved in overlying well water [19]. It should be noted that this type of separation only occurs at a migration front and that eventually a steady state condition should be reached where the input into the "column" has the same composition as the gas leaving the "column".

The possibility of carbon isotope fractionation of methane should also be mentioned. However, since the solubilities of $^{13}\text{CH}_4$ and $^{12}\text{CH}_4$ are almost identical, only a very slight fractionation between the two should ever be observed as methane bubbles rise through a water column. At seep site 3, where samples were taken at 1, 15, and 30 m below the surface, no isotope fractionation between methane samples could be detected within $\pm 0.1\%$. When samples of methane were equilibrated with water in the laboratory so as to dissolve over 75% of the gas, a fractionation of only 0.3‰ was observed, so it is unlikely that significant isotope fractionation of methane occurs during ascent of the bubble or during storage before analysis.

The only other gas in question is the sample from seep 10, in which propane is also detectable and ethane concentration is unusually high for a gas considered to be biogenic on the basis of its isotopic composition (-63%). While the methane could possibly be isotopically fractionated during migration to produce an anomalously negative $\delta^{13}\text{C}$ value, any sediment capable of depleting $^{13}\text{CH}_4$ would certainly retain higher hydrocarbons as well, producing a seep gas with a much higher $C_1/(C_2 + C_3)$ ratio than observed. The mixing of biogenic and petrogenic gas is a more logical explanation and probably occurs in most gas seepage in the Gulf of Mexico to some extent. If hydrocarbon gas, thermocatalytic in origin, is diluted by microbially produced gas, the resulting methane will become isotopically lighter but higher-hydrocarbon concentrations

will be decreased only by the fraction of biogenic gas introduced. In this manner, a sample such as seep 10 which is isotopically in the biogenic range could have an appreciable thermocatalytic component. Similarly, the other seep gases reported with light isotope ratios of methane may be contaminated with small amounts of petrogenic gas, slightly raising the ethane concentrations but not shifting the isotope ratio out of the biogenic range. Since microbially produced methane with $\delta^{13}\text{C}$ values as light as -85% is commonly found in marine sediment cores [2], a considerable fraction of petrogenic hydrocarbon gas could be mixed with a given biogenic methane accumulation before shifting the isotopic ratio of the resulting methane mixture into the petrogenic region.

As indicated in Table 1, seep gas 3 had no measurable ^{14}C and was assigned an age greater than 30,000 years. This bubbling seep was located on East Flower Garden bank (EFG) which along with its neighbor West Flower Garden bank (WFG) are thought to be the northernmost thriving tropical shallow-water coral reefs off the eastern and southern coasts of North America. WFG and probably EFG are underlain by salt domes, whose tops are less than 2000 ft below the sediment-water interface [20]. The upward thrusting salt diapirs produce not only the mounds which form the substrate for reef building organisms, but also faults and fractures through which the seep gases may migrate. The $>30,000$ -year age for the methane does not eliminate microbial activity as the methane source as the salt diaphragm may have caused a recent rupturing of a deeply buried and old reservoir of biogenic methane. The $\delta^{13}\text{C}$ value of -51.3% and the substantial amounts of ethane (0.14%) and propane (12 ppm) in this seep gas suggest that it is composed of a mixture of biogenic and thermocatalytic gases whose carbon precursors were fixed more than 30,000 years ago.

5. Conclusions

The molecular and isotopic compositions of gas bubbles collected from bottom seepage along the outer continental shelf of the northwestern Gulf of Mexico do not always differentiate biological and thermocatalytic origins of the hydrocarbon gases. While $C_1/(C_2 + C_3)$ ratios greater than 1000 and $\delta^{13}\text{C}$ values lighter than -58% strongly suggest a biological origin for eight of

fourteen samples, half of the remaining six samples may also be microbially produced, despite $\delta^{13}\text{C}$ values in the petrogenic range. Only one gas sample (seep 5) has isotopic and molecular compositions unequivocally indicative of a thermocatalytic origin. Two other isotopically heavy samples (seeps 3 and 7) contain larger fractions of higher hydrocarbons than microbial degradation should produce, but if they are truly petrogenic, ethane and higher hydrocarbons have been depleted before analysis.

If the fourteen gas seep compositions reported here are representative of gas seepage in general, the use of hydrocarbon "sniffing" in offshore petroleum exploration must be reevaluated. High concentrations of dissolved methane in near-bottom waters produced from microbial processes could be misinterpreted as the result of seepage from petrogenic sources. In addition, dissolved higher hydrocarbons may not be detected near existing petrogenic seepage due to their very low concentrations at the sediment surface. Determination of light hydrocarbon concentrations along with isotopic ratios of methane in bubbling gas seepage should be more definitive for petroleum exploration, but even these analyses cannot always distinguish hydrocarbon gas sources.

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