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A GEOCHEMICAL MODEL FOR CHARACTERIZATION OF HYDROCARBON GAS SOURCES IN MARINE SEDIMENTS

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ABSTRACT

A geochemical model has been developed to distinquish biogenic from petroleum-related gas in marine sediments. Analyses of seep and sediment gases from the Gulf of Mexico indicate that the characteristic composition of petrogenic gas can be altered during migration through sediments and by mixing with biogenic gas. Measurements of carbon isotopic ratios of methane and hydrocarbon ratios generally provide a definitive interpretation of hydrocarbon gas sources. It is suggested that prospecting for reservoired hydrocarbons include coring on or near observed geologic features to first establish the source of existing hydrocarbon gas in a region.

INTRODUCTION

An extensive review of major petroleum provinces by Link (1952) indicates that most important oil-producing regions have been associated with oil and gas seepage. Thus, the detection of seepage has provided the initial clues to the discovery of most of the world's major oil fields. Over the past twenty years, various geochemical methods of prospecting for oil and gas seepage from reservoirs have been introduced, including measurements of adsorbed and occluded hydrocarbons from soil (Horvitz, 1954) or marine sediments (Gérard and Feugére, 1968), "sniffing" for dissolved light hydrocarbons in seawater (Brooks and Sackett, 1973; Sigalove and Pearlman, 1975), and analysis of light hydrocarbons dissolved in inter-

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References and illustrations at end of paper.

stitial water (Carlisle *et al.*, 1975). These exploration techniques are made theoretically feasible because hydrocarbons from petroleum reservoirs migrate upward through faults, fractures, bedding planes, etc., and exude from surface sediments into the overlying waters. Thus, the detection and characterization of marine seepage may reveal the location of offshore oil and gas deposits.

In theory, petroleum-related (petrogenic) gas can be distinguished from microbially-produced (biogenic) gas by the presence of significant quantities of ethane-and-higher hydrocarbons. The analyses reported here suggest that the hydrocarbon composition of petrogenic gas can be altered to resemble biogenic gas during migration through the sediments, thus confusing interpretation. Moreover, mixtures of gases from the two sources can retain the character of petroleum-related gas in hydrocarbon composition while changing isotopically.

Since the measurement of one parameter such as hydrocarbon composition can be misleading, an examination of two or more parameters can aid in characterization of gas origin. Analyses of isotopic composition of methane from seepage and sediment gas in conjunction with molecular composition can provide more definitive interpretation.

GENERAL PRINCIPLES

Two types of hydrocarbon gas present in Gulf of Mexico sediments have been described by Bernard *et al.* (1976). Biogenic gas consists almost exclusively of methane, carbon dioxide, and hydrogen sulfide, having $C_1/(C_2+C_3)$ ratios greater than 1000

and carbon isotope ratios ($\delta^{13}C$ values) more nega-
tive than $-60°/_{oo}$. Petroleum-related hydrocarbon
gases generally have $C_1/(C_2+C_3)$ ratios smaller than
50 and isotopic ratios greater than $-50°/_{oo}$. Since
these two parameters should be diagnostic of the
origin of the gas in seep or sediment samples, a
simple geochemical model for the characterization
of hydrocarbon gas sources can be constructed from
the field of $C_1/(C_2+C_3)$ ratios and $\delta^{13}C$ values found
in marine natural gases.

SAMPLE COLLECTION AND ANALYSIS

Seep gas samples from the northwest Gulf of
Mexico and Mississippi Delta region were collected
by snorkel and scuba divers using inverted glass
jars. The jars were sealed while still immersed
in sea water and stored inverted with sea water
seals until analysis. The seeps were detected by
12 KHz acoustical reflection techniques and were
generally found over various topographical highs
in the Texas-Louisiana Shelf region. Analyses were
performed by injecting 100-microliter samples of
gas into the carrier stream of a Hewlett-Packard
5710A gas chromatograph, with component separation
on a 3-meter Porapak Q column thermostated at 60°C.
A flame ionization detector was used in conjunction
with a Hewlett-Packard 3380A electronic integrator
for analysis of hydrocarbon concentrations. Samples
were prepared for carbon isotope analysis by com-
bustion of several milliliters of methane to car-
bon dioxide at 800°C. Isotopic values were deter-
mined using a dual collecting Nuclide mass spectro-
meter (Sackett et al., 1970).

Gravity and piston cores on the Texas-Louis-
iana Shelf were obtained for sediment gas analysis.
Two-hundred-milliliter sections of sediment were
placed in 0.5-liter containers with 125-milliliters
of sodium azide poisoned, degassed water. The re-
maining head space was flushed with helium, and
hydrocarbon gases dissolved in the interstitial
water were partitioned into the helium phase by a
high-speed shaker. One-milliliter aliquots of the
headspace were injected into the carrier stream of
the gas chromatograph for analysis. Partition co-
efficients for the individual hydrocarbons were
determined by repeated equilibrations after re-
placement of the headspace gas with hydrocarbon-
free helium (McAuliffe, 1971). The partition co-
efficients per equilibration for methane, ethane
and propane were 93.9, 90.3 and 94.0%, respective-
ly. Carbon isotopic ratios were measured on sam-
ples containing at least 0.1 milliliters of
methane by sampling the headspace gas with an
evacuated glass bulb and combusting the methane
as described previously.

RESULTS AND DISCUSSION

Sediment Gas

The isotopic and molecular ratios of hydro-
carbon gas taken from a shelf sediment in the Miss-
issippi Delta region are plotted against depth of
burial in Fig. 1. An increase in $\delta^{13}C$ with increas-
ing sediment depth is evident, whereas the relative
fractions of hydrocarbon components do not change
significantly. Bore hole gases taken in the same
region showed a similar trend with an isotopic
enrichment from $-82°/_{oo}$ at 40 meters to $-60°/_{oo}$
at 60 meters depth. These values are represent-

ative of gas produced strictly by microorganisms.
The isotopic enrichment of the methane with depth
is not an indication of an increasing petrogenic
component in older sediments, as indicated by the
lack of significant fractions of higher hydrocar-
bons [high $C_1/(C_2+C_3)$ ratios] in the samples.
Rather, it may be the result of carbon-12 depletion
in the substrate on which the methanogenic bacteria
feed (Claypool and Kaplan, 1974; Bernard et al.,
1976). Biogenic methane is isotopically "light"
in carbon-13 compared to the substrate because
bacteria preferentially select carbon-12 in methane
production. Thus, the remaining substrate carbon
becomes increasingly enriched in carbon-13, and
ensuing methane must also become "heavier".

Examples of sediment gas composition typically
associated with petroleum are reported by Claypool
et al. (1973) on samples taken from a Deep Sea
Drilling Project bore hole over a presumed salt
dome in the Gulf of Mexico. Figure 2 illustrates
trends in $\delta^{13}C$ and $C_1/(C_2+C_3)$ ratios with depth in
this bore hole. Whereas the hydrocarbon ratios
for all but the top (58 meter) sample are positive
indicators of a petrogenic source, the isotopic
ratios of methane ranging from -50 to -60 $°/_{oo}$ are
suggestive of a mixture of gas from both biogenic
and petroleum-related sources.

Seep Gas

Seep gases with compositions typical of bio-
genic sources are plotted on Fig. 3. Despite the
fact that microbially produced sediment gas iso-
topically lighter than -80 $°/_{oo}$ is quite common in
marine sediments, there has never been a seep gas
lighter than $-67°/_{oo}$ reported. It may be that
biogenic seeps generally consist of the older,
carbon-13 enriched gas.

Gases from four underwater vents and three
seep gases of petrogenic origin are plotted on
Fig. 4. Vent gases are non-commercial by-products
of offshore petroleum production operations, and
the four samples are representative of isotopic
and molecular compositions normally associated
with oil and gas reservoirs. Whereas the isotopic
ratios of the three seep gases are characteristic
of petroleum-related methane, hydrocarbon ratios
on two of the samples are significantly higher than
vent gas ratios. The authors suggest that ethane
and higher hydrocarbons are retarded as the gases
migrate upward through the sediments, producing
seep gases deficient in the higher hydrocarbons
relative to initial reservoir compositions. Simi-
lar findings have been reported by Coleman (1976)
on gas sampled from an underground gas storage
reservoir and overlying well water.

SOURCE MODELING

A model for the source identification of sedi-
ment and seep gases is illustrated in Fig. 5. The
two sources of marine hydrocarbon gases are dis-
tinctly characterized by the two parameters, $\delta^{13}C$
values of methane and $C_1/(C_2+C_3)$ ratios, and alter-
ation trends are diagrammed. The depletion of car-
bon-12 in older biogenic gas is illustrated by a
shift to the left in the Biogenic Gas Zone, corre-
sponding to an increase in $\delta^{13}C$ values of methane
with no significant change in $C_1/(C_2+C_3)$ ratios.
The depletion of higher hydrocarbons during migra-

tion of petroleum-related gas is illustrated by an upward shift in the Petrogenic Gas Zone, corresponding to an increase in $C_1/(C_2+C_3)$ ratios with no significant change in $\delta^{13}C$ values of methane. Mixing of gases of both origins is represented by the dashed lines connecting the two source zones. These two lines were generated by hypothetically mixing a typical petrogenic gas ($\delta^{13}C$ value of $-45^\circ/\circ\circ$; $C_1/(C_2+C_3)$ ratio of 10) with two separate biogenic gases having $\delta^{13}C$ values of $-60^\circ/\circ\circ$ and $-80^\circ/\circ\circ$, respectively, and $C_1/(C_2+C_3)$ ratios of 10^4.

Positions corresponding to a mixture of equal (1:1) fractions from the two sources are marked on the mixing lines. It is clear from the diagram that petroleum-related gas can be diluted with biogenic gas as much as 1:1 without shifting the resulting $C_1/(C_2+C_3)$ ratio out of the petrogenic region. Isotopic values of methane in mixtures, on the other hand, are shifted almost linearly with mixing ratios. Thus, only small fractions of biogenic gas are required to cause a significant isotopic change in a predominantly petrogenic mixture. The isotopic and molecular ratios plotted from the five Deep Sea Drilling Project bore hole samples (marked by triangles) fall close to one of the hypothetical mixing curves, and can be interpretated as the result of mixing various fractions of petrogenic and biogenic gas with compositions shown in Fig. 5. The mixing model indicates that four of the five samples consist mostly of biogenic gas, regardless of low $C_1/(C_2+C_3)$ ratios.

CONCLUSIONS

It has been demonstrated that alterations in the compositions of both petrogenic and biogenic natural gas within marine sediments can hinder interpretation of gas sources if only one geochemical parameter is examined. These results should be of interest to exploration geochemists who consider hydrocarbon ratios in surface sediments or dissolved methane concentrations from bottom water in evaluation of reservoir potential of a region. The origin of hydrocarbon gas in marine sediments is more accurately determined by comparison of the isotopic and molecular compositions of the sample gas using the proposed model. In this regard, prospecting for reservoired hydrocarbons should include coring on or near geologic features such as unconformities, faults, bedding planes, or distinct gas seepage, to first establish the source of existing gas in the region. If the gas is of biogenic origin, as are most of the gas samples analysed from the northwest shelf of the Gulf of Mexico, reconsideration can be given to the petroleum potential of the area.

NOMENCLATURE

$$C_1/(C_2+C_3) = \frac{CH_4 \text{ concentration}}{C_2H_6 \text{ conc.} + C_3H_8 \text{ conc.}}$$

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

where the standard is PDB.

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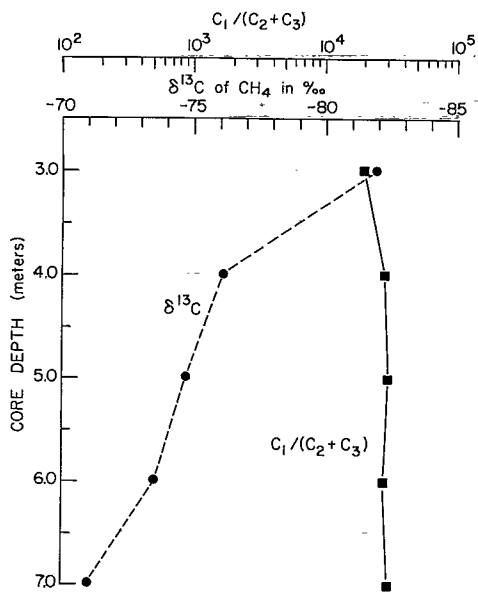
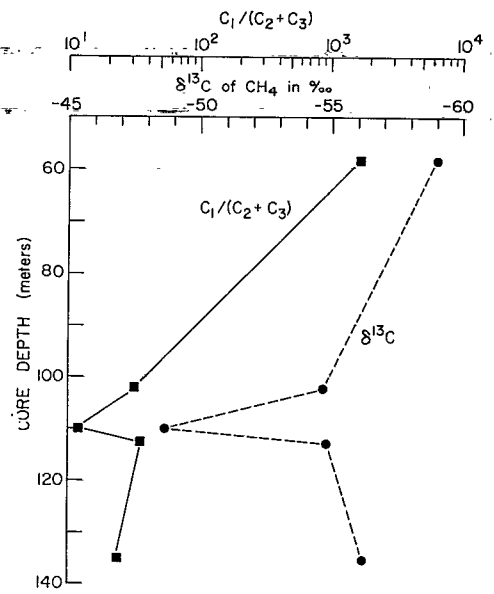FIG. 1 - DEPTH TRENDS OF BIOGENIC SEDIMENT GAS.

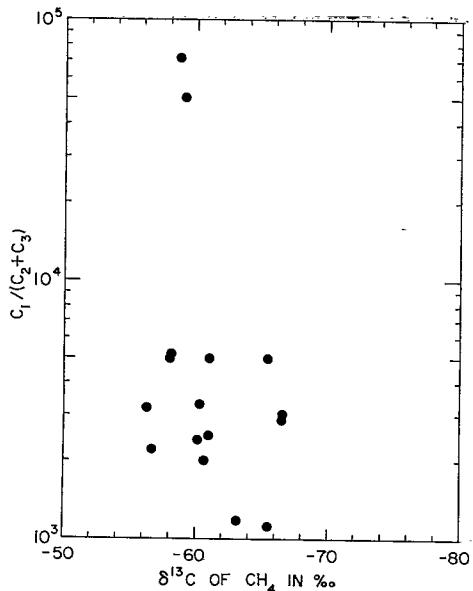FIG. 2 - DEPTH TRENDS OF DSDP SEDIMENT GAS.

FIG. 3 - COMPOSITIONS OF BIOGENIC SEEP GASES, AFTER BERNARD ET AL, 1976.
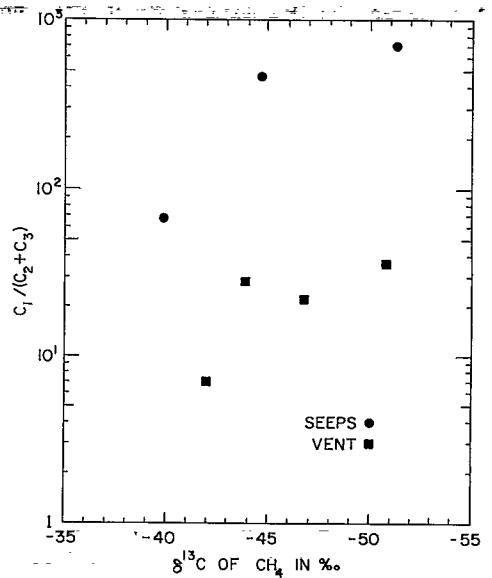

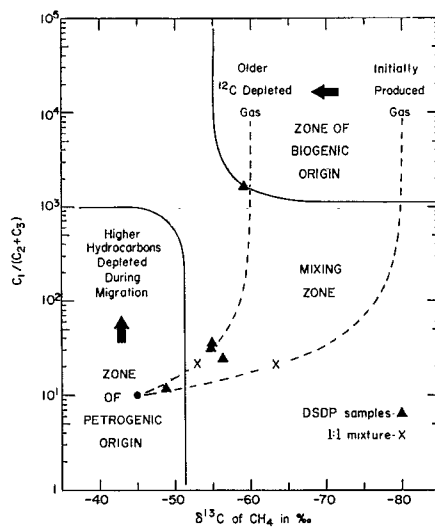FIG. 4 - COMPOSITIONS OF VENTS AND PETROGENIC SEEP GASES, AFTER BERNARD ET AL, 1976.

FIG. 5 - MODEL FOR SOURCE CHARACTERIZATION OF MARINE HYDROCARBON GASES.