

## 35. GAS ANALYSES IN SEDIMENT SAMPLES FROM LEGS 10, 11, 13, 14, 15, 18, AND 19<sup>1</sup>

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### INTRODUCTION

As a result of finding oil and gas on Leg 1 of the JOIDES exploratory drilling program, a decision was reached to undertake shipboard analyses for gas. The biogeochemistry laboratory at UCLA was asked to develop a rapid method for such analysis. Consequently, a technique was devised to capture gas, which was obviously visible as pockets in the transparent core liners. The gas was then analyzed on a calibrated gas chromatograph and the results immediately evaluated. Additional samples of the gas were sealed and forwarded to our laboratory for further analyses. Prior to Leg 10, no successful analyses were made and, for an unexplainable reason, no samples collected. This report deals with samples collected between Legs 10 and 19.

Methane (CH<sub>4</sub>) is the dominant constituent of the gas given off by freshly cored deep-sea sediment as it equilibrates to surface conditions. In some cases, outgassing may be prolonged and vigorous and cause spectacular pressure effects if the core liners are tightly sealed. More typically, the effects of the presence of gas in moderate quantities are disturbance of the sediment, creation of gas expansion pockets, and partial (up to 50%) extrusion of the sediment from the core liner. Undoubtedly, smaller quantities of gas are not routinely detected if visual evidence is not apparent.

While the production of methane in paddies, swamps, and marshes is commonly accepted as a consequence of organic decay under anaerobic conditions (hence the common name "marsh gas" for methane) the extent of methane occurrence in the marine environment has not been widely appreciated or understood (Atkinson and Richards 1967). Gassy sediments are occasionally encountered in shallow coring operations (Revelle 1950; Emery and Hoggan 1958; Nissenbaum et al. 1972), but with the advent of deep coring of the ocean floor by the Deep Sea Drilling Project (DSDP), gas is more frequently encountered, and at depths previously unattainable by gravity or piston coring devices. Through Leg 19, some 28 of 193 sites drilled encountered gas in sufficient quantity to enable successful sampling and analysis. The sediments which yield gas when brought to the surface share the following characteristics: the sedimentation rate has been sufficiently rapid to prevent complete oxidative decomposition of organic matter and biochemical reduction processes are in progress as evidenced by complete removal of sulfate from the pore water at some depth within the core. Typically, sediments of this type are deposited in environments where

the supply of organic detritus is high, generally around continental margins. The location of sites where sediment gas has been sampled and analyzed is given in Table 1.

### SAMPLING AND ANALYTICAL PROCEDURES

Sampling and preliminary analysis of gas samples was carried out by DSDP shipboard personnel. The presence of sediment gas was indicated by gas expansion pockets in the core. These were sampled by puncturing the core liner and withdrawing the gas into an evacuated glass container, as described by Gealy and Dubois (1971). This procedure invariably results in some atmospheric contamination, and, although the gases are sampled at atmospheric pressure, the sediments are still in the process of temperature equilibration and outgassing. Because of these shortcomings in the sampling procedure, it is difficult to obtain quantitative information on the sediment gases under in situ conditions or to directly relate gas volume to sediment volume.

### Gas Chromatography

In the shipboard analyses, a small sample of the gas was injected by syringe into a gas chromatograph equipped with Poropak Q column, thermal conductivity detector, and helium carrier gas. The gas samples were specifically analyzed for methane, CO<sub>2</sub>, and ethane. Mixtures of oxygen and nitrogen were detected as an undifferentiated "air" peak. The retention times of propane and higher hydrocarbon were so long under the usual operating conditions that, when present, they were usually undetected or appear as poorly resolved humps in random position in the chromatograms of subsequent gas analyses. A similar procedure was employed in laboratory shore analyses at UCLA on selected stored gas samples submitted to us. Exceptions to the shipboard procedures were the use of, first, a small evacuated manifold with a gas sampling valve to introduce a known quantity of gas into the chromatograph, second, both a Porapak and a molecular sieve column to separate N<sub>2</sub> and O<sub>2</sub>, and third, a flame ionization detector and programmed column temperature for samples which contained hydrocarbons heavier than methane.

The chemical composition of the gas samples, corrected for atmospheric contamination, was computed from the gas chromatographic analysis by the following procedure: (1) The peak areas were computed (peak height times peak width at 1/2 height, times attenuation factor) and normalized to the methane peak, i.e., expressed as ratios. (2) These raw peak area ratios were converted to volume/volume ratios by applying appropriate instrument response ratios obtained from calibration data. (3) The contribution of atmospheric contamination to the total CO<sub>2</sub>/CH<sub>4</sub> volume ratio was taken to be 0.00035 times "air"/CH<sub>4</sub> (or, in a limited number of cases, 0.00175 times O<sub>2</sub>/CH<sub>4</sub>) and

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TABLE 1  
Location of DSDP Cores for which Gas Samples have been Analyzed

Site	Latitude	Longitude	Water Depth (m)	Penetration (m)	Physiographic Description
<b>Leg 10</b>					
88	21° 22.93'N	94° 00.21'W	2532	135	Campeche-Sigsbee Knoll
90	23° 47.80'N	94° 46.09'W	3713	768	Sigsbee Plain
91	23° 46.40'N	93° 20.77'W	3763	900	Sigsbee Plain
<b>Leg 11</b>					
102	30° 43.93'N	72° 27.14'W	3426	661	Blake-Bahama Outer Ridge
103	30° 27.08'N	74° 34.99'W	3964	449	Blake-Bahama Outer Ridge
104	30° 49.65'N	74° 19.64'W	3811	617	Blake-Bahama Outer Ridge
106B	36° 25.28'N	69° 25.81'W	4504	1015	Lower Continental Rise, S.E. of New York
<b>Leg 13</b>					
128	35° 42.58'N	22° 28.09'E	4640	481	Hellenic Trench
<b>Leg 14</b>					
144A	09° 27.23'N	54° 20.52'W	2957	200	Demerara Rise
<b>Leg 15</b>					
147	10° 42.48'N	65° 10.48'W	892	162	Cariaco Trench
147C	10° 42.68'N	65° 10.45'W	892	198	Cariaco Trench
154	11° 05.11'N	80° 22.75'W	3338	278	Colombian Abyssal Plain
154A	11° 05.07'N	80° 22.82'W	3338	172	Colombian Abyssal Plain
<b>Leg 18</b>					
174A	44° 53.38'N	126° 21.40'W	2799	879	Astoria Submarine Fan
176	45° 56.0'N	124° 37.0'W	193	41	N. Oregon Continental Shelf
180	57° 21.76'N	147° 51.37'W	4923	470	E. Aleutian Trench
<b>Leg 19</b>					
185	54° 25.70'N	169° 14.59'W	2120	728	NE of Umnak Plateau
186	51° 07.81'N	174° 00.34'W	4532	926	Atka Basin
189	54° 02.14'N	170° 13.38'E	3447	697	Aleutian Ridge
191	56° 56.70'N	168° 10.72'E	3864	919	Kamchatka Basin

subtracted to give a corrected  $(\text{CO}_2/\text{CH}_4)_c$  volume ratio. (4) The relative proportions of three gases (methane, carbon dioxide, and ethane) were computed from the volume ratios using the following relations:

$$\text{vol. \%CO}_2 = \frac{(\text{CO}_2/\text{CH}_4)_{\text{corrected}}}{(\text{CO}_2/\text{CH}_4)_c + (\text{C}_2\text{H}_6/\text{CH}_4) + 1} \times 100$$

$$\text{vol. \%C}_2\text{H}_6 = \frac{\text{C}_2\text{H}_6/\text{CH}_4}{(\text{CO}_2/\text{CH}_4)_c + (\text{C}_2\text{H}_6/\text{CH}_4) + 1} \times 100$$

$$\text{vol. \%CH}_4 = \frac{1}{(\text{CO}_2/\text{CH}_4)_c + (\text{C}_2\text{H}_6/\text{CH}_4) + 1} \times 100$$

These are the percentages reported in Table 2, making use of both shipboard and laboratory analyses of DSDP gas

samples. Replicate analyses and comparison of shipboard and laboratory work indicate that gas analyses computed in this way have an absolute precision of about  $\pm 0.1$  percent for methane and about  $\pm 0.001$  percent for  $\text{CO}_2$  and ethane, at 2-sigma confidence level.

#### $\text{C}^{13}/\text{C}^{12}$ Measurements

Methane in the gas samples was purified from small amounts of  $\text{CO}_2$  and ethane, either by vacuum distillation at  $-190^\circ\text{C}$ , or by reaction with caustic to remove  $\text{CO}_2$  from samples with insignificant ethane content. Methane was quantitatively converted to  $\text{CO}_2$  for mass spectrometric analysis by combustion in an oxygen atmosphere at  $900^\circ\text{C}$  according to the procedure described by Kaplan, Smith, and Ruth (1970).

When sufficient quantities of  $\text{CO}_2$  and ethane were available, these gases were also separated and prepared for  $\text{C}^{13}/\text{C}^{12}$  measurement.

The methane (and air) was first removed by distillation from liquid nitrogen, and, if ethane was insignificant, the remaining  $\text{CO}_2$  was purified and analyzed directly. Mixtures

TABLE 2  
Chemical and Isotopic Composition of DSDP Gases

Sample	Depth Below Sea Floor (m)	Component (Volume %)			$\delta C^{13}$ (‰)
		CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	CO <sub>2</sub>	
<b>Leg 10</b>					
88-2	54	99.5	0.06	0.42	-59.0
3	102	96.6	3.03	0.32	-54.7
4-4	110	91.5	8.39 <sup>a</sup>	0.09	-48.7
4-6	113	97.0	2.67 <sup>a</sup>	0.30	-54.8
5	135	95.9	3.97 <sup>a</sup>	0.17	-56.3
90-3	130	99.4	n.d.	0.63	-83.0
11	678	99.9	0.01	0.14	-78.0
91-3	159	99.8	n.d.	0.19	-84.0
5	190	99.6	n.d.	0.45	-80.4
6	301	99.1	0.01	0.89	-81.0
7	412	99.7	0.01	0.32	-80.8
8	492	99.1	0.02	0.85	-80.0
11	774	99.3	0.01	0.72	-79.9
18	838	99.2	0.02	0.82	-78.7
<b>Leg 11</b>					
102-5	135	99.7	0.005	0.30	-88.4
11	350	99.6	0.005	0.44	-72.8
19	660	n.a.	n.a.	n.a.	-77.1
104-3	67	97.8	0.01	2.16	-76.3
7	300	97.8	0.06	2.18	-70.7
9	500	94.2	0.06	5.76	-70.1
106B-2	455	99.4	0.01	0.61	-86.1
5	940	84.0	0.10	15.9	-73.7
<b>Leg 13</b>					
128-3	26	99.9+	n.d.	0.03	-73.5
10	420	n.a.	n.a.	n.a.	-77.8
11	475	99.8	n.d.	0.18	-72.6
<b>Leg 14</b>					
144A-3	163	99.5	n.d.	0.52	-74.4
6	190	99.6	n.d.	0.39	-70.8
<b>Leg 15</b>					
147-6	46	98.9	0.02	1.08	-76.3
9	74	92.9	0.04	7.09	-65.0
12	100	93.8	0.04	6.19	-61.7
16	140	89.6	0:10	10.3	-60.6
17	150	85.6	0.07	14.4	-62.8
18	160	97.7	0.10	2.24	-65.0
147c-7	175	95.0	0.12	4.84	-64.7
154A-7	60	99.6	<0.005	0.40	-81.3
154-2	110	99.8	0.01	0.23	-74.8
5	190	99.9	0.04	0.10	-69.1
9	225	99.4	0.03	0.52	-71.9
10	235	99.8	0.01	0.19	-69.7
<b>Leg 18</b>					
174A-8	200	99.2	n.d.	0.84	-88.7
16	179	99.3	n.d.	0.70	-84.1
31	316	99.3	<0.001	0.73	-75.9
351	410	99.3	<0.001	0.65	-76.6
40-4	765	99.5	0.06	0.43	-80.4
40-5	766	99.5	0.10	0.42	-76.7
176-3	23	99.3	n.d.	0.73	-58.7
4	31	98.9	n.d.	1.15	-54.9
5	39	98.9	<0.002	1.13	-47.1

TABLE 2—Continued

Sample	Depth Below Sea Floor (m)	Component (Volume %)			$\delta C^{13}$ (‰)
		CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	CO <sub>2</sub>	
180-15	245	98.1	n.d.	1.91	-75.7
17	266	98.1	n.d.	1.89	-76.5
18	272	97.8	n.d.	2.19	-72.6
22	441	99.5	n.d.	3.11	-80.8
<b>Leg 19</b>					
185-20	665	99.7	0.035	0.288	-72.1
23	685	n.a.	n.a.	n.a.	-71.4
186-3	20	99.9	n.d.	0.121	-78.8
6	110	99.5	trace	0.466	-68.4
9	167	99.4	n.d.	0.553	-71.6
19	450	99.7	trace	0.263	-71.3
28	920	99.9	0.009	0.110	-62.7
189-6	250	99.5	0.004	0.544	-75.8
8	375	99.7	0.010	0.284	-70.8
10	560	99.8	0.019	0.149	-71.0
191-4	80	98.8	n.d.	1.17	-77.4
8	275	99.0	<0.001	1.03	-75.4
10	388	98.6	<0.001	0.351	-75.4

n.d. = not detected; n.a. = not analyzed.

<sup>a</sup>Includes propane and higher hydrocarbons.

of CO<sub>2</sub> and ethane were separated by exposing the gas to Ba(OH)<sub>2</sub> solution. The unreacted ethane was then recovered and converted to CO<sub>2</sub> by the combustion method referred to above and the reacted CO<sub>2</sub> recovered by acidifying the Ba(OH)<sub>2</sub>-BaCO<sub>3</sub> solution.

The  $\delta C^{13}$  was measured and reported according to the usual conventions (Kaplan, Smith and Ruth, 1970) in the delta notation relative to the PDB standard.

## RESULTS

The chemical composition of the DSDP sediment gases and the  $\delta C^{13}$  values of the methane in the gas is given in Table 2. The gas samples, excluding air gases, are composed predominantly of methane and, with few exceptions, minor or trace amounts of carbon dioxide. In rare cases, the gas contains significant amounts of either CO<sub>2</sub> or ethane. Although H<sub>2</sub>S odors are sometimes associated with the freshly cored sediment, it has not been detected analytically. The range of chemical composition of DSDP gases is indicated by the triangular diagram, Figure 1.

In Figure 2, the  $\delta C^{13}$  of the methane is plotted versus depth of burial, with different symbols indicating each core. Whereas the methane from a single location does not vary by more than 15 percent the combined range for methane samples is about 40‰, from -89 to -47‰. The total  $\delta C^{13}$  variation is apparent within the shallowest 200 meters of sediment, not necessarily because methane is more variable at shallow depths, but probably because of the larger number of samples and the fact that drilling was terminated at shallow depths in holes where isotopically heavy methane was encountered (Sites 88, 147, and 176).

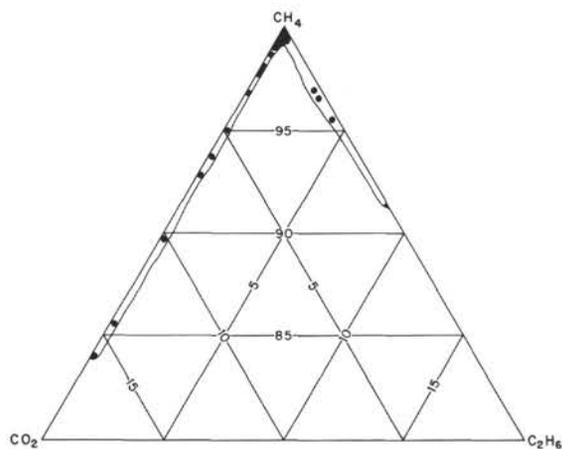


Figure 1. Triangular plot of gas composition in terms of methane, ethane, and carbon dioxide.

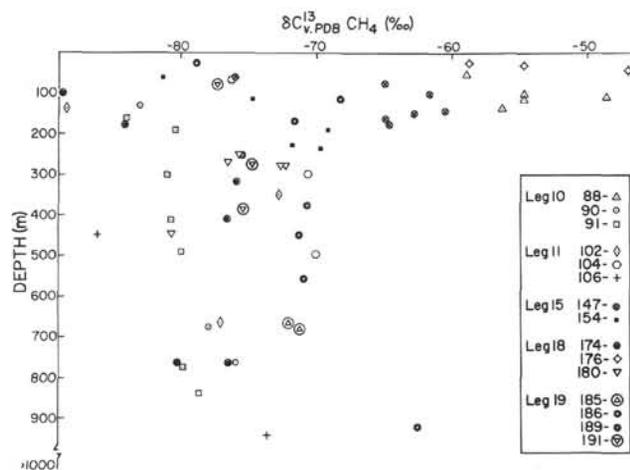


Figure 2. Distribution of  $\delta C^{13}$  in methane in various samples from Legs 10, 11, 15, 18, and 19.

The wide  $\delta C^{13}$  range of methane in marine sediments may be due to different mechanisms of origin. For example, the gas from Site 88, drilled over a presumed salt dome in the Gulf of Mexico, contains appreciable amounts (up to 8%) of ethane and higher hydrocarbons. The heavier ( $-59$  to  $-49\text{‰}$ )  $\delta C^{13}$  values of the methane and the "wet" chemical composition is more typical of gas associated with liquid petroleum (Silverman 1971).

At the other extreme, the majority of the gas samples are isotopically very light ( $-90$  to  $-70\text{‰}$ ) methane with no detectable higher hydrocarbons. These samples are chemically and isotopically similar to methane of bacterial origin (Rosenfeld and Silverman 1959; Oana and Deevey 1960).

Most of the samples with intermediate  $\delta C^{13}$  values ( $-70$  to  $-60\text{‰}$ ) are from the sediments of the Cariaco Basin

(Site 147). Bacterial methane production in this environment may proceed under slightly different conditions than in typical deep-sea sediments, resulting in heavier  $\delta C^{13}$  values. Site 176, drilled in only 200 meters of water on the shelf off the coast of northern Oregon, has gas of unique composition. The methane is isotopically heavy ( $-56$  to  $-47\text{‰}$ ) and ethane is below or just at the level of detection. These samples may represent gases which contain methane related to liquid petroleum, but without significant amounts of ethane or higher hydrocarbons, or, alternatively, they represent an extreme case of bacterial methane production in shelf sediments.

In Table 3, the  $\delta C^{13}$  values of ethane (plus higher hydrocarbons) and gaseous  $CO_2$  are shown for the few samples which contained a sufficient amount of the minor components to permit separation and isotopic analysis. Four of the five ethane samples are within a two per mil range, around  $-34\text{‰}$ , or very similar to ethane separated from Italian natural gases and reported by Columbo et al. (1965). The  $CO_2$  from the gas samples is much more variable in  $\delta C^{13}$  than the ethane. The total range is about forty per mil, with the  $\delta C^{13}$  values of the  $CO_2$  roughly paralleling that of the coexisting methane, and the lightest  $CO_2$  at the shallowest depths in the sediment.

For three of the  $CO_2$  samples separated from the gases of Site 147,  $\delta O^{18}$  of the  $CO_2$  was also measured and values near  $+7\text{‰}$  (vs. PDB) obtained.  $CO_2$  in equilibrium with interstitial water with the oxygen isotopic composition of seawater should be about  $+12\text{‰}$ . Therefore, either the interstitial water is about five per mil depleted in  $\delta O^{18}$  relative to seawater, or the  $CO_2$  in the gas is not in equilibrium with interstitial water and the lighter oxygen reflects some biogenic influence.

TABLE 3  
Isotopic Composition of Minor  
Components of DSDP Gases

Sample	$\delta C^{13}$ (‰)		$\delta O^{18}$ PDB ( $CO_2$ )
	$C_2H_6+$	$CO_2$	
88-4-4	-33.1	-11.2	
4-6	-35.4		
5	-35.0		
91-3	-34.3		
102-5		-32.1	
102-19	-25.4	-7.9	
104-3		-23.2	
7		-14.6	
9		-14.4	
106B-2		-23.2	
5		-7.4	
144A-6		-20.2	
147-9		+3.7	-6.7
12		+6.5	-7.5
18		+10.5	-6.3
147c-7		+6.9	
154A-7		-23.8	
154-5		-22.4	
154-9		-24.8	

It was not possible to obtain reliable values for nitrogen gas, because of air contamination problems during sampling. An attempt was made to correct the data by applying the value for the oxygen peak on the gas chromatograms and assuming oxygen is a contaminant. The results of this correction were ambiguous, indicating  $N_2$  production in some cases and consumption in others. Because of this, it was assumed that changes in  $N_2$  concentration were not large and that the results were masked by the lack of precision in the measurement. As a consequence of the above difficulties, it was decided not to quote nitrogen data.

## DISCUSSION

The analytical results show that methane is by far the most important gas generated in marine sediments. The origin of methane can be bacteriological fermentation and reduction of carbon dioxide or thermal degradation of high-molecular-weight organic compounds.

During early diagenesis of organic matter, under anaerobic conditions, bacterial degradation initially involves sulfate reduction. During this process, organic matter can be partially degraded by dehydrogenation and decarboxylation. Carbon dioxide and hydrogen sulfide are released. Both are reactive and highly soluble gases and apparently do not exist in a sufficiently high concentration to become significant gas components. The hydrocarbon gases are inert and very insoluble, and therefore become concentrated in the gas phase when the cores are brought to the surface.

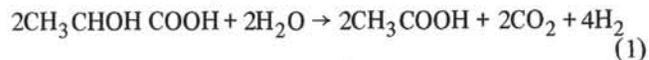
Bacterial methane production begins after sulfate reduction is essentially complete. The maximum amount of dissolved  $CO_2$  generated (as  $HCO_3^-$ ) is  $2^\circ SO_4 = 56$  mM/liter. It is apparent from studies undertaken on dissolved bicarbonate in interstitial water (see Presley and Kaplan, 1972) that methane production in DSDP sediments is associated with a decrease in the concentration and in  $C^{12}$  isotopic content of the total dissolved  $CO_2$ . This isotopic effect has been interpreted by Nissenbaum et al. (1972) as resulting from the preferential reduction of  $C^{12}$ -enriched  $CO_2$  by methanogenic bacteria to form methane. Methane can also be formed from simple alcohols, such as methanol, and simple acids, such as acetic and formic acids. It may therefore be considered the end product of anaerobic carbon degradation.

Thermal degradation of organic matter will result in the formation of low molecular-weight organic compounds, primarily methane, ethane, and in decreasing amounts, the higher hydrocarbons. Thus, the presence of small quantities of ethane in the gas phase in the range ethane:methane  $10^{-5}$  and  $10^{-6}$  would indicate an admixture of small quantities of thermally produced products with microbiological methane. Where the ratio rises to  $10^{-4}$  or greater, it could indicate production of hydrocarbons due to high temperatures at depth, or else upward diffusion from a petroleum reservoir. The data shown in Figure 3 for Leg 19 demonstrates the data which may be expected in a zone of high heat flow, as in the Aleutian Trench and Arc system. The quantity of ethane present showed excellent correlation with the inferred temperature flux. With the exception of Site 88, which is located above a presumed salt dome and has ethane present in the gas at a level 100 times that of gas

from other locations, increase in ethane with depth in all samples could be due to in situ generation along the natural geothermal gradient and does not necessarily reflect migrated hydrocarbons from a petroleum reservoir.

In general,  $\delta C^{13}$  of methane may be an indicator of its source. Thermal degradation of organic matter does not produce the same enrichment in  $C^{12}$  as biologically produced methane. The results for DSDP gases suggest a general relationship between isotopically heavier methane and increase in concentration of ethane, but with important exceptions. Thus, heavier methane occurred at Sites 88 and 147 where the highest ethane concentrations were recorded. However, at several locations (e.g., Sites 102, 147, 174, and 180) ethane content increases regularly with depth, but the  $\delta C^{13}$  of the methane is constant or decreases (enrichment in  $C^{12}$ ). Furthermore, at Site 176 where the heaviest  $\delta C^{13}$  methane values were observed, ethane was undetectable. Based on this limited sampling, it is likely that the observed variations in the isotopic and chemical composition of DSDP gas samples are primarily due to differences in the conditions of bacterial methane formation (i.e., isotopic composition of carbon substrate, and fractionation factor) and secondarily due to admixture of gases from higher temperature origin.

From the measured results, it is not possible to accurately determine the concentration of methane in the sediments studied. However, it may be possible to assign some limits. If it is assumed that methane production proceeds by reduction of the products generated during sulfate reduction, we may begin with oxidation of lactic acid as a typical substrate for sulfate-reducing bacteria. The reactions shown in equations 1 through 5 may then depict the terminal stages of carbon diagenesis (per mole of  $SO_4 =$  reduced, sulfate reduction to sulfide by active hydrogen not shown).



If dissolved carbon dioxide derived from equation 1 is hydrated and disproportionated to bicarbonate, it is probable that only 1 mole  $CO_2$ /mole  $SO_4$  reduced will be used for methane production, and the lower limit would then be 28 mM/liter interstitial water. However, an equivalent amount of methane and additional  $CO_2$  could be generated by degradation of the acetic acid. Furthermore, other fermentation processes in the sediment are producing  $CO_2$ , alcohols, and low-molecular-weight acids. The extent of this degradation is unknown, but it may be assigned a value equal to that produced by sulfate reduction. The methane produced in the sediment may therefore range from 28 mM/liter (0.63 liter  $CH_4$ /liter  $H_2O$ , from equation 4) to 112 mM/liter (2.5 liter  $CH_4$ /liter  $H_2O$ ). This range is equivalent to 0.31 to 1.25  $m^3CH_4/m^3$  sediment (on the

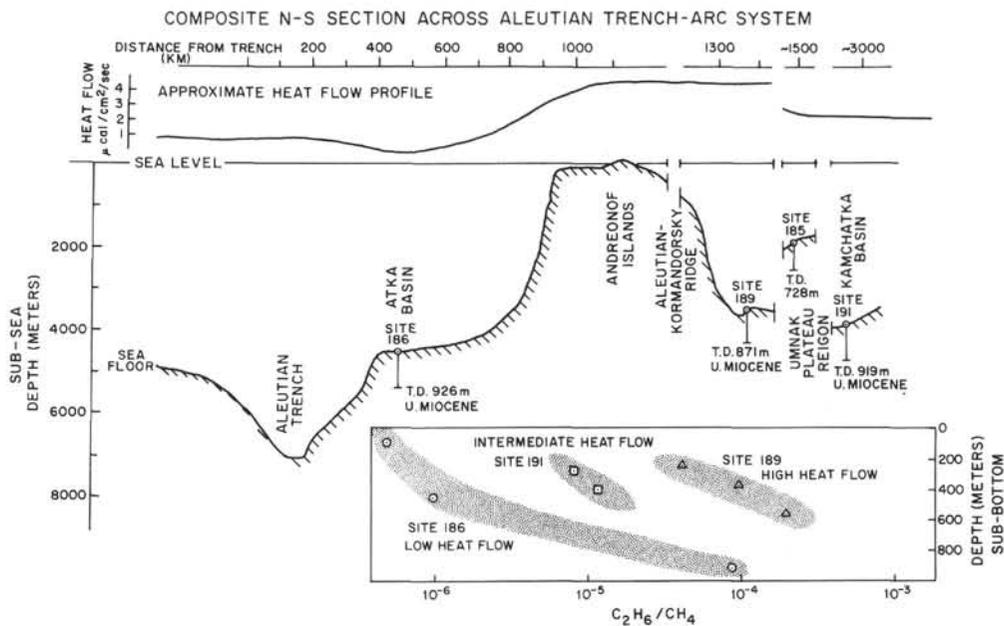


Figure 3. Variation in ethane/methane ratios with depth as a function of the geographic location of drilling in the Aleutian Trench-Arc System. It is believed that this relationship is directly related to the heat flow at the drilling site.

basis of 33% water content), which would indicate that low temperature bacterial generation of methane could be responsible for production of significant quantities of natural gas.

#### REFERENCES

- Atkinson, L. P. and Richards, F. A., 1967. The occurrence and distribution of methane in the marine environment. *Deep Sea Res.* 14, 673.
- Columbo, U., Gazzarrini, F., Gonfiantini, R., Sironi, G. and Tongiorgi, E., 1965. Measurements of  $C^{13}/C^{12}$  isotope ratios on Italian natural gases and their geochemical interpretation. *Advances in Organic Geochemistry*, 1964. Oxford (Pergamon Press). 279.
- Emery, K. O. and Hoggan, D., 1958. Gases in marine sediments. *Bull. Am. Assoc. Petrol. Geologists.* 42, 2174.
- Gealy, E. L. and Dubois, R., 1971. Shipboard geochemical analysis, Leg 7, *Glomar Challenger*. In Winterer, E. L., Reidel, W. R., et al., 1971. Initial Reports of the Deep Sea Drilling Project, Volume VII. Washington (U. S. Government Printing Office). 863.
- Kaplan, I. R., Smith, J. W. and Ruth, E., 1970. Carbon and sulfur concentration and isotopic composition in Apollo 11 lunar samples. *Geochim. Cosmochim. Acta*, Supplement I.
- Nissenbaum, A., Presley, B. J. and Kaplan, I. R., 1972. Early diagenesis in a reducing fjord, Saanich Inlet, British Columbia - I. Chemical and isotopic changes in major components of interstitial water. *Geochim. Cosmochim. Acta.* 36, 1007.
- Oana S., and Deevey, E. S., 1960. Carbon 13 in lake waters, and its possible bearing on paleolimnology. *Am. J. Sci.* 258-A, 253.
- Presley, B. J. and Kaplan, I. R., 1972. Interstitial water chemistry: Deep Sea Drilling Project, Leg XI. In Hollister, C. D., Ewing, J. I. et al., 1972. Initial Reports of the Deep Sea Drilling Project, Volume XI. Washington (U. S. Government Printing Office). 1009.
- Revelle, R., 1950. Sedimentation and oceanography: survey of field observations. *Geol. Soc. Am. Mem.* 43. 1.
- Rosenfeld, W. D. and Silverman, S. R., 1959. Carbon isotope fractionation in bacterial production of methane. *Science.* 130, 1658.
- Silverman, S. R., 1971. Influence of petroleum origin and transformation on its distribution and redistribution of sedimentary rocks. *World Petroleum Cong. Proc.* 8th, Moscow, 1971, 2, 47.