

24. GEOCHEMISTRY OF INTERSTITIAL GASES IN SEDIMENTARY DEPOSITS OF THE GULF OF CALIFORNIA, DEEP SEA DRILLING PROJECT LEG 64¹

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ABSTRACT

We analyzed interstitial gases from holes at Sites 474, 477, 478, 479, and 481 in the Gulf of California, using gas chromatography and stable isotope mass spectrometry to evaluate their composition in terms of biogenic and thermogenic sources. The hydrocarbon gas (C₁-C₅) concentrations were comparable to the shipboard data, and no olefins could be detected. The $\delta^{13}\text{C}$ data for the CH₄ confirmed the effects of thermal stress on the sedimentary organic matter, because the values were typically biogenic near the surface and became more depleted in ¹²C versus depth in holes at Sites 474, 478, and 481. The CH₄ at Site 477 was the heaviest, and in Hole 479 it did not show a dominant high-temperature component. The CO₂ at depth in most holes was mostly thermogenic and derived from carbonates. The low concentrations of C₂-C₅ hydrocarbons in the headspace gas of canned sediments precluded a stable carbon-isotope analysis of their genetic origin.

INTRODUCTION

Recent tectonic activity in the Gulf of California has generated extremely diverse thermal conditions within the sedimentary sequences. Some of these sediments show considerable thermal gradients, and already at a depth of several hundred meters sub-bottom, the *in situ* temperatures correspond to a platform sedimentary sequence that has subsided to a depth of many thousand meters. But the same sedimentary basin has other regions where the heat-flow values do not significantly exceed normal levels. Thus, the geological conditions permit the study of the thermal effects on the transformation of organic matter and the composition of the products resulting from this transformation versus the background of other, more or less constant, conditions (e.g., lithology-facies composition, age of deposits, and the type and source of organic matter).

METHOD

Interstitial gas samples were collected on board in vacutainers (commercial, evacuated test tubes) and then analyzed on board. Using gas chromatography for C₁-C₈ hydrocarbons under higher gas chromatographic resolution, we reanalyzed the samples. The gas had been stored in the same vacutainers until delivery to the laboratory for analysis.

Quantitative hydrocarbon gas data were obtained using a Hewlett-Packard 5830A gas chromatograph connected to a Model 18850A control terminal. We used locking gas-tight syringes (Precision Series A - 5.0, 1.0, and 0.25 ml) for sample injections. The Model 5830A is a dual-column gas chromatograph with a flame ionization detector (FID) for the analysis of C₁-C₈ hydrocarbons (100-pg detection limit) and a thermal conductivity detector (TCD) for H₂, CO, CO₂, CH₄, N₂, and O₂ determinations (100-ng detection limit).

The FID was operated only, using the following GC conditions: injection temperature at 180°C; helium carrier gas (3.6 ml/min. flow

rate; 20 ml/min. air); column oven programmed -50° (2 min. isothermal) to +10°C at 10°C/min., +10° to 100°C (45 min. isothermal) at 4°C/min.; Durapak stainless steel column (*n*-octane/Porosil C, 5 m × 0.76 mm I.D.).

We identified the compounds by comparing their retention times with those of the natural gas components. The individual compounds of natural gas had been identified by gas chromatography-mass spectrometry (Rohrbach, 1979). The results of these GC analyses are found in Table 1, and they confirm the shipboard data (see site chapters).

The carbon isotope compositions of CH₄ and CO₂ were measured in the Laboratory of Carbon Geochemistry of the Institute of Geochemistry and Analytical Chemistry, USSR Academy of Sciences. Barium hydroxide, injected into the vacutainers, bound the carbon dioxide. We then introduced 5 cm³ of the remaining gas, sampled by syringe, into the vacuum system to be incinerated to CO₂ in the reactor that consisted of copper oxide heated to 800°C. The system had appropriate traps for removing N₂O, SO₂, and other impurities. When the precipitated barium carbonate (BaCO₃) was dry, we then treated it with ortho-phosphoric acid in the standard system; the released CO₂ was used to analyze the carbon isotopes. The carbon isotopic composition measurements were performed on a Varian MAT 230 mass spectrometer with an accuracy of ±0.1‰ (Galimov et al., 1980). Table 2 is a compilation of the results and gives the "δ" notation versus the PDB standard.

The headspace of canned sediment samples was analyzed by gas chromatography and the stable carbon and oxygen isotope compositions on CH₄ and CO₂ determined. The $\delta^{18}\text{O}$ versus standard mean ocean water (SMOW) is also given.

RESULTS AND DISCUSSION

Table 1 shows the results of the interstitial gas analyses. The concentrations of CH₄, C₂H₆, C₃H₈, and total C₄H₁₀ and C₅H₁₂ compare with the shipboard data (see site chapters and Simoneit, this volume). No olefinic hydrocarbons are detectable.

Mouth of the Gulf

Sites 474 through 476 are at the mouth of the Gulf of California and within the boundary of the continental slope. They lie under water depths of 2500 to 3000 meters. The sedimentary sequence in Holes 474 and 474A

¹ Curray, J. R., Moore, D. G., et al., *Init. Repts. DSDP*, 64: Washington (U.S. Govt. Printing Office).

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Table 1. Hydrocarbon (C₁-C₅) and carbon dioxide in interstitial gas samples from the Gulf of California (DSDP Leg 64).

Section	Sub-bottom Depth (m)	Methane Concentration (mg/l)	Ethane (μg/l)	C ₂ /C ₁ × 10 ⁻⁴	Propane (μg/l)	C ₄ H ₁₀ Total (μg/l)	C ₅ H ₁₂ Total (μg/l)	Neopentane (μg/l)	Carbon Dioxide Concentration (%) ^a	Approximate Thermal Gradient Estimate ^b
474-3-3	14.5	375	75	2.3	10	2.5	8	0.1	4	1
474A-9-4	245	355	240	8.1	49	15	1.5		4	1
474A-12-4	272	83	42	6.0	12	5	3.5		4	2
474A-24-3	375	361	299	10.0	50	17			2	3
474A-26-2	393	221	149	8.1	20	8	7		1	5
474A-28-2	413	267	175	7.8	25	13			1	5
474A-40-3	529	0.1			0.5					5
477-7-1	50	0.8	5	81	0.3	0.05	1.5		0.2	1
477-16-2	117	5.2	39	90	30	21	2		8	3
477-19-3	147	118	1865	190	161	16	0.5	0.1	32	5
477-20-2	155	74	462	75	14		0.5		16	8
477-23-1	182	62	159	31	3.5		0.9		1.2	10
478-11-3	92	55	5	1.0	4	0.3			2	1
478-14-3	121	455	35	0.9	27	7	9		12	1
478-17-3	149	378	34	1.1	26	8	9		12	2
478-20-4	170	348	42	1.4	32	1			20	3
478-22-1	184	204	35	2.0	22	3		0.05	6	4
478-28-3	244	285	200	8.4	22	5	0.05		2	6
478-31-1	260	122	62	6.1	5	1			1	6
478-33-3	282	68	35	6.1	5	0.9	0.6		2	6
478-36-2	309	99	39	4.7	6	0.6	1.0		2	6
479-14-6	125	237	90	4.5	10	0.4	1.5		30	1
479-18-2	161	252	119	5.7	19	0.3	2		38	1
479-20-5	180	281	110	4.7	16	0.3	1.3		32	1
479-22-5	198	109	121	13	19	0.4	1.5		33	1
479-24-5	217	260	107	5	12	0.2	1.5		29	2
479-25-2	225	224	106	5.7	9	0.3	1.5		33	2
479-27-5	246	246	146	7	9	0.7	0.5		27	2
479-29-5	266	240	185	9.3	8	1.0	0.7		25	3
479-31-5	285	265	323	14	10	1.0	1.8		24	4
479-34-5	314	213	285	15	9	1.0	0.3		41	5
479-36-2	329	85	159	22	6	0.9	0.9		44	6
479-40-4	370	155	610	47	39	16.5	3.5		33	6
479-43-2	394	173	309	21	19	25	2.5		15	6
479-47-3	435	173	482	21	38	47	5.5		25	6
480-21-2	101	3.6	1	2.8	0.2		0.5		1.5	1
480-25-1	119	278	125	5.4	22	3	3	0.2	6	1
481A-4-1	70.5	233	214	11	6	2	6		2	1
481A-5-3	83	401	468	14	11	6	6		5	1
481A-7-6	106	389	391	12	44	195	43	0.2	6	1
481A-9-5	125	109	336	37	6	0.1	4	0.05	5	2
481A-10-5	135	372	1097	35	139	177	34	0.2	7	2
481A-12-5	152	473	4388	112	215	164	38	0.3	1	3
481A-13-2	159	485	2347	58	102	248	144	3.1	2	4
481A-13-4	162	64	354	66	17	56	119	2.5	1	5
481A-14-3	169	161	284	21	37	55	16	0.3	1	5
481A-22-4	246	423	103	3	29	26	7		8	6
481A-22-6	248	263	77	3.5	22	20	6		8	6
481A-24-6	269	491	115	2.8	34	25	6		6	6
481A-25-6	278	495	124	3.0	34	25	7		6	7
481A-26-6	287	434	111	3.1	29	18	10		6	7
481A-27-6	297	459	107	2.8	26	9	4		4	7
481A-28-6	306	366	118	3.9	29	10	5		2	8
481A-30-7	326	125	339	33.0	50	89	11	0.01	4	8

^a The CO₂ data are from shipboard analyses (see site chapters).

^b Very qualitative and based on shipboard temperature estimates (1 = low thermal stress; 10 = high thermal stress).

generally consists of hemipelagic diatomaceous ooze with thick interlayers of turbidites; the sequence varies in age from early Pliocene to Recent. Below 521 meters, the lithology changes to interlayered dolerites and basalt at a depth of 562.5 meters.

The methane concentration shows no trend with depth (Fig. 1), but ethane increases in concentration down to

about 300 meters and then drops to a minimum value above the basalt. This was first explained by the high density and cementation of the sediment below 300 meters, which decelerated the liberation of ethane from the core (see site chapter). Some data support this explanation. In fact, the density of the sediment increases from 1.6 g/cm³ in the upper part of the sequence to 1.8 g/cm³

in the lower part. The upper part also contains a considerable amount of dissolved silicic acid, which is depleted at depth.

But this chapter shows that the carbon isotope composition of the methane, which does not depend on emanation conditions, reveals the same trend as that of the ethane concentration (Fig. 1). In the upper part of the sequence, the methane has a $\delta^{13}\text{C}$ value (Fig. 1) typical for gases of a microbiological origin ($\delta^{13}\text{C} = -75\text{‰}$) (Galimov, 1975; Simoneit et al., 1979). But in the zone with the high concentration of ethane, the methane is enriched in the ^{13}C isotope, and downward in the sequence it again becomes isotopically lighter (Fig. 1). The $\delta^{13}\text{C}$ values, measured in the lower part of the sequence, correspond to the common case: methane depleted in the light isotope with depth (Galimov, 1975). The methane with an isotopic composition of about -40‰ does not fit this tendency and should therefore be regarded as allogenic. We know that methane with a similar isotopic composition is derived from mature organic matter by thermal transformation. The gas is relatively high in heavy hydrocarbons at this depth (272 m). In this context, the higher content of ethane can be accounted for by a lateral migration of hydrocarbon gas. Coarse sandy layers were encountered at a depth of 260 to 280 meters in Hole 474A. They could be permeable horizons, providing for the lateral migration of hydrocarbons. The samples recovered from that interval had the maximum $\delta^{13}\text{C}$ value of the CH_4 and highest $\text{C}_2\text{-C}_5$ concentrations.

Holes 475 and 476 contained no interstitial gas.

Guaymas Basin

Holes 477, 478, and 481 are in the Guaymas Basin in water depths of approximately 2000 meters. The structural geology of the region is determined by two, short, rifting axes separated by a short minor transform fault and confined by two long transform faults. The basin is in an active rift zone and has a typical oceanic crust

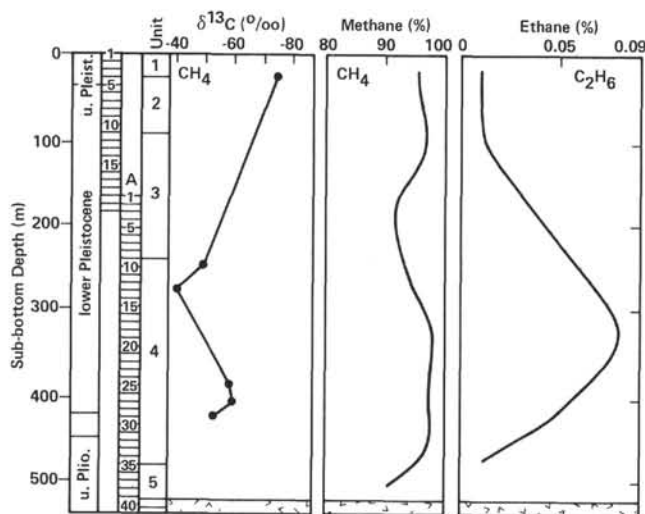


Figure 1. Plots of $\delta^{13}\text{C}$ and concentrations of methane and ethane versus depth, Holes 474 and 474A.

(Moore et al., 1978). The heat flow in the basin is uneven and ranges up to about $30 \mu\text{cal cm}^{-2} \text{g}^{-1}$. The basin has a rather high rate of sediment accumulation ($2.7 \text{ m}/10^3 \text{ yr}$) associated with high biological productivity and, as a consequence, a rapid burial of unoxidized organic matter. The region offers an opportunity to investigate the effect of increased temperatures on diagenetically unaltered organic matter (Einsele et al., 1980).

Hole 477 is in the southern rift zone. Measurements showed extremely high values of heat flow. At a depth of 260 meters, the temperature exceeds 135°C . The lithologic sequence consists of an upper, unaltered member of diatom turbidites (0–58 m), a dolerite intrusion (58–105.5 m), and a lower, altered member of turbidites. The lower turbidite member has undergone extensive hydrothermal alteration.

The methane concentration in the upper section decreases with depth toward the dolerite intrusion; in the lower sequence, it increases with depth, away from the dolerite intrusion (Fig. 2). The change in carbon dioxide concentration in the sediment is exactly the opposite. The interstitial gas contains a peculiarly high concentration of CO_2 . Its concentration adjacent to the intrusion is 90%. We found no ethane in the upper section, but below the sill, the ethane concentration increases and then decreases (Fig. 2).

The carbon isotopic analysis shows that the methane in the lower part of the sequence is depleted in the light isotope and has $\delta^{13}\text{C}$ values corresponding to gases generated from organic matter at a medium stage of metamorphism (Fig. 2). Methane of similar isotopic compositions frequently accompanies crude oil (Galimov, 1975).

The gas from Core 477–19 reveals the highest value of $\delta^{13}\text{C}$ and the maximum content of ethane. Thus, the lower sequences of Holes 477 and 477A contain hydrocarbon gases generated by the destruction of organic matter under extreme hydrothermal conditions.

The change in isotopic composition of the carbon dioxide (Table 2) is shown in Figure 2. The CO_2 concentration decreases toward the sill and becomes isotopically heavier. The CO_2 possibly resulted from a partial decomposition of carbonates from hydrothermal alteration. The increase in the concentration of CO_2 may account for the enrichment of CO_2 in the ^{13}C isotope near the intrusion.

Hole 478 is near the transform fault between the rifts of the Guaymas Basin. Unlike Hole 477, it has a moderate heat flow value. The sediments show no effects of hydrothermal alteration. They consist of a 300-meter-thick deposit of turbidites, overlying dolerite sills. The sediment in the upper section (0–188 m) comprises diatomaceous ooze, with interlayers of turbidite sand. They are underlain by various dolomite sandstones and include two dolerite sills (188–260 m). The lower portion of the sediment contains homogeneous diatom claystones with interlayered dolomite (260–342.5 m). The density of the sediments does not exceed that of the Hole 474 sequence and is typical for oceanic deposits. The change in the physical boundaries of sediment throughout the sequence is less pronounced than in Hole 477. The tem-

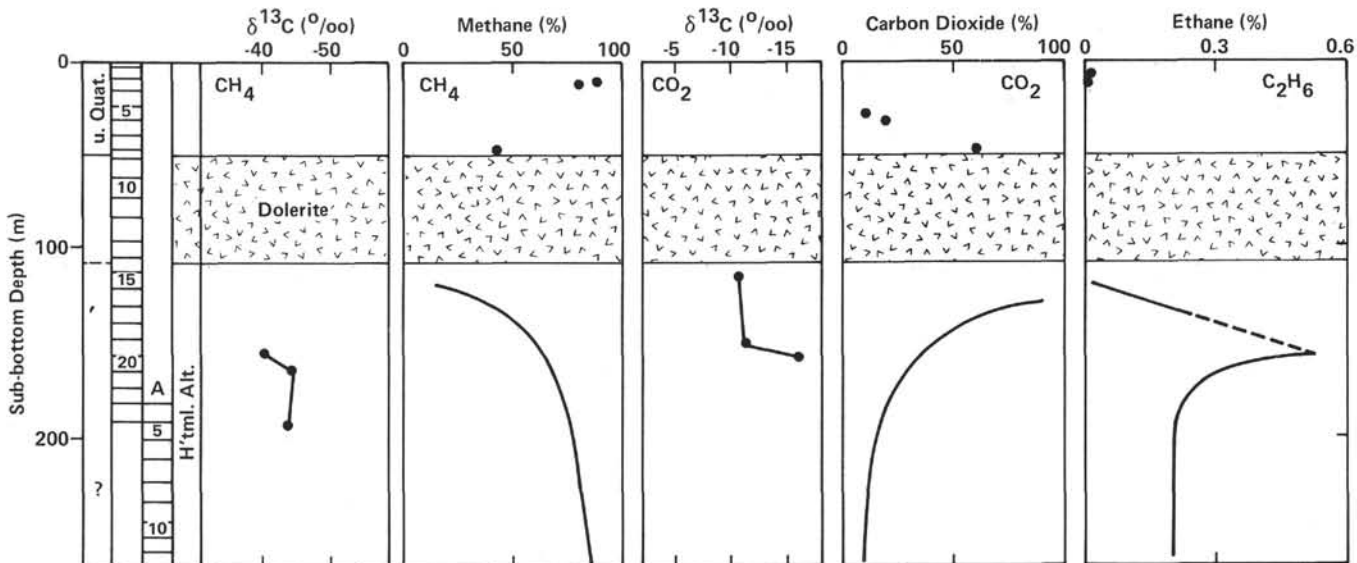


Figure 2. Plots of $\delta^{13}\text{C}$ and concentrations of methane and ethane versus depth, Hole 477.

perature effects of the intrusions are limited to the immediate contact zone (several cm).

Gas composition varies only slightly throughout the sequence (Fig. 3). Ethane increases slightly with depth, but below the dolerite intrusion, it passes through a minimum.

The isotopic composition of the CH_4 has a relatively low $\delta^{13}\text{C}$ value, typical for methane generated from immature organic matter by microbiota. The upper part of the sequence reveals a rather rapid change in the isotopic composition of CH_4 from -79.17 to -62.46% with depth (Fig. 3). These values compare with the mean ($\delta^{13}\text{C} = -71\%$) for CH_4 in surface sediments at station 30G in the northern rift (Simoneit et al., 1979). Farther down, the isotopic composition of methane varies approximately around the mean. These isotopic data indicate an autochthonous origin for the methane when under conditions of a moderate thermal gradient. The CO_2 concentration ranges from 10 to 20% above the sills, and the $\delta^{13}\text{C}$ values range from -6.3 to -9.7% (Table 2). As in Hole 477, this CO_2 may be derived from partial decomposition of carbonates.

Hole 481A is in the northern rift of the Guaymas Basin. In the sediment above the dolerite sill, the ethane increases in concentration with depth to a maximum at about 150 meters sub-bottom (Fig. 4). Below the upper sill, the C_2H_6 concentration passes through a minimum. The CH_4 concentration is approximately constant from 50 to 130 meters. It increases slightly toward the upper sill (Fig. 4) and below it passes through a maximum.

The carbon isotopic composition of the CH_4 above the upper sill lightens rapidly (Fig. 4). This change is more distinct than in Hole 478. Values to about 100 meters sub-bottom are typically biogenic (Claypool and Kaplan, 1974) and compare to the $\delta^{13}\text{C} = -71\%$ for the CH_4 in the surface sediment at station 30G, about 8 km to the northeast (Simoneit et al., 1979). The CH_4 near the top of the upper dolerite sill approaches the isotopic composition of approximately -44% , which is

typical of thermogenesis from mature organic matter and which corresponds to the initial phase of oil generation (Galimov, 1975). The isotopic composition of CH_4 in the lower part of the sequence changes unevenly with depth, remaining, with one exception, within the range characteristic of methane at the early stage of transformation of organic matter. The presence of CH_4 at 278 meters sub-bottom with $\delta^{13}\text{C} = -44.4\%$ appears to be a significant relict thermogenic component. Most of the gas below the upper sill probably formed under milder thermal regimes from relatively unaltered organic matter.

The CO_2 concentrations throughout the hole are less than 10%, and the $\delta^{13}\text{C}$ values are scattered from -3.3 to -20.3% (Table 2)—data insufficient to indicate processes.

Continental Slope

Holes 479 and 480 are on the continental slope of the northeastern flank of the Guaymas Basin in water depths of 650 to 750 meters. The lithology of the sediment in Hole 479 consists of hemipelagic diatomaceous ooze and claystone with interlayered dolomite beds. The carbonate is less abundant in the upper part (0–250 m) than in the middle part (250–355 m). The amount of carbonates increases further in the lower part (355–440 m).

The CH_4 concentration decreases to about 60% with depth and then fluctuates between 45 and 70% (Fig. 5). Ethane remains low and essentially constant, not exceeding 0.02% to a depth of about 260 meters (Fig. 5). But at greater depth, the C_2H_6 concentration increases to $>0.1\%$ and accompanies the simultaneous increases of the C_3 – C_5 hydrocarbons (Simoneit, this volume). Drilling in Hole 479 stopped at 400 meters because of a continuing increase in the concentrations of heavy hydrocarbons.

The isotopic composition of the CH_4 varies within the range of -50 to -70% (Fig. 5). The isotopic composition of the CH_4 remains generally unaltered and

Table 2. Carbon isotope composition of CH₄ and CO₂, Gulf of California (DSDP Leg 64).

Section	CH ₄ δ ¹³ C(‰) ^a	CO ₂ δ ¹³ C(‰) ^a
474-3-3	-75.34	— ^b
474A-9-4	-49.65	—
474A-12-4	-40.35	—
474A-24-3	-59.00	—
474A-26-2	-59.96	—
474A-28-2	-53.61	—
474A-40-3	— ^b	—
477-7-1	—	—
477-16-2	—	-10.87
477-19-3	-39.99	-11.05
477-20-2	-44.40	-16.43
477-23-1	-42.94	—
478-11-3	-79.17	—
478-14-3	-72.38	-8.91
478-17-3	-68.66	-8.09
478-20-4	-62.46	-6.31
478-22-1	-64.36	-9.73
478-28-3	-61.93	—
478-31-1	-65.38	—
478-33-3	—	—
478-35-2	-59.75	—
479-14-6	-55.62	+3.29
479-18-2	-58.41	—
479-20-5	-61.78	-0.85
479-22-5	-55.48	+0.80
479-24-5	-52.04	+0.06
479-25-2	-61.78	-2.47
479-27-5	-61.56	-2.71
479-29-5	-57.45	-1.78
479-31-5	-51.63	-3.77
479-34-5	-60.76	-6.57
479-36-2	-58.95	-3.67
479-40-4	-54.87	-4.63
479-43-2	-60.76	-8.53
479-47-3	-60.38	-9.57
480-21-2	—	—
480-25-1	-66.96	-4.38
481A-4-1	-77.32	—
481A-5-3	-70.32	-7.28
481A-7-6	-69.75	-11.95
481A-9-5	—	—
481A-10-5	-59.20	—
481A-12-5	-54.66	—
481A-13-2	-55.22	—
481A-13-4	—	—
481A-14-3	-44.18	—
481A-22-4	-59.84	—
481A-22-6	—	-3.25
481A-24-6	-57.75	-20.28
481A-25-6	-44.36	—
481A-26-6	-56.29	-9.49
481A-27-6	-56.06	-12.60
481A-28-6	-61.05	—
481A-30-7	-53.66	—

^a Versus PDB Standard.

^b Insufficient sample for determination.

does not reflect a ¹³C-enrichment that can be related to the increase of the C₂-C₅ hydrocarbon concentration. The scatter throughout the sequence is less than 10‰, and the range is within values typical for CH₄ derived from immature organic matter. Such a striking difference in the chemical composition of the gas and the isotopic composition of the methane can be attributed,

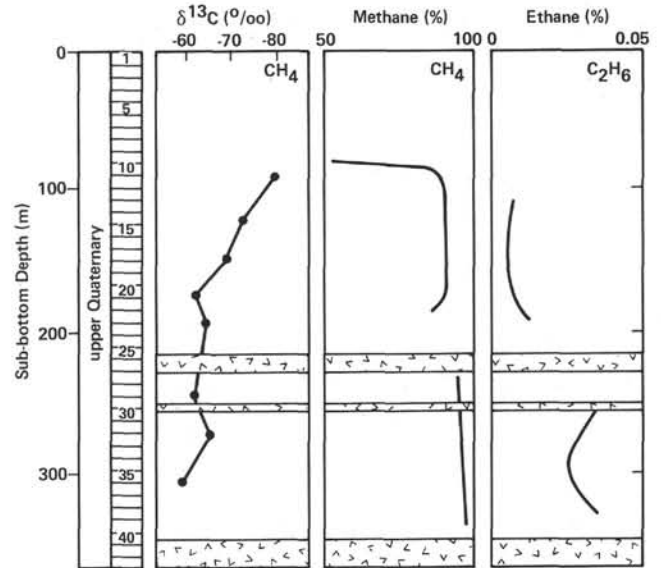


Figure 3. Plots of δ¹³C and concentrations of methane and ethane versus depth, Hole 478.

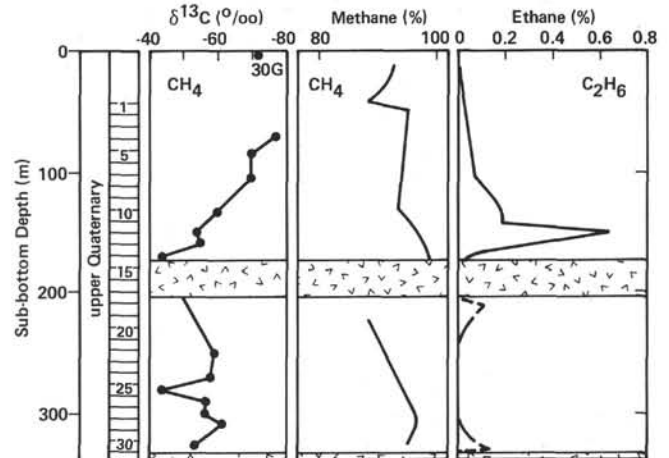


Figure 4. Plots of δ¹³C and concentrations of methane and ethane versus depth, Hole 481.

in principle, to a diffusion of thermogenic hydrocarbons from the underlying deposits. Compared to the gas content of the sediment, the gas influx from this origin could be minor (not exceeding several percent). Therefore, the change in the isotopic composition of the CH₄ could be imperceptible. But the influx of even 1% of gas with a 5% constituent of ethane, where the ethane concentration made up 0.01%, could quintuple the ethane proportion of the gas; and this could explain the data.

The CO₂ in Hole 479 varies in concentration from 10 to 50% and has the highest values of δ¹³C (Fig. 5 and Table 2). The CO₂ isotopic composition shows a tendency to depletion of the heavy carbon isotope in the sequence. Calculations of average values from the data for all three lithologic complexes gives the following results: δ¹³C = 0.31‰ for all the upper complex, -3.9‰ for the middle, and -7.58‰ for the lower.

Isotopically heavy CO₂ may result from the decomposition of oxygen-bearing organic compounds (e.g.,

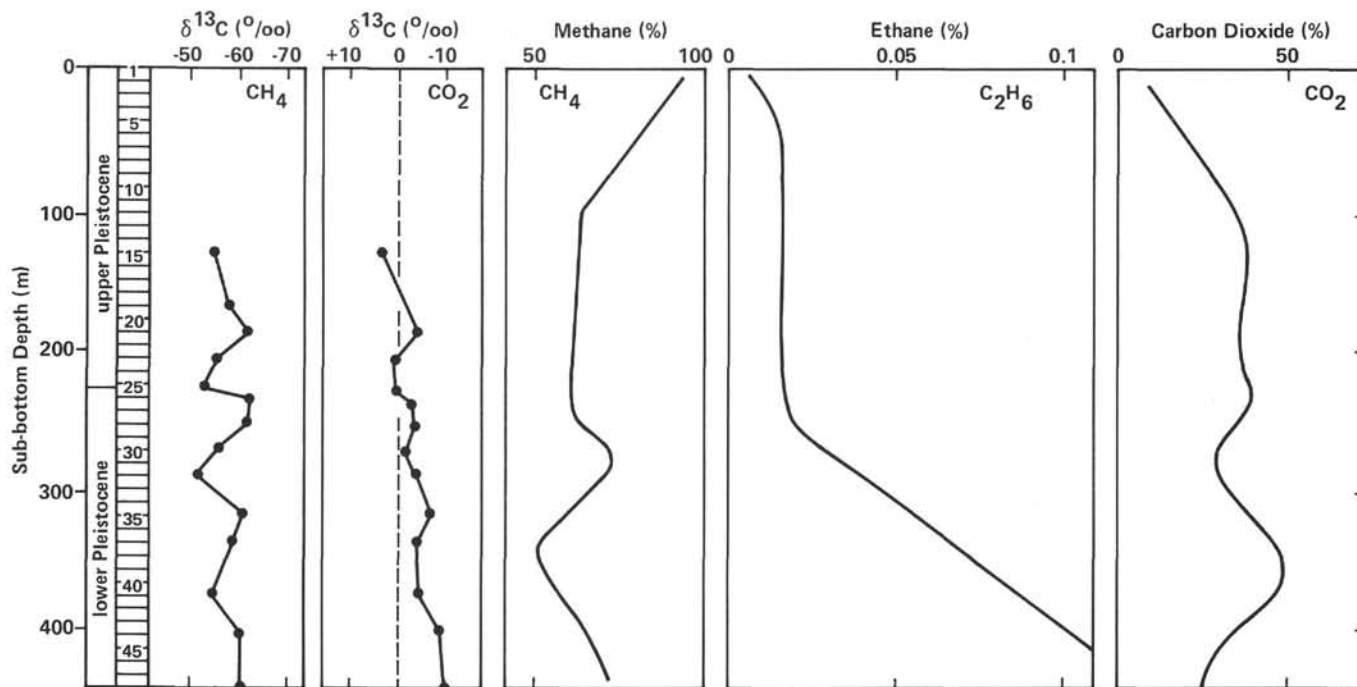


Figure 5. Plots of $\delta^{13}\text{C}$ and concentrations of methane, carbon dioxide, and ethane versus depth, Hole 479.

decarboxylation) in reducing environments (Galimov, 1974) and from the microbiological reduction of some carbon dioxide to methane (Claypool and Kaplan, 1974). The high biological productivity and high rates of organic matter burial imply that sedimentation in the Site 479 hole took place in environments with an oxygen deficiency. This is confirmed by the relatively high values of $\delta^{13}\text{C}$ for the CO_2 , particularly in the upper part of the sequence. Because of the high carbonate concentration at greater depths, the CO_2 isotopic composition may possibly become a function of fractionation in the isotope exchange system ($\text{CO}_2 \rightleftharpoons \text{CO}_3^-$). Analyzing this assumption requires more comprehensive data on the carbonate content and the isotopic composition of the sediment.

Hole 480 is in the same region of the marginal plateau as Hole 479. A single analysis of the interstitial gas from 119 meters sub-bottom gave the values of $\delta^{13}\text{C} = -66.96\text{‰}$ for CH_4 and -4.38‰ for CO_2 . These values are slightly lower than those from Hole 479 at a corresponding depth (about 120 m).

Canned Samples

Table 3 presents the results of the headspace analyses of the canned samples. The purpose of the analysis was to obtain $\delta^{13}\text{C}$ data for the $\text{C}_2\text{-C}_5$ hydrocarbons, but the small concentrations precluded such determinations. The gas data are similar to that of Hole 479: $\delta^{13}\text{C}$ values of the methane are essentially in the biogenic range, and the CO_2 is depleted in ^{13}C at depth.

CONCLUSIONS

The concentrations of the interstitial hydrocarbon gases ($\text{C}_1\text{-C}_5$) determined onboard were confirmed, and we detected no olefinic hydrocarbons.

The carbon isotopic composition of methane shows a trend toward a depletion of the light isotope with depth in the sedimentary sequence (Galimov, 1975). Galimov et al. (1980) also established this same tendency for a deep oceanic sedimentary sequence. This depletion results from the fact that the methane, generated at different stages of transformation of the organic matter, differs in the isotopic composition of the carbon. The following are ranges of CH_4 isotopic composition (corresponding to the successive stages of organic matter transformation):

- 1) initial (biogenic; consisting only of methane) $\delta^{13}\text{C} = < -60\text{‰}$;
- 2) early (onset of $\text{C}_2\text{-C}_5$ hydrocarbon generation) $\delta^{13}\text{C}$ from -40‰ to -60‰ ;
- 3) mature (main phase of oil formation) $\delta^{13}\text{C}$ from -30‰ to -40‰ ; and
- 4) late (termination of liquid hydrocarbon generation; amorphous stage of organic matter metamorphism) $\delta^{13}\text{C} = > -30\text{‰}$.

In most of the holes, the isotopic composition of methane in the upper sections, composed of sediment unaffected by thermal events caused by intrusions, corresponds to a microbiological origin (i.e., the initial stage of organic matter transformation). This is also true for the CH_4 in the surface sediment from station 30G in the northern rift of the Guaymas Basin (Simoneit et al., 1979). But near intrusions, the methane is generally depleted in the light carbon isotope. In these sections, the change in the methane isotopic composition increases with depth. The highest values of $\delta^{13}\text{C}$ for CH_4 occur in Hole 477, the area with the highest heat flow values. The isotopic composition of CH_4 ranges from -40 to -44‰ at depths below 200 meters. Thus, the isotopic composition of methane, as a rule, accords with the thermal history of the surrounding sediment.

Table 3. Headspace analyses of canned sediment samples from Holes 479, 481, and 418A.

Section	Quantitative Analysis ^a						Stable Isotope Composition ^b		
	Methane	Ethane	Propane	Total C ₄	C ₅ ⁺	CO ₂	Methane δ ¹³ C	Carbon δ ¹³ C	Dioxide δ ¹⁸ O
479-19-7	381	0.34	0.07	—	—	9.7	-59.89	-3.78	-1.29
479-28-7	102	0.28	0.04	—	—	4.9	—	-5.53	-1.35
481-4,CC	3190	—	0.08	—	—	2.3	-70.08	-4.01	-1.34
481A-24,CC	486	0.45	0.15	0.09	0.16	1.7	-58.34	-10.93	-0.58

^a Hydrocarbon concentrations are in parts per million by volume; carbon dioxide values are volume percentage.

^b Stable isotope data are in parts per thousand; carbon is relative to PDB and oxygen is relative to SMOW.

Some sediment revealed examples of gas migration. Two holes were typical. The CH₄ in Hole 474, at a depth of 250 to 280 meters, was depleted in the light carbon isotope (δ¹³C from -40 to -50‰) in the overlying and underlying gases. This possibly resulted from horizontal migration of methane derived from the transformation of mature organic matter. Hole 479 is another example of this sequence not revealing any considerable change in the isotope composition of the methane with depth. But, a considerable increase in the concentration of hydrocarbons at depths below 300 meters implies a vertical gas diffusion from a source with a high content of heavy hydrocarbons.

Considerable concentrations of CO₂ were encountered in some of the interstitial gas. In most of the cases, the isotopic composition of the CO₂ carbon varies downhole without any obvious trend. The values of δ¹³C, ranging from -7 to -12‰, are common. They are close to the value of -9‰, which corresponds to the average value of the CO₂ of organic and inorganic origins. In sections with considerable carbonate concentrations, the isotopic composition of CO₂ should be controlled by an exchange in the system (CO₂ ⇌ CO₃²⁻). The enrichment of CO₂ with the heavy carbon isotope (e.g., as in Hole 479) is possibly determined by generation of this ¹³C by the anaerobic decomposition of organic matter in a sedimentary environment of acute oxygen deficiency. The CO₂ may be enriched in ¹³C in two ways. First, the carbon may combine with oxygen (e.g., carboxyl) in the biogenic organic compounds and become enriched in the ¹³C isotope by a specific intramolecular distribution of carbon isotopes (Galimov, 1974, 1975). Second, the microbiological reduction of CO₂ presumably generates a kinetic isotope effect, leading to the concentration of the ¹³C isotope in the residual carbon dioxide (Claypool and Kaplan, 1974). The CO₂ enriched in the light carbon isotope (-16 to -20‰) is probably a product of organic matter oxidation, and it inherits the isotopic composition of the total organic carbon.

The headspace gas of canned sediment samples contained insufficient C₂-C₅ hydrocarbons for stable carbon isotope analysis. The CH₄ was primarily biogenic, and the CO₂ was partly thermogenic.

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