

23. ISOTOPIC COMPOSITION OF METHANE CARBON AND THE RELATIVE CONTENT OF GASEOUS HYDROCARBONS IN THE DEPOSITS OF THE MOROCCAN BASIN OF THE ATLANTIC OCEAN (DEEP SEA DRILLING PROJECT SITE 415 and 416)

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INTRODUCTION

At Site 415, drilling was planned to penetrate 3000 meters of oceanic sediments, thus affording a unique opportunity to study the geochemical evolution of organic matter in basin conditions. Drilling such a deep borehole made especially acute the problem of preventing a possible blowout of hydrocarbons. The program of geochemical investigations aboard *Glomar Challenger* therefore was devised to produce the necessary information to ensure drilling safety and prevent ocean pollution. One of the principal methods serving this purpose was the chromatographic analysis of gases.

Drilling to the contemplated depth proved impossible: Hole 415A penetrated 1079 meters sub-bottom, and Hole 416A achieved a total depth of 1624 meters. The gas content and composition in the sediment did not reach parameters which could be regarded as critical. However, the experience of applying chromatographic analysis of gases aboard ship proved it to be a very useful method of estimating hydrocarbon types and concentrations, thereby allowing uninterrupted drilling with minimal risk of blowout.

As a result of gas analysis aboard ship, data were obtained on the content of gas in the profile and its hydrocarbon composition. Gas samples in sealed vacuum containers were delivered to the Carbon Geochemistry Laboratory (GEOCHI, Moscow) where the isotopic composition of carbon in the gases was measured.

EXPERIMENTAL PROCEDURE

The gas samples were taken aboard ship by piercing the plastic jacket of the core sampler with the needle of a vacuum-tight syringe. The gas was transferred from the syringe into a pre-vacuumized test tube closed with an airtight rubber stopper. From this test tube, the gas was analyzed chromatographically. For shore-based analysis, the gas was stored and transported in the same tube.

Aboard ship, gas analysis was conducted on two chromatographs using the same analytical procedure employed on Leg 47. The CH₄ and CO₂ analysis was performed utilizing the Carl Model 8000 gas chromatograph with a catarometer as the detector. The column (5 ft long, with 1/8 in. o.d., packed with 8% Carbowax 1540 on Anacrome ABC, 90 to 100 mesh) was kept at a constant temperature of 40°C. The analysis of hydrocarbons, from C₂ to C₅, was conducted on a Hewlett Packard Model 5710A chromatograph with a flame-

ionization detector and a system of dual columns to work in the compensational mode of operation. This dual system involved one column (4 ft long, with 1/8 in. o.d., packed with Spherosyl) joined with another column (12 ft long, with 1/8 in. o.d., packed with 20% OV 101 on Anacrome 11/110 AC). Helium served as the carrier gas; the flow rate was 20 cm³/min. The furnace temperature was programmed as follows: initially at 60°C for 4 min, then increased to 200°C at the rate of 16°/min, then kept constant at 200°C for 16 min. The sample previously had been drained of air and methane by being passed through a coil cooled to -70°C.

The isotopic analysis of gas was performed on a Varian MAT-230 mass spectrometer. Prior to analysis, the gas from the vacuum container was passed through an ascarite tube to be purified of carbon dioxide and through a cold trap for methane to be separated from higher hydrocarbons. Methane then was oxidized to CO₂ in the circulation system of a reactor filled with CuO at 800°C. The CO₂ obtained was freed of air and water impurities in cold traps, and of N₂O in a furnace with elementary copper at 500°C. Analysis of the isotopic composition of methane carbon was conducted with an accuracy of ±0.1 per mill. The results are given in δ¹³C values as related to the PDB standard.

RESULTS

Tables 1 and 2 show the results of the chromatographic analysis of gas samples from Holes 415A and 416A. Methane concentration in the samples varies from immeasurably low content to 50 to 60 per cent. The content of carbon dioxide in all the samples is low, barely exceeding the background values in the laboratory air. The hydrocarbon fraction of the gas is represented almost entirely by methane. The content of total heavy hydrocarbons in all the samples is less than 1 per cent.

The hydrocarbon composition of gas in samples that were analyzed immediately after recovery is different from the composition in the same samples after being stored for several hours at room temperature. In the latter case, as shown in Table 3, the samples are almost twice as rich in heavy hydrocarbons. This is evidently caused by the different time needed for different hydrocarbons to evolve from the sediment. The hydrocarbon composition of the gas analyzed after a certain period of time seems to be truer to *in situ* conditions. Accordingly, only the analyses of these gases are included in the tables presented in this report.

TABLE 1
Concentration of CH₄ and CO₂ and C₂-C₅ Hydrocarbons in the Samples of Site 415

Core	Stratigraphy	Sub-Bottom Depth (m)	CH ₄ CO ₂		C ₂ H ₆	C ₃ H ₈	<i>i</i> -C ₄ H ₁₀	<i>n</i> -C ₄ H ₁₀	<i>i</i> -C ₅ H ₁₂	<i>n</i> -C ₅ H ₁₂
			(% vol)							
415-3	Miocene	137.5-147	0.3	0.16	0.0	0.0	0.0	0.0	0.0	0.0
415-5	Miocene	273.5-283	0.3	0.08	2.9	0.0	0.0	0.0	0.0	0.0
415A-5	Paleocene	443.0-452	27.3	0.14	83.2	0.0	0.0	0.0	0.0	0.0
415A-6	Paleocene	452.0-509.5	20.2	0.25	54.8	0.0	0.0	0.0	0.0	0.0
415A-7	M.-U. Cret.	509.5-519	4.7	0.13	43.7	2.1	0.0	0.0	0.0	0.0
415A-8	M.-U. Cret.	519-585.5	16.7	0.29	126.2	11.6	2.7	2.2	1.3	0.6
415A-9	Cenomanian	642-652	29.8	0.20	239.0	31.0	11.6	6.8	5.6	2.8
415A-10	Cenomanian	709-718.5	57.5	0.16	414.3	55.6	19.2	8.4	7.0	1.7
415A-11	Cenomanian	794-804	49.6	0.17	733.6	113.4	60.0	22.0	18.5	8.4
415A-12	Cenomanian	880-889.5	34.1	0.20	424.2	63.0	28.2	10.9	9.0	4.5
415A-13	Cenomanian	956-965.5	26.0	0.16	588.0	97.4	53.1	19.2	18.0	6.7
415A-14	Albian	1032-1041.5	59.8	0.25	1222.3	142.0	70.4	24.3	20.1	7.8

TABLE 2
Concentration of CH₄ and CO₂ and C₂-C₅ Hydrocarbons in the Samples of Site 415

Core	Stratigraphy	Sub-Bottom Depth (m)	CH ₄ CO ₂		C ₂ H ₆	C ₃ H ₈	<i>i</i> -C ₄ H ₁₀	<i>n</i> -C ₄ H ₁₀	C ₅ H ₁₂
			(% vol)						
416A-1	M.-U. Miocene	146-155.5	0.0	0.13	0.0	0.0	0.0	0.0	0.0
416A-2	L. Miocene	293-307.5	0.0	0.13	0.0	0.0	0.0	0.0	0.0
416A-3	U. Oligocene	450-459.5	11.4	0.36	18.0	0.0	0.0	0.0	0.0
416A-5	Alb.-l. Eocene	754-763.5	10.7	0.09	35.0	0.5	0.0	0.0	0.0
416A-6	L. Aptian	887-896.5	22.0	0.11	46.7	0.5	0.0	0.0	0.0
416A-7	Hauterivian	991.5-1093	0.5	0.09	2.4	0.5	0.5 ^a	0.0	0.4
416A-9	Hauterivian	1176.9-1185.4	0.28	0.10	4.0	0.0	0.0	0.0	0.0
416A-11	Hauterivian	1194.8-1204.3	0.06	0.09	5.0	0.0	0.0	0.0	0.0
416A-12	Hauterivian	1204.3-1213.8	0.17	0.05	11.1	1.5	0.6	0.4	0.36
416A-13	Hauterivian	1213.8-1222.1	0.08	0.05	3.8	0.2	0.0	0.0	0.0
416A-14	Valanginian	1223.4-1232.9	0.08	0.04	5.0	0.3	0.0	0.0	0.0
416A-15	Valanginian	1232.9-1242.5	0.10	0.08	3.2	0.07	0.0	0.0	0.0
416A-16	Valanginian	1242.5-1252.0	0.19	0.06	5.3	0.15	0.0	0.0	0.0
416A-17	Valanginian	1252.0-1261.5	0.09	0.06	5.0	0.60	0.0	0.0	0.0
416A-18	Valanginian	1261.5-1271.0	0.09	0.08	2.4	0.3	0.0	0.0	0.0
416A-19	Valanginian	1271-1277.5	0.09	0.06	3.2	0.6	0.0	0.0	0.0
416A-20	Valanginian	1277.5-1287.0	0.15	0.08	4.5	0.7	0.21	0.17	0.12
416A-21	Valanginian	1290-1299.5	0.07	0.05	5.2	1.8	0.45	0.31	0.3
416A-22	Valanginian	1299.5-1309.1	0.23	0.13	9.2	3.3	0.97	0.93	1.1
416A-23	Valanginian	1309.1-1318.6	0.15	0.08	6.1	2.1	0.64	0.56	0.88
416A-24	Valanginian	1318.6-1324.7	0.11	0.08	5.4	1.9	0.56	0.54	0.74
416A-25	Valanginian	1327.7-1336.7	0.08	0.07	3.3	1.4	0.35	0.70	0.70
416A-26	Valanginian	1337.2-1346.7	0.09	0.08	3.0	1.0	0.35	0.5	0.85
416A-28	Valanginian	1356.4-1365.9	0.04	0.07	1.3	0.45	0.22	0.22	0.52
416A-29	Valanginian	1365.7-1375.2	0.04	0.05	3.3	1.8	0.45	0.45	0.8
416A-30	Valanginian	1375.2-1384.6	0.04	0.05	2.6	1.0	0.43	0.69	1.11
416A-31	Valanginian	1384.6-1394.1	0.02	0.04	0.9	0.35	0.0	0.0	0.0
416A-32	Valanginian	1394.1-1403.6	0.03	0.04	1.9	1.0	0.1	0.32	0.4
416A-34	Valanginian	1406.8-1416.4	0.12	0.04	4.8	2.4	0.7	0.85	1.3
416A-36	Valanginian	1425.4-1435.0	0.018	0.04	0.7	0.4	0.0	0.0	0.0
416A-40	Valanginian	1454.5-1463.9	0.02	0.04	0.9	0.4	0.04	0.2	0.47
416A-45	Valanginian	1501.2-1510.6	0.001	0.01	0.99	0.78	0.05	0.24	0.29
416A-49	Berriasian	1539.1-1548.6	0.033	0.06	0.5	0.26	0.34 ^a	0.2	0.2
416A-50	Berriasian	1548.6-1558.0	0.036	0.07	0.73	0.38	0.14	0.29	0.3
416A-51	Berriasian	1558.0-1567.4	0.052	0.05	1.0	0.32	0.22	0.17	0.38
416A-52	Berriasian	1567.4-1576.8	0.052	0.05	0.95	0.59	0.16	0.13	0.34
416A-53	Tithonian-Berrias	1576.8-1586.2	0.02	0.08	0.56	0.37	0.1	0.17	0.3

^aIsobutane + *n*-butane.

TABLE 3
Comparison Between Hydrocarbon Composition of Gas Samples Taken Immediately After Recovery and After Standing at Room Temperature for Two Hours

Core	Section	Mode of Sampling	CH ₄	C ₂ H ₆	C ₃ H ₈	<i>i</i> -C ₄ H ₁₀	<i>n</i> -C ₄ H ₁₀	<i>i</i> -C ₅ H ₁₂	<i>n</i> -C ₅ H ₁₂
			(%)						
415A-13	1	Immediately	42.6	595.3	69.0	32.6	12.2	11.8	3.4
	2	After 2 hr standing	30.4	627.0	94.0	57.2	19.2	19.2	7.3
415A-14	1	Immediately	62.4	1044.3	96.6	40.3	14.1	12.3	6.7
	1	After 2 hr standing	59.8	1222.3	142.0	70.4	24.3	20.7	7.8

The values of absolute gas concentrations reflect only an approximation of the distribution throughout the section. The content of gas in the sample depends not only on its concentration in the sediment, but also on the conditions of core and gas sampling. Consequently, relative values are more reliable for discussion. These relative values are reflected in the content of heavy hydrocarbons in per cent of the total C₂ to C₅ in Tables 4 and 5, as well as a number of individual hydrocarbon ratios in Tables 6 and 7.

The results of methane carbon isotopic composition measurements are given in Tables 8 and 9. The amount of higher methane homologues in all the samples was too small to be measured.

Much like the chemical composition, the isotopic composition depends to some extent on the sampling conditions (Table 10). Methane carbon from the gas sample taken after holding the core at room temperature for several hours is richer in the ¹³C isotope by approximately 1 per mill.

DISCUSSION

Figures 1 and 2 give an idea of gas content variations throughout the drilled interval of Holes 415A and 416A. As already mentioned, the methane content is characterized by relative values. With the core-sampling technology presently used, a considerable portion of sediment gas is lost in the course of drilling and recovery. These figures, therefore, provide no more than a qualitative picture of gas distribution throughout the section.

Gas content in the top 200 to 300 meters of the section is only slight. This is characteristic of both Holes 415A and 416A. Further downhole, gas content begins to increase and, in Hole 415A, remains high over the whole section. In Hole 416A, the interval with a noticeable gas content is replaced at the depth of 900 to 1000 meters by a profile section extremely poor in gas.

A successive appearance of increasingly heavier gaseous hydrocarbons is observed at both sites. In Hole 415A, ethane was first detected in the interval from 273.5 to 283 meters, with hydrocarbons heavier than ethane being completely absent. At a depth of 509.5 to 519 meters, propane appears for the first time. Similarly, the first appearance of ethane has been recorded in Hole 416A at a depth of 450 to 459.5 meters. Measurable concentrations of propane were found in the next core sample (416A-5 at 754 to 763.5 m), and butane and propane appear at the depth of about 1000 meters.

A picture thus emerges of consecutive actuation of the mechanisms whereby organic matter generates increasingly heavier hydrocarbons with depth. The regularity in the growth of the content of heavy hydrocarbons with depth becomes especially clear in the lower portions of Hole 416A.

The total gas content in the profile of Hole 416A, as already has been noted for the whole turbiditic profile, is very low starting from Core 416A-7 (991.5 to 1093 m). It stays within 0.01 to 0.2 per cent down to the deepest deposits. Despite low gas concentration, there is a clearly defined tendency for the content of heavy hydrocarbons to increase with depth. From Figure 3 it is seen that at a depth of 1250 meters (from Cores 416A-13 to 416A-19) the C₂ to C₅ fraction consists mainly of ethane. With increasing depth, the ethane fraction decreases until it constitutes less than half of the gas samples from the deposits lying below 1400 meters. Especially striking is the increase of pentane content; at these depths it becomes the main component of the C₂ to C₅ fraction of the gas. Since pentane essentially starts the gasoline series of liquid hydrocarbons, its high relative concentration may be regarded as an indication of the capability of organic matter to generate liquid hydrocarbons at corresponding depths.

In this respect, one's attention is also attracted by the inversion of the ratio *i*-C₄/*n*-C₄ at depths of more than 1300 to 1350 meters (Figure 4). In the upper portion of the section, isobutane predominates; in the lower portion, the inverse relationship is observed. It is to be noted that the ratio *i*-C₄/*n*-C₄ in oils is generally less than unity.

The picture of the distribution of carbon isotopes in gases for the sections investigated (Figure 5) has the following noteworthy characteristic features:

- 1) The deposits in the upper 1000 meters of both sites contain methane which is isotopically very light.
- 2) The methane isotopic composition in both sites changes progressively with depth.
- 3) The gradient of isotopic composition variation is not the same in the profiles of Sites 415 and 416.
- 4) At about 1300 meters in Hole 416A, a gas was encountered whose isotopic composition is close to that of the gases of oil deposits.

The variation of gas isotopic composition with depth towards the depletion of the light isotope is characteristic of the gases of the sedimentary crust in general (Galimov, 1969). We believe the most probable explanation

TABLE 4
Concentration of C₂ to C₅ Hydrocarbons on the Methane = Free Basis in the Samples of Site 415

Core	Stratigraphy	Sub-Bottom Depth (m)	C ₂ H ₆	C ₃ H ₈	<i>i</i> -C ₄ H ₁₀	<i>n</i> -C ₄ H ₁₀	<i>i</i> -C ₅ H ₁₂	<i>n</i> -C ₅ H ₁₂
415-3	Miocene	137.5-147	n.d. ^a	n.d.	n.d.	n.d.	n.d.	n.d.
415-5	Miocene	273.5-283	100	n.d.	n.d.	n.d.	n.d.	n.d.
415A-5	Paleocene	443-452	100	n.d.	n.d.	n.d.	n.d.	n.d.
415A-6	Paleocene	452-509.5	100	n.d.	n.d.	n.d.	n.d.	n.d.
415A-7	M.-U. Cret.	509.5-519	95.0	5.0	n.d.	n.d.	n.d.	n.d.
415A-8	M.-U. Cret.	519-585.5	87.3	8.0	1.9	1.5	0.9	0.4
415A-9	Cenomanian	642-652	80.5	10.4	3.9	2.3	1.9	1.0
415A-10	Cenomanian	709-718.5	81.8	11.0	3.8	1.7	1.4	0.3
415A-11	Cenomanian	794-804	76.7	11.9	6.3	2.3	1.9	0.9
415A-12	Cenomanian	800-889.5	78.6	11.7	5.2	2.0	1.7	0.8
415A-13	Cenomanian	956-965.5	75.1	12.4	6.8	2.5	2.3	0.9
415A-14	Albian	1032-1041.5	82.2	9.5	4.7	1.6	1.4	0.6

^an.d. = not detected.

TABLE 5
Concentration of C₂ to C₅ Hydrocarbons on the Methane-Free Basis in the Samples of Site 416

Core	Stratigraphy	Sub-Bottom Depth (m)	C ₂ H ₆	C ₃ H ₈	<i>i</i> -C ₄ H ₁₀	<i>n</i> -C ₄ H ₁₀	C ₅ H ₁₂
416A-1	M.-U. Miocene	146-155.5	n.d. ^a	n.d.	n.d.	n.d.	n.d.
416A-2	L. Miocene	298-307.5	n.d.	n.d.	n.d.	n.d.	n.d.
416A-3	U. Oligocene	450-459.5	100	n.d.	n.d.	n.d.	n.d.
416A-5	Alb.-I. Eocene	454-763.5	98.6	1.4	n.d.	n.d.	n.d.
416A-6	L. Aptian	877-896.5	98.9	1.1	n.d.	n.d.	n.d.
416A-7	Hauterivian	991.5-1093	62.8	13.6	13.1 ^b	n.d.	10.5
416A-9	Hauterivian	1176.9-1185.4	n.d.	n.d.	n.d.	n.d.	n.d.
416A-11	Hauterivian	1194.8-1204.3	n.d.	n.d.	n.d.	n.d.	n.d.
416A-12	Hauterivian	1204.3-1213.8	79.5	10.7	4.3	2.9	2.6
416A-13	Hauterivian	1214.8-1224.4	95.0	5.0	n.d.	n.d.	n.d.
416A-14	Valanginian	1223.4-1232.5	94.0	6.0	n.d.	n.d.	n.d.
416A-15	Valanginian	1232.9-1242.5	98.0	2.0	n.d.	n.d.	n.d.
416A-16	Valanginian	1242.5-1252.0	97.0	3.0	n.d.	n.d.	n.d.
416A-17	Valanginian	1252.0-1261.5	89.0	11.0	n.d.	n.d.	n.d.
416A-18	Valanginian	1261.5-1271	89.0	11.0	n.d.	n.d.	n.d.
416A-19	Valanginian	1271-1277.5	84.0	16.0	n.d.	n.d.	n.d.
416A-20	Valanginian	1277.5-1287	78.9	12.3	3.7	3.0	2.1
416A-21	Valanginian	1290-1299.5	64.6	22.3	5.6	3.8	3.7
416A-22	Valanginian	1299.5-1309.1	59.4	21.3	6.2	6.0	7.1
416A-23	Valanginian	1309.1-1318.6	59.3	20.4	6.2	5.6	8.5
416A-24	Valanginian	1318.6-1327.7	59.1	20.8	6.1	5.9	8.1
416A-25	Valanginian	1327.7-1336.7	51.2	21.7	5.4	10.8	10.9
416A-26	Valanginian	1337.2-1346.7	52.1	17.5	6.1	8.8	14.9
416A-28	Valanginian	1356.4-1365.9	47.9	16.6	8.1	8.1	19.3
416A-29	Valanginian	1365.7-1375.2	48.5	26.5	6.6	6.6	11.8
416A-30	Valanginian	1375.2-1384.6	44.6	17.2	7.4	11.8	19.0
416A-31	Valanginian	1384.6-1394.1	n.d.	n.d.	n.d.	n.d.	n.d.
416A-32	Valanginian	1394.1-1403.6	51.1	26.9	2.7	8.6	10.7
416A-34	Valanginian	1406.8-1416.4	47.8	23.9	7.0	8.5	12.8
416A-36	Valanginian	1425.4-1435.0	n.d.	n.d.	n.d.	n.d.	n.d.
416A-40	Valanginian	1454.5-1463.9	44.8	19.9	2.0	9.9	23.4
416A-45	Valanginian	1501.2-1510.6	42.1	33.2	2.1	10.2	12.4
416A-49	Berriasian	1539.1-1548.6	38.5	20.0	26.2 ^b	15.4	15.4
416A-50	Berriasian	1548.6-1558.0	39.6	20.6	7.6	15.8	16.3
416A-51	Berriasian	1558.0-1567.1	47.8	15.3	10.5	8.1	18.2
416A-52	Berriasian	1567.4-1576.8	43.8	27.2	7.4	6.0	15.6
416A-53	Tithonian-Berriasian	1576.8-1586.2	37.3	24.7	6.7	11.3	20.0

^an.d. = not detected.

^bIsobutane + *n*-butane.

of this phenomenon is that at great depths there generally is a more transformed, organic-matter-generated methane which is less enriched in the light isotope. This phenomenon is associated with the nature of the intramolecular distribution of carbon isotopes in biological systems (Galimov, 1973).

At the early stages of organic matter transformation, usually in the top 500 meters of the sedimentary crust, methane is encountered whose isotopic composition is from -80 to -60 per mill. The gases of the brown coal stage are somewhat poor in the light isotope: the $\delta^{13}\text{C}$ of

TABLE 6
Hydrocarbon Ratios for the Gas Samples of Site 415

Core	Stratigraphy	Sub-Bottom Depth (m)	$\frac{C_1}{C_{2+}}$	$\frac{C_2}{C_3}$	$\frac{C_3}{(i+n)C_4}$	$\frac{i-C_4}{n-C_4}$
415-3	Miocene	137.5-147	n.d.	n.d.	n.d.	n.d.
415-5	Miocene	273.5-283	n.d.	n.d.	n.d.	n.d.
415A-5	Paleocene	443-452	3284.0	n.d.	n.d.	n.d.
415A-6	Paleocene	452-509.5	3686.0	n.d.	n.d.	n.d.
415A-7	M.-U. Cret.	509.5-519	1230.0	20.6	n.d.	n.d.
415A-8	M.-U. Cret.	519-585.5	1156.0	10.9	2.4	1.2
415A-9	Cenomanian	642-652	980.0	7.7	1.7	1.7
415A-10	Cenomanian	709-718.5	1135.0	7.4	2.0	2.2
415A-11	Cenomanian	794-804	519.0	6.5	1.4	2.7
415A-12	Cenomanian	880-889.5	632.0	6.7	1.6	2.6
415A-13	Cenomanian	956-965.5	332.0	6.0	1.3	2.7
415A-14	Albian	1032-1041.5	402.0	8.6	1.5	2.9

methane is -60 to -50 per mill. With a still higher degree of organic matter transformation, corresponding to the main stage of oil formation, methane is characterized by $\delta^{13}\text{C}$ values in the range of -50 to -35 per mill. An isotopically heavier methane (-35 to -20 per mill) most frequently is associated genetically with coals of high degrees of metamorphism. In natural conditions, such correlation can be disturbed by the gas-migration processes, as well as by certain peculiarities of the geological history of specific deposits.

All other things being equal, the gas isotopic composition must depend on the extent to which the reservoir rock is capable of retaining gas. In the course of geological time, gas of different generation stages is accumulated successively in the rock. The isotopically lighter methane of the early generation stages is gradually diluted with the isotopically heavier one. For one or more reasons (e.g., diffusion, filtration, break-through along fractures, etc.), the previously generated gas is lost. It is obvious that the rock contains an isotopically heavier methane than would be the case if it retained all the gas formed in the course of the evolution of organic matter.

We believe that these considerations can serve as the basis to explain a sharper change of the gas isotopic

TABLE 7
Individual Hydrocarbon Ratios

Core	Stratigraphy	Sub-Bottom Depth (m)	C_1	C_2	C_3	$i-C_4$
			C_{2+}	C_3	$(i+n)C_4$	$n-C_4$
416A-1	M.-U. Miocene	146-155.5	n.d. ^a	n.d.	n.d.	n.d.
416A-2	L. Miocene	298-307.5	n.d.	n.d.	n.d.	n.d.
416A-3	U. Oligocene	450-459.5	6300.0	n.d.	n.d.	n.d.
416A-5	Alb.-l. Eocene	754-763.5	3100.0	70	n.d.	n.d.
416A-6	L. Aptian	887-896.5	4660.0	93	n.d.	n.d.
416A-7	Hauterivian	991.5-1093	2080.0	4.6	1.0	1.6
416A-9	Hauterivian	1176.9-1185.4	700.0	n.d.	n.d.	n.d.
416A-11	Hauterivian	1194.8-1204.3	120.0	n.d.	n.d.	n.d.
416A-12	Hauterivian	1204.3-1213.8	122.0	7.4	1.5	1.5
416A-13	Hauterivian	1213.8-1222.4	200.0	19.0	n.d.	n.d.
416A-14	Valanginian	1223.9-1232.9	151.0	16.6	n.d.	n.d.
416A-15	Valanginian	1232.9-1242.5	300.0	45.0	n.d.	n.d.
416A-16	Valanginian	1242.5-1252.0	348.0	35.0	n.d.	n.d.
416A-17	Valanginian	1252.0-1261.5	160.0	8.3	n.d.	n.d.
416A-18	Valanginian	1261.5-1271.0	330.0	8.0	n.d.	n.d.
416A-19	Valanginian	1271.0-1277.5	236.0	5.3	n.d.	n.d.
416A-20	Valanginian	1277.5-1287.0	263.0	6.4	1.8	1.2
416A-21	Valanginian	1290.0-1299.5	86.0	2.9	0.7	1.0
416A-22	Valanginian	1299.5-1309.1	150.0	2.8	1.7	1.0
416A-23	Valanginian	1309.1-1318.6	149.0	2.9	1.7	1.1
416A-24	Valanginian	1318.6-1327.7	122.0	2.8	1.7	1.0
416A-25	Valanginian	1327.7-1336.7	122.0	2.4	1.3	0.5
416A-26	Valanginian	1337.2-1346.7	157.0	3.0	1.2	0.7
416A-28	Valanginian	1356.4-1365.9	147.0	2.9	1.0	1.0
416A-29	Valanginian	1365.7-1375.2	59.0	1.8	2.0	1.0
416A-30	Valanginian	1375.2-1384.6	69.0	2.6	0.9	0.6
416A-31	Valanginian	1384.6-1394.1	130.0	2.5	n.d.	n.d.
416A-32	Valanginian	1394.1-1403.6	81.0	1.9	2.4	0.3
416A-34	Valanginian	1406.8-1416.4	120.0	2.0	1.5	0.8
416A-36	Valanginian	1425.4-1435.0	160.0	1.8	n.d.	n.d.
416A-40	Valanginian	1454.5-1463.9	100.0	2.2	1.7	0.2
416A-45	Valanginian	1501.2-1510.6	4.0	1.3	2.7	0.2
416A-49	Berriasian	1539.1-1548.6	253.0	1.9	0.8	n.d.
416A-50	Berriasian	1548.6-1558.0	195.0	1.9	0.9	0.5
416A-51	Berriasian	1558.6-1567.4	248.0	3.1	0.8	1.3
416A-52	Berriasian	1567.4-1576.8	240.0	1.6	2.0	1.3
416A-53	Tithonian-Berrias	1576.8-1586.2	133.0	1.5	1.4	0.6

^an.d. = not detected.

TABLE 8
Carbon Isotope Composition of Methane
From the Gas Samples of Site 415

Core	Sub-Bottom Depth (m)	Stratigraphy	$\delta^{13}C$ (‰)
415-5	273.5-283	Miocene	-71.08
415A-6	452-509.6	Paleocene	-70.64
415A-8	519-585.5	M.-U. Cret.	-69.97
415A-9	642-652	Cenomanian	-68.81
415A-10	709-718.5	Cenomanian	-65.60 ^a
415A-12	880-889.5	Cenomanian	-62.89 ^a
415A-13	956-965.5	Cenomanian	-62.57 ^a
415A-14	1032-1041.5	Albian	-61.39 ^a

Note: All samples taken immediately after recovery.

^aMean Value for two different sections of a core.

composition with depth throughout Hole 416A as compared with Hole 415A. In the Cretaceous deposits of Hole 416A, a considerable portion of earlier-generation gas probably has been lost. This is also confirmed by the very low overall gas concentration in these deposits.

It should be said that, for all the sections of oceanic deposits, in which up to now the isotopic composition of methane has been studied, great enrichment in the light carbon isotope was observed. The only exceptions were the profiles of Site 83 (Leg 10) and Site 176 (Leg 18), where at depths of less than 100 meters a gas was encountered whose isotopic composition is about -50

TABLE 9
Carbon-Isotope Composition of Methane
From Gas Samples of Site 416

Core	Sub-Bottom Depth (m)	Stratigraphy	$\delta^{13}C$ (‰)
416A-3	450-459.5	U. Oligocene	-82.06
416A-5	454-763.5	Alb.-l. Eocene	-73.81
416A-6	887-896.5	L. Aptian	-71.56
416A-7	991.5-1093	Hauterivian	-61.90
416A-15	1232.9-1242.5	Valanginian	-57.29
416A-22+23	1299.5-1309.1	Valanginian	-49.18

Note: All samples taken after standing more than 2 hours at room temperature.

TABLE 10
Variations of $\delta^{13}C$ of Methane Depending on
Conditions of Sampling

Core	Section	Sampled Immediately After Recovery	Sampled After Standing 2 to 4 hr in the Closed Core Barrel Section
415-5		-71.08	-70.80
415-11	1	-66.52	-
	2	-64.66	-
415-13	1	-62.25	-61.12
	2	-62.90	-
415-14	1	-61.48	-60.97
	2	-61.30	-

per mill (Claypool et al., 1973). This gas is almost certainly of migratory origin. In most cases, methane had an isotopic composition of -80 to -60 per mill. The deposits of the top 1000 meters of Holes 415A and 416A contained methane with isotopic composition from -80 to -60 per mill. By way of comparison, in the upper-zone deposits of the continental sedimentary profiles, methane is somewhat less rich in the light isotope. It is also characteristic that the variation of its isotopic composition with depth manifests itself much more clearly in continental profiles. In connection with the reasoning presented here, such a difference in the distribution of methane isotopic composition over the profile of oceanic and of continental sedimentary deposits can be attributed to two causes: (1) the variation of degree of organic-matter transformation with depth in oceanic deposits is, on the average, smaller than in the deposits of a continental profile; (2) oceanic deposits, on the average, retain the gas generated by them better than the deposits of a continental profile.

Both causes are plausible. The first one is probable because organic-matter transformation in poorly consolidated sediments of the upper portion of the oceanic sedimentary profile actually occurs at a comparatively slower rate (see Galimov et al., this volume). The second cause seems probable due to the possibility of gas hydrates being formed. A combination of low temperatures and high pressures in the upper zone of the oceanic sedimentary profile makes it thermodynamically admissible that a deep gas-hydrate zone should be formed in

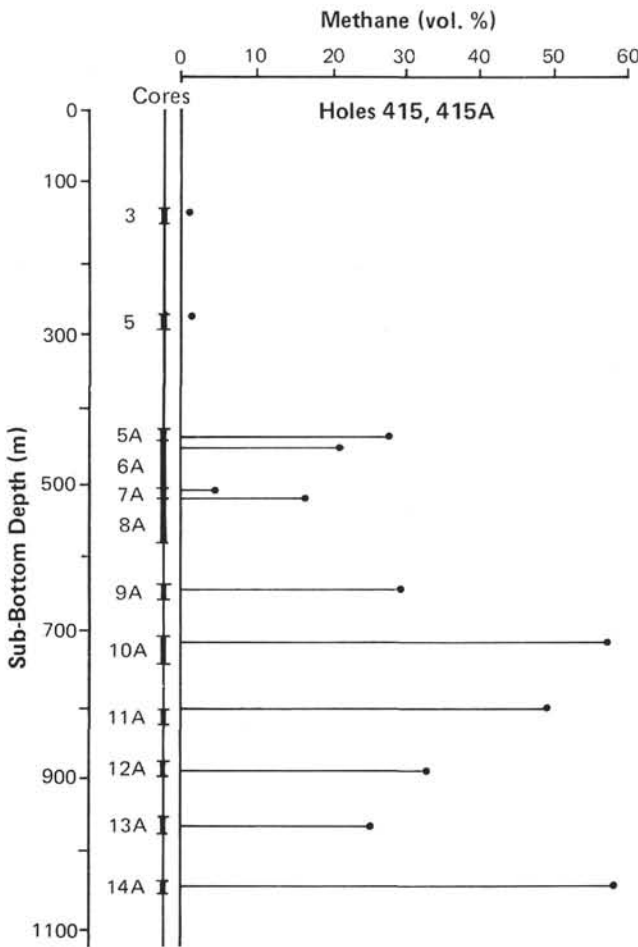


Figure 1. Methane content in gas samples, Holes 415 and 415A.

many areas of the ocean. With ocean depths of more than 2500 meters, the thickness of the gas-hydrate zone can reach 500 meters. The mobility of gas in the hydrate state is incomparably lower than in the free state.

Finally, the presence of methane, comparatively poor in the light isotope, at depths of about 1300 meters agrees with the data on the chemical composition of gas at these depths. The scarcity of the light isotope in methane, as well as the appearance in C₂ to C₅ hydrocarbons of heavy components in appreciable concentrations, indicate that these depths correspond to the uppermost boundary of the zone where the petroleum-formation process develops.

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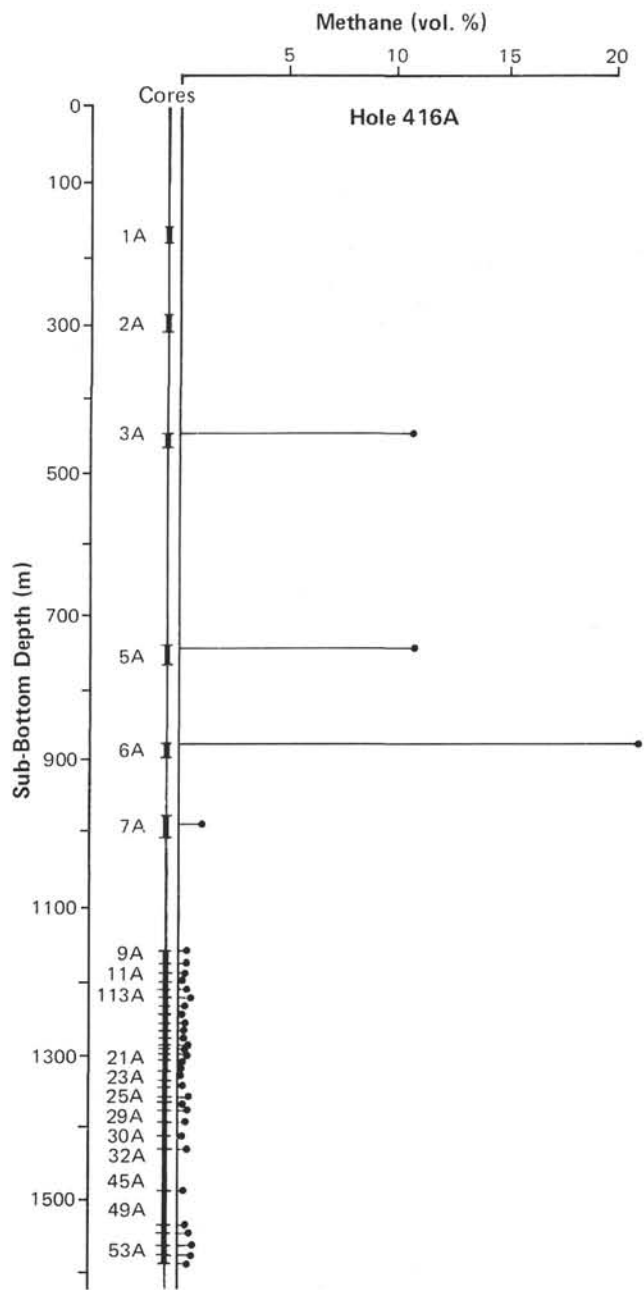


Figure 2. Methane content in gas samples, Hole 416A.

Reports of the Deep Sea Drilling Project, v. 19: Washington (U.S. Government Printing Office), p. 879-885.
 Galimov, E. M., 1969. The Isotopenzusammensetzung des Kohlenstoffs in den Gasen der Erdkruste. *Zeitschrift für angewandte Geologie*, B. 15, v. 2, p. 63-69.
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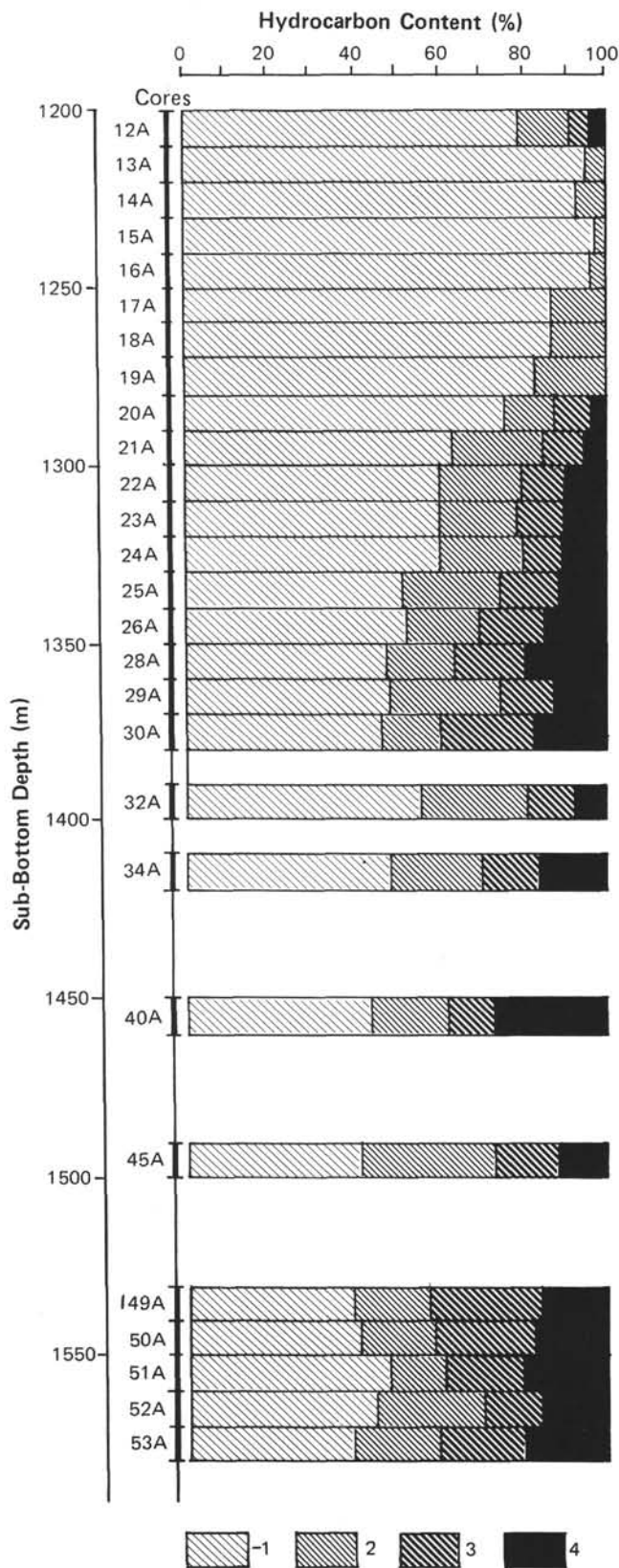


Figure 3. Percentage of the C_2 to C_5 hydrocarbons on methane-free basis, Hole 416A. 1 = C_2H_6 ; 2 = C_3H_8 ; 3 = C_4H_{10} ; 4 = C_5H_{12} .

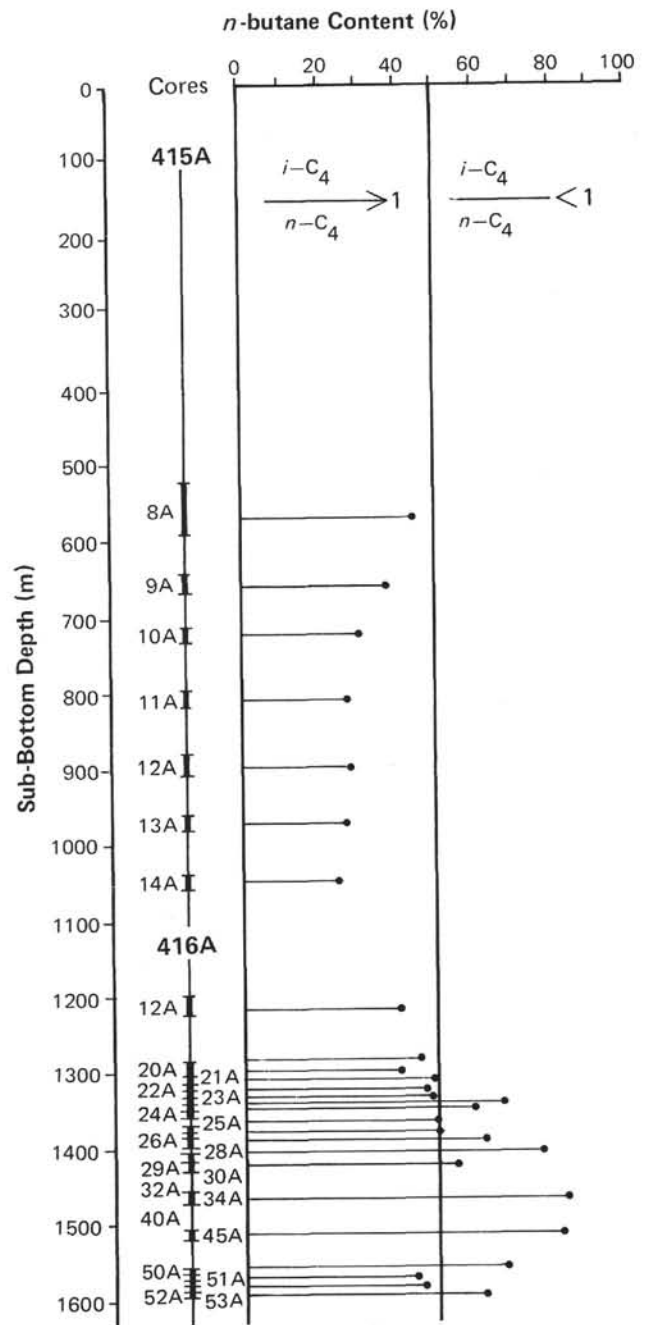


Figure 4. Percentage of n -butane relative to the sum of butane isomers, Holes 415A and 416A.

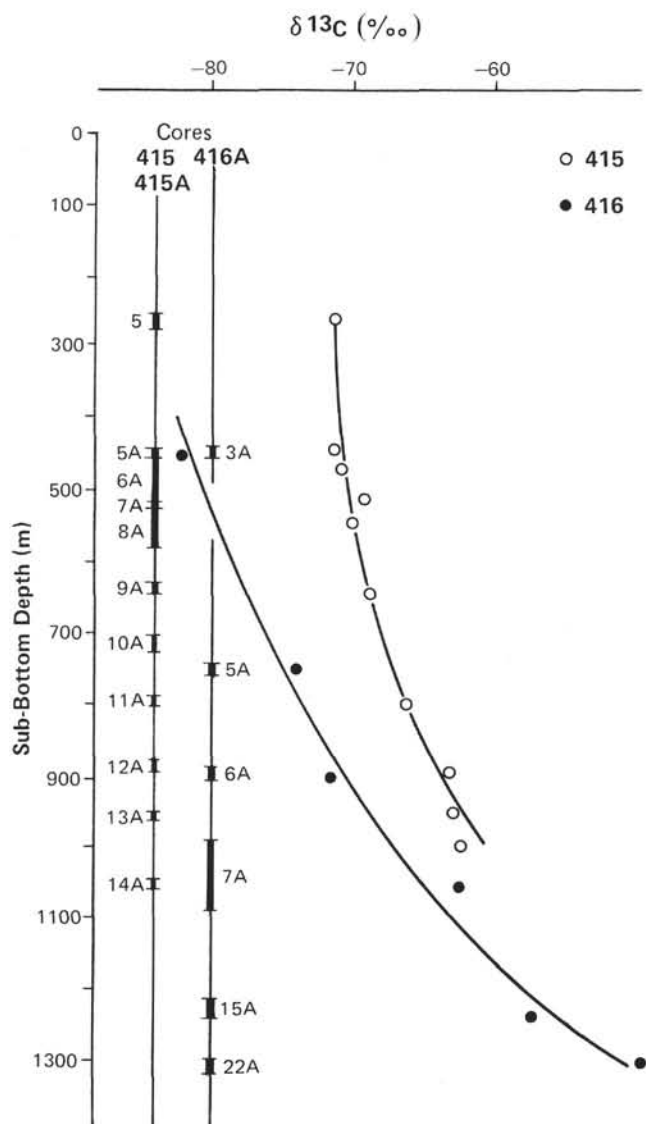


Figure 5. Variations in carbon isotopic composition of methane with depth, Holes 415A and 416A.