

10. CONCENTRATIONS AND CARBON ISOTOPIC COMPOSITIONS OF CH₄ AND CO₂ IN GAS FROM SEDIMENTS OF THE BLAKE OUTER RIDGE, DEEP SEA DRILLING PROJECT LEG 76¹

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ABSTRACT

The principal gaseous carbon-containing components identified in the first 400 m of sediment at Deep Sea Drilling Project Site 533, Leg 76, are methane (CH₄) and carbon dioxide (CO₂). Below a sub-bottom depth of about 25 m, sediment cores commonly contained pockets caused by the expansion of gas upon core recovery. The carbon isotopic composition ($\delta^{13}\text{C}$ ‰ relative to PDB standard) of CH₄ and CO₂ in these gas pockets has been measured, resulting in the following observations: (1) $\delta^{13}\text{C}_{\text{CH}_4}$ values increase with depth from approximately -94‰ in the uppermost sediment to about -66‰ in the deepest sediment, reflecting a systematic but nonlinear depletion of ¹²C with depth. (2) $\delta^{13}\text{C}_{\text{CO}_2}$ values also increase with depth of sediment from about -25‰ to about -4‰, showing a depletion of ¹²C that closely parallels the trend of the isotopic composition of CH₄. The magnitude and parallel distribution of $\delta^{13}\text{C}$ values for both CH₄ and CO₂ are consistent with the concept that the formation of the CH₄ resulted from the microbiological reduction of CO₂ from organic substances. These results imply that CH₄ and CO₂ incorporated in gas hydrates at this site are biogenic.

INTRODUCTION

The Blake Outer Ridge is a large bathymetric feature rising up to 1500 m above the abyssal plain of the Atlantic Ocean as a submarine, spitlike extension of the continental rise offshore the southeastern United States (Fig. 1). The Ridge probably formed in the late Cenozoic through accretion of hemipelagic mud deposited by contour-following currents (Heezen et al., 1966). Seismic reflection profiling over the Ridge has shown an anomalous acoustic reflector that subparallels the seafloor at a sub-bottom depth of about 600 m (Markl et al., 1970; Tucholke et al., 1977; Shipley et al., 1979). This bottom-simulating reflector (BSR) has been observed in seismic profiles over an area of about 80,000 km² of the Blake Outer Ridge, as shown in Figure 1 (Dillon et al., 1980). One explanation for the anomalous acoustic reflector is that it corresponds to the base of a zone containing gas hydrate and represents the boundary between sediment containing gas hydrate and sediment lacking gas hydrate (Ewing and Hollister, 1972; Tucholke et al., 1977; Shipley et al., 1979).

More than 10 yr. ago, DSDP Leg 11 cored sediment samples from the Ridge in order to investigate the nature of the anomalous acoustic reflector (Ewing and Hollister, 1972). Sediment samples recovered at Sites 102, 103, and 104 (Fig. 1) across the Ridge yielded high concentrations of gas (Lancelot and Ewing, 1972). The dominant component in the gas was CH₄, and the balance was mainly CO₂ (Claypool et al., 1973). Although no obvious gas hydrates were recovered at these sites, the high gas concentrations and the anomalous acoustic

reflector were cited as evidence of the presence of gas hydrates (Ewing and Hollister, 1972; Lancelot and Ewing, 1972).

Site 533 of DSDP Leg 76 was selected to attempt to document geochemically the postulated presence of gas hydrates in sediment of the Blake Outer Ridge. Part of the geochemical program included a detailed examination of the gases recovered from cored sediments. As in the case of the results from Leg 11, the main carbon-containing gases in sediments from Site 533 are CH₄ and CO₂, and this report focuses on the concentrations and carbon isotopic compositions of these gases and the significance of these compositions relative to the processes involved in the origin of these gases.

METHODS

Gases were recovered directly from separations in the sediment that developed as gases expanded while the sediment was confined in the core liner. These gas pockets were sampled by means of a hollow punch equipped with a valve to prevent the immediate release of gas. After the punch penetrated the core liner, gas was vented through the valve into 20-ml evacuated containers, henceforth called vacutainers. The vacutainers are under partial vacuum with a residual background of air that affects the volumetric measurements of gases from the sediment. Gas was collected in three sets of vacutainers for use as follows: (1) shipboard chemical analyses, (2) shore-based analyses, and (3) carbon isotopic measurements.

CH₄ and CO₂ were measured aboard ship on a Carle Model 800 gas chromatograph (thermal conductivity detector) utilizing a 1/8 in. × 5 ft. column, packed with 8% carbowax 1540 on 90-100 mesh Anachrom ABS, operated isothermally at 40°C. A sample size of 250 µl of gas was removed from each vacutainer for analysis. Areas of peaks on chromatograms were measured by a CSI Model 38 integrator, and from these areas concentrations were calculated.

To determine carbon isotopic compositions, CH₄ and CO₂ were removed from the vacutainers, and these gases were separated by binding CO₂ with barium hydroxide in a vacuum chamber. CH₄ was combusted in pure oxygen to CO₂. The $\delta^{13}\text{C}$ of the CO₂ released from the barium hydroxide and the $\delta^{13}\text{C}$ of the CO₂ formed from CH₄ were determined separately on a Varian MAT 230 mass spectrometer with

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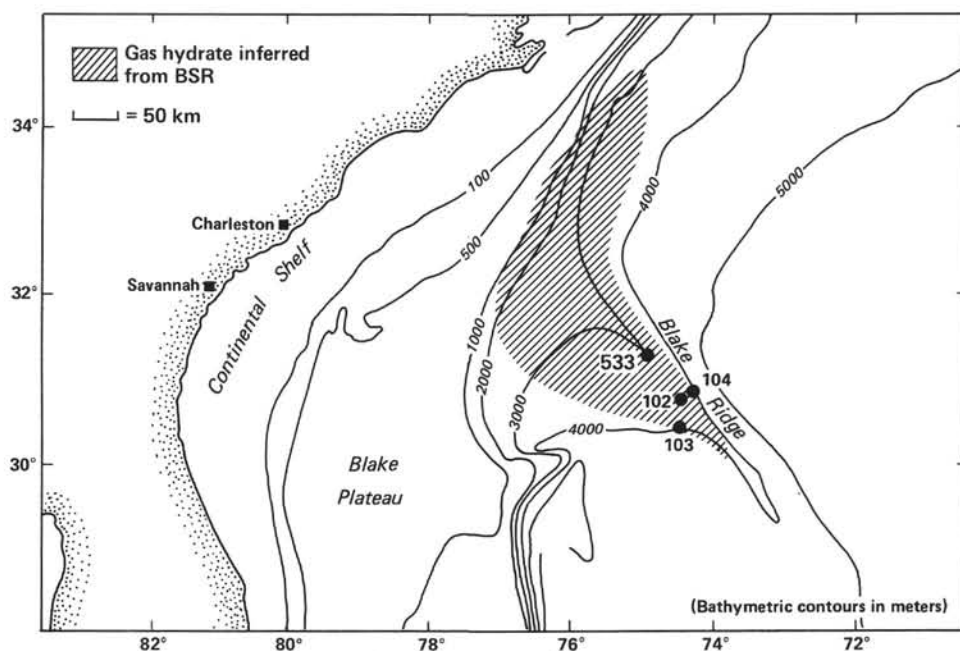


Figure 1. Map showing locations of Site 533, Leg 76, and Sites 102, 103, and 104, Leg 11. (Pattern shows the extent of the anomalous bottom-simulating reflector [BSR] possibly marking the base of gas hydrate [Dillon et al., 1980].)

an accuracy of $\pm 0.1\%$. Values of $\delta^{13}\text{C}$ in parts per thousand (‰) are referenced to the PDB standard. Details of the method have been described previously [Galimov and Simoneit, 1982].

RESULTS

Two holes were drilled at Site 533. The first (Hole 533) was continuously cored with an hydraulic piston core from the surface to a sub-bottom depth of 168 m. A second hole (Hole 533A) at this site was rotary cored from 57 m with continuous core recovery from 143 to 399 m sub-bottom. The cores of near-surface samples (0–25 m) did not contain sufficient gas to produce gas pockets in the core liners; therefore recovery of gas by vacutainers was not possible for this sediment interval. Gas pockets occurred sporadically in cores from 25 to 50 m sub-bottom. Most of the cores from depths between 50 and 399 m contained gas pockets from which samples could be removed for analysis.

Table 1 shows the shipboard measurements of the concentrations of CH_4 and CO_2 in the gas mixture of the vacutainers used to collect gas released from the sediment. The total concentrations of these gases range from 4.2 to 99.2%. Besides less than 1% hydrocarbons heavier than CH_4 , the balance of most of the gas in the vacutainers is likely air. This air results from the residual background gas in the vacutainers before their use, air that enters the core liners during sampling, and air that is incorporated during analysis. Sampling and analysis were done as systematically as possible to minimize introduction of air and to provide comparative results. Therefore the concentration of CH_4 and CO_2 are semi-quantitative and relative, but the overall trends in concentrations with depth are likely real. CH_4 concentra-

tions range from 4 to 98%, and below 50 m CH_4 concentrations were all greater than 47% with three exceptions. In general, the concentrations of recovered CH_4 tend to decrease slightly with depth below 50 m. CO_2 is much less abundant than CH_4 , and concentrations of CO_2 range from 0.2 to 10%. Below 50 m depth, CO_2 concentrations exceed 1%, with four exceptions, and tend to increase with depth.

Table 1 also shows the shore-based laboratory measurements of carbon isotopic compositions of CH_4 and CO_2 from all sediment intervals where samples could be collected by vacutainers. The $\delta^{13}\text{C}_{\text{CH}_4}$ values are not significantly affected by the air incorporated during sampling because the amount of CH_4 in air is too small. However, the $\delta^{13}\text{C}_{\text{CO}_2}$ values may be affected by the 0.03% CO_2 in air for those samples at depths less than 60 m where air possibly constitutes more than about 90% of the gas mixture. In fact, as much as 10 to 15% of the CO_2 in these samples may be atmospheric with a $\delta^{13}\text{C}_{\text{CO}_2}$ value of about -7% . Thus the isotopic values recorded in Table 1 for these samples are probably too heavy. For example, the carbon isotopic composition of CO_2 in the topmost sediment may actually be 2 or 3‰ lighter than the -24.50% measured. $\delta^{13}\text{C}_{\text{CH}_4}$ values increase from about -94% at 25 m to about -66% at 394 m. The values decrease systematically but nonlinearly to a depth of about 250 m; below this depth the $\delta^{13}\text{C}_{\text{CH}_4}$ values average about -66% (Fig. 2). $\delta^{13}\text{C}_{\text{CO}_2}$ values also increase with depth following a trend that closely parallels the trend of $\delta^{13}\text{C}_{\text{CH}_4}$ values (Fig. 2). The carbon isotopic composition of CO_2 is heavier than CH_4 and ranges from about -25% to about -4% . The differences in $\delta^{13}\text{C}$ values of CH_4 and CO_2 in a given sam-

Table 1. Concentrations and carbon isotopic compositions of CH₄ and CO₂, Blake Outer Ridge, Site 533.

Hole-core section	Sub-bottom depth (m)	CH ₄		CO ₂	
		% (vol.)	δ ¹³ C (‰)	% (vol.)	δ ¹³ C (‰)
533-9-1	24.9-26.4	4	-93.8	0.2	-24.5
533-9-2	26.4-27.9	10	-89.3	0.6	—
533-11-1	33.9-35.4	7	-91.3	0.3	-23.4
533-15-2	53.0-54.5	80	-84.0	1.8	-17.4
533-16-3	58.0-59.5	5	-81.6	0.3	-14.5
533-17-2	61.0-62.5	78	-81.3	1.7	—
533A-1-6	64.5-66.0	56	-80.6	1.8	-12.7
533-20-1	73.0-74.5	81	-79.7	1.5	-12.7
533-21-1	77.5-79.0	80	-79.2	1.9	-11.3
533-22-1	82.0-83.5	90	-78.9	2.1	—
533-23-2	88.0-89.5	89	-78.1	1.1	-13.8
533-24-2	92.5-94.0	72	-76.5	1.3	—
533-25-2	97.0-98.5	72	-76.7	1.3	-10.3
533-26-1	100.0-101.5	76	-76.7	1.5	-10.1
533-27-2	106.0-107.5	60	-75.4	1.4	-9.6
533-28-3	112.0-113.5	79	-75.0	1.3	-9.5
533-29-1	113.5-115.0	47	-75.1	0.9	-7.8
533-30-2	119.5-121.0	66	-74.9	1.4	-7.6
533-31-2	124.0-125.5	98	—	1.2	-7.6
533-32-1	127.0-128.5	65	-73.0	1.5	-7.2
533-33-1	131.5-133.0	84	-72.3	2.5	-5.8
533-34-1	136.0-137.5	69	-72.1	2.4	-4.0
533-37-1	146.5-148.0	83	-71.8	2.2	-6.4
533-38-2	151.0-152.5	95	-71.5	1.9	-5.9
533A-3-2	153.5-154.0?	78	-71.2	4.5	-3.2
533A-3-3	154.0?-154.5	63	-70.1	2.5	-4.6
533A-4-3	157.5-159.0	62	-71.2	2.7	—
533-40-2	160.0-161.5	80	-69.9	4.4	-3.6
533-41-2	164.5-166.0	85	-69.9	3.5	-5.1
533A-5-6	169.0-170.5	67	-70.1	1.8	-7.7
533A-6-1	171.0-172.5	7	—	0.5	—
533A-11-4	223.0-224.5	70	-67.4	4.7	-4.4
533A-13-1	237.5-239.0	63	-68.6	1.7	-6.9
533A-15-2	258.0-259.5	74	-66.6	3.8	-4.6
533A-16-6	273.5-275.0	71	-66.5	5.8	-1.8
533A-17-5	281.5-283.0	77	-65.4	9.3	-2.4
533A-18-4	289.5-291.0	82	-66.7	7.8	—
533A-19-7	303.5-304.0	84	-66.9	4.3	-4.2
533A-20-6	312.0-313.5	76	-67.3	5.2	-6.2
533A-21-6	321.0-322.5	81	-66.6	9.4	-3.9
533A-22-4	327.5-329.0	4	-66.7	0.5	—
533A-22-6	330.5-332.5	48	-66.5	4.6	-5.0
533A-24-5	347.0-348.5	70	-66.6	6.4	-4.7
533A-25-2	353.0-354.5	69	-66.7	6.2	-6.2
533A-26-4	365.5-367.0	54	-65.8	6.2	-5.0
533A-27-6	378.0-379.5	69	-66.1	5.6	-6.4
533A-29-1	392.5-394.0	71	-65.9	10.0	-3.5

Note: — indicates data not available.

ple gradually decrease from approximately 68‰ in the shallower sediments to approximately 61‰ in the deeper sediments.

DISCUSSION

Site 533 provided a good opportunity to collect information relevant to the possible occurrence of gas hydrates in sediments of the Blake Outer Ridge. The site was located in 3184 m of water near the crest of the Ridge about 50 km northwest of Sites 102, 103, and 104 (Fig. 1), where high amounts of CH₄ in sediments had previously been found (Ewing and Hollister, 1972; Lancelot and Ewing, 1972). Seismic reflection profiles crossing

Site 533 clearly showed the anomalous acoustic reflector at a depth of about 600 m. Downhole temperature measurements showed a maximum temperature of 19°C at 399 m, and the geothermal gradient toward the bottom of the hole was determined to be about 36°C/km (Sheridan, Gradstein, et al., this volume). Thus pressure and temperature conditions at this site fall within the stability field for CH₄ gas hydrates (Katz et al., 1959), and the acoustic anomaly supports the assumed presence of gas hydrates.

Finding high concentrations of CH₄ in sediments at Site 533 therefore came as no surprise. Finding unequivocal evidence of gas hydrates was more difficult. In fact, only one small (~25 cm³) sample of demonstrable gas-hydrate-containing sediment was recovered at a sub-bottom depth of 238 m, although disrupted sediment was observed in the interval from 152 to 240 m, suggesting the possible presence of gas hydrates that had decomposed during core recovery (Kvenvolden and Barnard, this volume). Gas hydrates at this site apparently are distributed unevenly and are finely dispersed throughout the sediment. The CH₄ and CO₂ observed in sediments here may be related to gas hydrates, but the exact relationships are not known.

The very light δ¹³C values for CH₄ (as light as about -94‰) in the shallow sediments are typical of CH₄ generated by microbiological processes (Rosenfeld and Silverman, 1959). Likewise, the very light δ¹³C values for CO₂ in the shallow sediments (at least as light as about -25‰) suggest that the CO₂ came from organic substances that at Site 533 have carbon isotopic compositions ranging from -21 to -25‰ (Brooks et al., this volume). The closely parallel distribution of δ¹³C values for CH₄ and CO₂ with depth at Site 533 (Fig. 2) agrees with the concept of Claypool and Kaplan (1974) that CH₄ can form in anoxic sediments from the microbiological reduction of CO₂ in the following manner: CO₂, initially generated during the process of sulfate reduction at the expense of organic substances, has accumulated and becomes available for CH₄ generation after sulfate is depleted. The CO₂ should have, at this stage, a carbon isotopic composition close to that of the organic substances from which it was derived, that is, -20 to -25‰. CH₄ generation from CO₂ involves a large carbon isotopic fractionation resulting initially in CH₄ enriched in ¹²C by as much as 60 to 70‰ relative to CO₂. As the process of CH₄ formation continues, CO₂ is gradually depleted in ¹²C and, accordingly, CH₄ is also depleted in ¹²C, with the carbon isotopic compositions of both CH₄ and CO₂ in isotopic balance.

This process, if operating alone, would lead to a decrease in concentrations of CO₂ relative to CH₄ as the CO₂ becomes enriched in ¹³C. Contrary to this prediction, CO₂ in sediments at Site 533 becomes enriched in ¹³C as the concentrations of CO₂, relative to CH₄, increase with depth (Table 1). In addition, the apparent asymptotic approach of δ¹³C_{CH₄} and δ¹³C_{CO₂} to values of about -66 and -4‰, respectively, with depth (Fig. 2), would not be expected, but rather the rate of change of δ¹³C_{CH₄} and δ¹³C_{CO₂} would increase rather than decrease with depth if CO₂ were simply converting to CH₄.

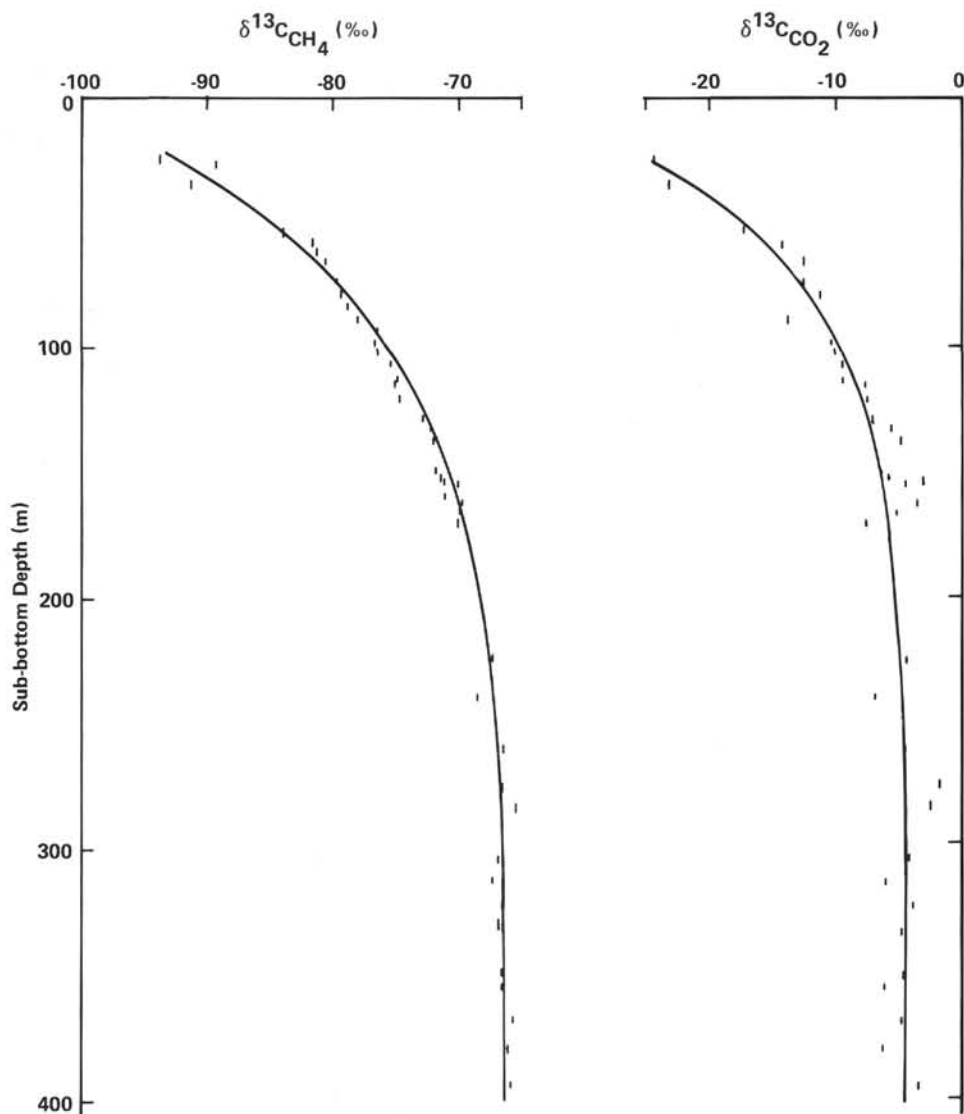


Figure 2. Variations with depth in the carbon isotopic compositions of CH_4 and CO_2 from Site 533 sediments.

Therefore, the process must be more complex than described and must, at a minimum, involve additional CO_2 generation during CH_4 formation.

The difference between the $\delta^{13}\text{C}$ values for CH_4 and CO_2 in sediments at a given depth in the shallow sediments at Site 533 is about 68‰. This difference decreases with depth to about 61‰. This decrease of 7‰ may be a manifestation of the temperature dependence of the isotopic effect.

If CH_4 and CO_2 at Site 533 are included in gas hydrates, their carbon isotopic compositions should not be directly influenced as a result of their hydrated state. However, CH_4 and CO_2 in gas hydrates have less opportunity to escape because they are held in a water clathrate. Accumulated CH_4 represents a product from different stages in the process of CH_4 formation. The earliest stages are characterized by isotopically light CH_4 , and in later stages the CH_4 becomes isotopically heavier. Therefore, CH_4 in zones of gas hydrate may be slight-

ly enriched in ^{12}C compared to CH_4 found in shallow-water sedimentary situations without gas hydrates, because the escape of isotopically light CH_4 from the gas hydrate has been inhibited.

The rather light $\delta^{13}\text{C}$ values of CH_4 recorded in the shallow sediments at Site 533 (as light as -94‰) may be the result of a combination of circumstances. First, the isotopically light CO_2 (as light as -25‰) formed in the process of sulfate reduction participated in the earliest stages of the formation of the isotopically light CH_4 , most or all of which was held in the sediment. Second, recycled CO_2 derived from the oxidation of CH_4 in the shallowest sediments could serve as the source for additional isotopically light CH_4 . Third, the low temperatures dominating the upper layers of these deep-water oceanic sediments have specified the maximum value of the isotopic effects accompanying CH_4 formation. Finally, the presence of gas hydrates may have inhibited the escape of CH_4 , leading to some enrichment in ^{12}C .

Neither the concentrations nor the carbon isotopic compositions of CH_4 and CO_2 reported here specifically indicate that gas hydrates are present at Site 533. But our results do show that if CH_4 gas hydrates are dispersed in the first 400 m of sediment of the Blake Outer Ridge, the source of CH_4 is probably CO_2 and the process of CH_4 formation is microbiologically controlled.

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