# 16. LIGHT HYDROCARBONS IN SEDIMENTS OF THE SULU SEA BASIN (SITE 768): GENETIC CHARACTERIZATION BY MOLECULAR AND STABLE ISOTOPE COMPOSITION<sup>1</sup>

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#### ABSTRACT

Geochemical investigations on gases and interstitial waters from ODP Site 768 (Sulu Trench/Philippines) demonstrate the application of molecular gas composition in combination with stable isotope analyses to the genetic classification of light hydrocarbons.  $^{13}C/^{12}C$  and D/H ratios of methane from gas pockets in cores and gases desorbed from frozen sediments by a vacuum/acid treatment suggest a microbial generation of methane by a CO<sub>2</sub> reducing process in sediments with low sulfate concentrations. Isotope data and molecular composition of sediment gases liberated by the vacuum/acid treatment seem to be affected by a secondary desorption process during sampling. A comparison between the D/H ratios of methane from gas pockets and interstitial H<sub>2</sub>O points to an in-situ generation of methane down to a sub-bottom depth of approx. 720 m. Below this depth hydrogen isotope data indicate a migration of light hydrocarbons into pyroclastic sediments at this site. The occurrence of higher hydrocarbons (propane to pentane) in gases from gas pockets coincides with the vertical distribution of mature organic matter. Gases within the zone of mature organic matter are gases of a mixed microbial and thermal origin.

### INTRODUCTION

During ODP Leg 124, where an objective was to determine the ages of the Celebes and Sulu Seas, a total of five sites was drilled in Philippine waters. Organic geochemical investigations on board the ODP drill ship were carried out with the purpose of safety monitoring (Rangin, Silver, von Breymann, et al., 1990). Shore-based studies on gases from Site 768 demonstrate the genetic characterization of light hydrocarbons by analyses of molecular compositions of gases in combination with stable isotope ratios. These investigations continue the work by Whiticar et al. (1986) and authors cited therein.

#### METHODS

Gases from visual gas pockets of the sediment cores of Site 768 were expanded into vacutainers on board JOIDES Resolution before cutting the liners. In addition, gases of selected frozen (at -20°C) sediments from Site 768 were desorbed in the Bundesanstalt für Geowissenschaften und Rohstoffe (BGR) laboratory by a vacuum/acid treatment described by Faber and Stahl (1983). This vacuum/acid procedure liberates a combination of free and adsorbed gases from the sediments. These gases are referred to as "total" gases. A total of 46 gas samples was analyzed for their molecular composition, their carbon, and depending on the amount, for their hydrogen isotope ratios at the BGR laboratory.

The molecular composition of hydrocarbon gases was determined by standard Flame Ionization Detector (FID) analyses utilizing a Siemens Sichromat 2 gas chromatograph provided with a capillary pre-column (50 m) and a Al<sub>2</sub>O<sub>3</sub>-filled capillary main-column (50 m). Nitrogen was used as a carrier gas at a flow rate of 2.93 mL/min. The chromatographic separation was carried out isothermally at 90°C.

For the isotope analyses the individual gas components were separated chromatographically and subsequently combusted to CO<sub>2</sub> and H<sub>2</sub>O using a preparation line described by

Dumke et al. (1989). The combustion product H<sub>2</sub>O is reduced to H<sub>2</sub>O by reaction with zinc in sealed glass tubes at 450°C.

Interstitial fluids of Site 768 were collected using pressure filtration of the sediments (see Rangin, Silver, von Breymann, et al., 1990). The D/H ratio of the interstitial water was determined on H2 generated following the in-vitro reduction of H<sub>2</sub>O on zinc (Dumke et al., 1989).

The stable isotope measurements on CO<sub>2</sub> from combustion of hydrocarbons were carried out using a Finnigan MAT 250 mass spectrometer. For the D/H analyses a Finnigan Delta mass spectrometer was used. Isotope ratios are reported in the usual  $\delta$ -notation relative to the PDB (Pee Dee Belemnite) standard for carbon and SMOW (Standard Mean Ocean Water) standard for hydrogen:

$$dR = [[(R_a/R_b)_{\text{sample}}/(R_a/R_b)_{\text{standard}}] - 1] \cdot 1000$$
(1)

where  $R_a/R_b$  is <sup>13</sup>C/<sup>12</sup>C and D/H, respectively.

# **RESULTS AND DISCUSSION**

#### **Analyses on Gas Pockets**

The hydrogen and carbon isotope ratios of methane from gas pockets of Site 768 collected below the sulfate reduction zone (Rangin, Silver, von Breymann et al., 1990) indicate a bacterial methane generation (Fig. 1, Table 1) through CO<sub>2</sub> reduction (Whiticar et al., 1986). The bacterial origin of methane is also confirmed by the combination of gas ratios of methane over the sum of ethane and propane and carbon isotope data of methane (Fig. 2, Table 1). Methane is the dominant component in all gas pockets, but hydrocarbons ethane to pentane are observed also.

The isotope profile of methane at Site 768 shows a steady decrease of the <sup>13</sup>C isotope with depth (Fig. 3, Table 1). This trend with depth is opposite to that which would result from the fractionation depletion model of Claypool and Kaplan (1974). In this model there is an increase of the <sup>13</sup>C isotope in bacterial methane with increasing depth, due to a depletion of the <sup>12</sup>C isotope in the substrate CO<sub>2</sub> that is preferentially consumed by bacteria during methanogenesis. The vertical variation of carbon isotope ratios of methane at Site 768 there-

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Figure 1. Hydrogen and carbon isotope ratios of methanes from gas pockets indicate a bacterial methane generation through  $CO_2$  reduction (diagram modified after Whiticar et al., 1986).



Figure 2. Carbon isotope ratios of methane and molecular ratios indicate a bacterial origin of methane from gas pockets (diagram modified after Bernard, 1979).

fore cannot be explained by such a model. We either have to assume that if the methane isotope values reflect the primary isotope ratios of the substrate  $CO_2$ , which would be the case if the methane was generated *in situ*, this substrate has been affected by a mechanism other than <sup>12</sup>C depletion through bacterial activity or that the methane was not generated "in place." As there is not sufficient data on the dissolved  $CO_2$  of pore waters in this depth range, because only small quantities of water could be obtained, we cannot solve the problem by comparing methane and  $CO_2$  carbon isotope data.

In addition to a bacterial generation of methane, thermogenic hydrocarbon generation is detected at a sub-bottom depth greater than 450 m (Table 1) where, according to Bertrand et al. (this volume), the maturity of the organic matter reaches more than 0.5% vitrinite reflectance. The occurrence of higher hydrocarbons coincides with the zone of mature organic matter. We conclude from the molecular composition of gases from the thermogenic zone that these gases are mixed gases of microbial and thermal origins. Although methane is the dominant compo-



Figure 3. Isotope profile of methane from gas pockets at Site 768 shows a steady decrease of the  $^{13}$ C isotope with depth.



Figure 4. Carbon isotope ratios of methane and molecular ratios indicate a correlated decrease of the light isotope with decreasing methane concentrations in "total" gases.

nent in gas pockets, significant amounts of ethane to pentanes were also detected (Table 1).

### Analyses on "Total" Gases

The hydrogen and carbon isotope ratios of methane of total gases released from sediments of Site 768 by the vacuum/acid treatment indicate a bacterial origin (Table 2) through  $CO_2$  reduction (Whiticar et al., 1986). Obviously, the datum points deviate from those of the gas pockets to more positive carbon values, indicating a depletion of the light isotope <sup>12</sup>C (Fig. 4). The ratio of methane to the sum of ethane and propane in combination with the carbon isotope data of methane (Fig. 4, Table 2) shows that the methane of the desorbed gases is different from

Sample 124-768C-	Depth (mbsf)	CH <sub>4</sub> (%)	C <sub>2</sub> H <sub>6</sub> (ppm)	C <sub>3</sub> H <sub>8</sub> (ppm)	i-C <sub>4</sub> (ppm)	n-C <sub>4</sub> (ppm)	i-C5 (ppm)	n-C5 (ppm)	$\frac{C_1}{C_2 + C_3}$	δ <sup>13</sup> C CH <sub>4</sub> (‰)	δD CH <sub>4</sub> (‰)
8R2-145	423.65	99.95	464	3	1	0	8	0	2140	-72.6	_
9R2-43	432.13	99.95	474	3	3	0	0	1	2095	-72.0	-184
10R3-51	443.41	99.95	459	2	2	0	0	0	2168	-72.4	-183
11R3-67	453.27	99.95	475	3	0	0	0	0	2091	-72.3	-183
12R1-124	460.44	99.94	540	6	6	0	0	0	1830	-70.2	-181
13R2-103	471.43	99.94	604	5	6	0	0	0	1641	-71.2	-185
14R1-60	479.10	99.94	569	25	9	0	0	0	1682	-72.0	-183
15R3-59	491.79	99.94	580	5	3	0	0	0	1708	-72.4	-187
17R2-71	509.71	99.94	556	12	5	0	0	0	1760	-72.5	-185
18R2-38	519.08	99.93	684	19	9	0	0	0	1421	-72.3	-184
19R1-135	528.25	99.93	703	17	9	0	0	0	1388	-72.5	-187
19R2-20	528.60	99.93	637	16	7	0	0	0	1530	-72.5	-185
26R4-32	599.42	99.90	886	65	26	0	0	0	1050	-73.3	-190
27R4-2	608.82	99.88	1060	82	33	1	4	0	875	-73.1	-190
28R5-56	620.46	99.88	1097	96	34	2	7	0	837	-70.3	-184
29R2-21	625.21	99.88	1066	89	30	0	8	1	865	-73.4	-189
31R1-88	643.68	99.87	1179	96	30	2	4	0	783	-72.0	-186
33R6-27	669.87	99.85	1310	110	30	2	6	0	703	-71.1	-185
37R2-112	703.42	99.84	1430	116	35	0	10	0	646	-74.3	-190
38R2-90	712.90	99.84	1426	37	9	3	9	0	682	-74.3	-188
39R1-80	721.00	99.59	1600	300	0	14	0	0	524	-73.6	-178
39R3-112	724.32	99.97	248	0	2	0	0	0	4031	-73.6	-188
40R2-56	731.96	99.85	1360	100	30	0	0	0	684	-74.4	-182
41R5-6	745.66	99.79	1800	0	300	0	10	0	554	-73.1	-162
42R2-100	751.80	99.61	2200	400	300	0	0	0	383	-73.4	-167
43R2-23	760.23	99.10	8900	0	100	0	0	0	111	-73.4	
63R3-52	953.82	99.83	1700	0	0	0	0	0	587	-77.5	-176
65R4-5	974.25	99.84	1500	0	100	0	0	0	666	-78.0	-176

Note: ppb =  $(g_{gas}/g_{wet sediment}) \times 10^9$ 

the methane of the gas pockets. The observed depletion of the light carbon isotope in the methane of the desorbed gases with decreasing methane concentration points to a secondary alteration of the methane. This observation can be attributed either to bacterial oxidation or to a degassing fractionation of methane as both processes result in a loss of the light isotope (Faber and Stahl, 1984; Whiticar and Faber, 1986). The time between collection of the sediment sample from the core and freezing of the sediment is too short (5 to 10 min.) to allow oxidizing bacteria to consume significant quantities of methane in the presence of oxygen, but within this time interval it is likely that a significant quantity of methane is lost by desorption from the sediment and diffusion into the air. This process can lead to an increase of the heavy <sup>13</sup>C and D isotopes in the gas fraction remaining in the sediment because of the lower desorption capacity of molecules containing heavy isotopes.

Because of the possible secondary alteration of total sediment gases they are excluded from the further discussion.

# Comparison of Hydrogen Isotope Data of Pore Waters and Methane of Gas Pockets

No dissolved CO<sub>2</sub> could be obtained from pore waters of the hydrocarbon- bearing sediments of Site 768. For the differentiation of autochthonous and allochthonous bacterial methane, a comparison between the hydrogen isotope ratios of the substrate water and the methane is essential. The hydrogen isotopic composition of autochthonous biogenic methane is related to the isotopic composition of the substrate H<sub>2</sub>O on which the bacteria live (Whiticar et al., 1986), whereas the isotope ratios of allochthonous gases are expected to show no relationship to the isotopic compositions of the water. For the purpose of comparing hydrogen isotope ratios of interstitial waters and methane (because samples of water and methane are not from the same depth) we first have to describe the change of the D/H ratio of water with increasing depth for Site 768. The D/H ratios of interstitial waters decrease with increasing depth from +6% to -6 ‰ over a depth range of 600 m (Fig. 5A, Table 3). Similar findings have been reported from other DSDP/ODP sites (Lawrence, 1989 and literature cited therein). The most likely explanation for this observation is a diffusion of isotopically light water from the basaltic basement rather than an isotopic shift due to mineral alteration or temperature-induced isotope differentiation through diffusion (Lawrence, 1989). The observed vertical isotope variation can be approximated by the linear regression function

$$Depth = -53.91 \ \delta D_{H,O} + 264.95. \tag{2}$$

From the hydrogen isotope fractionation function of water and methane for methane formation from  $CO_2$  reduction (Whiticar et al., 1986)

$$dDCH_4 = \delta D_{H_2O} - 180 \pm 10, \tag{3}$$

it is possible to predict the hydrogen isotopic variation with depth for an *in-situ* generation of methane at Site 768 by rearranging (3) and substituting into (2). This calculated depth trend for the hydrogen isotopic variation of methane (extrapolated to a depth of 800 m) is shown in Figure 5B and compared to the measured hydrogen isotope ratios of methanes from gas pockets of Site 768 (Table 1). Obviously, the measured data follow the predicted isotope trend between 400 and 700 m. Gases from deeper 700 m deviate from the calculated trend toward more positive isotope ratios. The observed coincident of the set of the

toward more positive isotope ratios. The observed coincidence of calculated and measured isotope values of methane between 400 and 700 m indicates that bacterial methane at this depth interval was generated *in situ*. Gases that deviate from the calculated isotope trend in the lowermost part of the sediment section toward positive values are likely to be allochthonous. These gases are found in turbidites and pyro-

Table 2. Molecular composition and isotope data of total gases in Holes 768B and 768C.

Sample 124-	Depth (mbsf)	CH <sub>4</sub> (ppb)	C <sub>2</sub> H <sub>6</sub> (ppb)	C <sub>3</sub> H <sub>8</sub> (ppb)	i-C <sub>4</sub> (ppb)	n-C <sub>4</sub> (ppb)	$\frac{C_1}{C_2 + C_3}$	δ <sup>13</sup> C CH <sub>4</sub> (‰)	δD CH <sub>4</sub> (‰)
768B-3H-CC, 21-23	23.46	6.61	3.59	2.16	0.00	0.00	2.44	_	_
768B-5H-CC, 11-13	42.18	15.45	10.68	6.42	0.00	0.00	1.92		-
768B-9H-CC, 27-29	80.52	18.10	13.02	8.57	0.00	0.00	1.79	-35.9	-
768B-13H-CC, 29-31	118.53	49.80	36.69	22.78	0.00	0.00	1.78		_
768B-19H-CC, 41-43	173.82	10.68	4.48	10.65	0.00	0.00	1.70	<u> </u>	_
768B-22H-CC, 38-40	200.99	25.15	1.95	0.80	0.00	0.00	18.90	-	-
768B-28X-CC, 37-39	247.00	9.21	0.78	0.00	0.00	0.00	22.04		_
768B-34X-CC, 35-37	300.26	200.05	2.35	0.59	0.00	0.00	135.83	-71.7	_
768C-1R-CC, 14-16	359.86	76.83	9.12	13.48	14.91	17.27	7.86	-62.8	_
768C-7R-CC, 14-16	419.19	507.75	16.32	1.64	1.22	0.68	54.50	-66.1	_
768C-13R-CC, 18-20	474.26	46.51	1.50	0.44	0.44	0.23	48.55	-67.8	
768C-19R-CC, 15-17	529.85	250.86	14.42	3.46	6.63	0.59	28.01	-70.7	-
768C-22R-CC, 15-17	559.30	58.48	3.86	3.00	3.60	1.02	18.55	-63.4	
768C-22R-CC, 13-15	623.17	714.46	27.34	10.36	8.70	1.15	39.01	-67.0	-165
768C-34R-CC, 16-18	681.07	395.19	42.19	33.06	29.83	5.32	11.44	-69.4	_
768C-37R-CC, 12-14	709.15	45.97	11.96	13.29	12.45	3.35	4.10	-62.4	_
768C-43R-CC, 13-15	762.32	52.32	2.31	2.07	1.68	0.77	26.28	-71.0	_
768C-48R-CC, 0-2	813.91	10.43	2.48	0.86	0.00	0.00	6.38	-54.5	
768C-54R-CC, 44-46	871.00	30.48	2.00	0.30	0.00	0.00	25.88	-72.6	_
768C-60R-CC, 13-15	931.31	110.75	1.81	0.39	0.00	0.00	100.00	-	-
768C-65R-CC, 33-35	977.12	752.22	0.85	0.30	0.00	0.00	1427.42	-78.19	-159
768C-72R2, 66-68	1039.06	104.86	10.69	5.23	0.00	0.00	13.79	-63.19	_

Table 3. Hydrogen isotope data from pore waters in Holes 768B and 768C.

Sample 124-	Depth (mbsf)	δD H <sub>2</sub> O (‰)
768B-1H-2, 145-150	2.95	1.9
768B-2H-5, 145-150	11.45	3.0
768B-3H-5, 145-150	20.95	4.9
768B-4H-5, 145-150	30.45	5.5
768B-5H-4, 145-150	38.45	6.0
768B-6H-5, 145-150	49.45	4.0
768B-7H-5, 145-150	58.95	4.1
768B-8H-5, 145-150	68.45	4.4
768B-9H-5, 145-150	77.95	4.2
768B-10H-5, 145-150	87.45	3.7
768B-13H-5, 145-150	115.95	3.1
768B-16H-5, 145-150	144.45	2.5
768B-19H-5, 140-150	172.90	-0.5
768B-22H-4, 140-150	198.70	-0.5
768B-26X-2, 140-150	222.20	-0.5
768B-28X-4, 140-150	244.50	-0.4
768B-31X-5, 140-150	274.90	-1.8
768B-34X-2, 140-150	299.30	-1.7
768B-37X-2, 140-150	328.40	0.1
768C-1R-3, 140-150	357.60	-0.2
768C-4R-1, 140-150	383.50	-2.6
768C-7R-3, 140-150	415.50	-4.4
768C-10R-3, 140-150	444.30	-3.5
768C-13R-3, 140-150	473.30	-3.6
768C-16R-1, 140-150	499.30	-3.3
768C-19R-1, 140-150	528.30	-2.8
768C-22R-2, 140-150	558.70	-2.7
768C-26R-4, 140-150	600.50	-5.3
768C-28R-4, 140-150	619.80	-3.1

clastics with TOC values below 0.1% (Rangin, Silver, von Breymann et al., 1990).

These findings coincide with results from shipboard analyses of headspace gases concentrations (Rangin, Silver, von Breymann et al., 1990). Below 700 m, gas concentrations in sediments that are lean in organic matter are, on average, one order of magnitude higher than gas concentrations in sediments with TOC values between 0.2% and 3.85% (Rangin, Silver, von Breymann et al., 1990). This observation clearly indicates that gases of the lowermost sediment section at Site 768 were not generated *in situ*.

The observed hydrogen isotope shift in gases of the lower section toward positive isotope values cannot be attributed to an admixture of thermal methane with higher deuterium concentration. Theoretically, this result would be possible, as organic matter at Site 768 has the appropriate maturity to generate thermal hydrocarbons (see below). In this case, however, the carbon isotope values also should increase but do not. A comparison of Figures 3 and 5B shows that the two isotope species show diverse trends. The high D/H ratios of the allochthonous gases, which are similar and/or more positive than values from gases from the initial zone of methanogenesis of Site 768, indicate that these gases were generated from pore waters with low D/H ratios similar to those of the upper part of the bacterial methane zone. But generally, a direct extrapolation of the generation depth from hydrogen isotope values of the methane is not possible because the vertical distribution of D/H ratios of the pore waters in the sediment column of the Sulu Trench may vary locally.

The gases were most likely transported by advective flows from higher structures of the Sulu Trench Basin into deeper structures, possibly via permeable turbidites and/or pyroclastics that are present in this basin. The allochthonous gases detected at Site 768 were likely generated in the Sulu Trench Basin itself and not on the near Cagayan Ridge because the two sites drilled on the Cagayan Ridge (Site 769 and Site 771), which terminated in basaltic rocks, showed background methane concentrations in sediments associated with high amounts of sulfate in pore waters (Rangin, Silver, von Breymann et al., 1990).

#### CONCLUSIONS

1. Carbon and hydrogen isotope ratios of methane in sediments at Site 768 point to methane formation through microbial reduction of  $CO_2$ .

2. A comparison between calculated D/H ratios of methane deduced from the isotope ratios of interstitial  $H_2O$  and measured deuterium concentration of methane points to an *in-situ* generation of methane down to a sub-bottom depth of approximately 700 m.

3. Below 700 mbsf, hydrogen isotope data indicate a migration of light hydrocarbons into pyroclastic sediments.

#### HYDROCARBON MOLECULAR AND ISOTOPIC COMPOSITION

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Figure 5. The D/H ratios of interstitial waters (A) decrease with increasing depth from +6% to -6% over a depth range of 600 m. A calculated depth trend (B) for the hydrogen isotopic variation of methane deduced from the D/H ratios of pore waters is compared to the measured hydrogen isotope ratios of methane from gas pockets at Site 768.