

24. ISOTOPE COMPOSITIONS OF GASES IN SEDIMENTS FROM THE CHILE CONTINENTAL MARGIN¹

Amane Waseda² and Borys M. Didyk³

ABSTRACT

Molecular and isotope measurements of gases from gas pockets at ODP Leg 141 Sites 859, 860, 861, and 863 are reported. The $\delta^{13}\text{C}$ values of methane range between -86‰ and -61‰ . The δD values of methane range between -249‰ and -163‰ . The $\text{C}_1/(\text{C}_2 + \text{C}_3)$ ratios of all samples are higher than 300. These data indicate methane is mainly produced by bacterial activity, and the primary methanogenic pathway is CO_2 reduction. The $\delta^{13}\text{C}$ values of ethane range between -70‰ and -44‰ . These values are among the lightest carbon isotope values reported for ethane in natural gas, indicating the origin of ethane is also predominantly bacterial. In deeper strata below 200 m below seafloor (mbsf) at Site 860, the $\delta^{13}\text{C}$ values of ethane become heavier from -60‰ to -45‰ and the C_1/C_3 ratios decrease with increasing depth. This indicates the presence of a small amount of thermogenic hydrocarbons. The low degree of maturation of the organic matter suggest the thermogenic hydrocarbon components are not generated in situ but have migrated from more mature strata, possibly driven by active fluid flow in these strata.

INTRODUCTION

Seismic sections across the Chile margin in the forearc region indicate the presence of bottom-simulating reflectors (BSRs). BSRs are thought to mark the base of a layer of gas hydrates (Shipley et al., 1979), and have been associated with actual recovery of hydrates (Shipley and Didyk, 1982). Hydrates are ice-like solids that contain large concentrations of gas, predominantly methane (Kvenvolden and Barnard, 1983). The hydrate layer is thought to be in pressure-temperature equilibrium with free hydrocarbon gases (Miller et al., 1991). Ocean Drilling Program (ODP) Leg 141 in the vicinity of the Chile Triple Junction (Fig. 1) has, for the first time, intentionally penetrated the base of the hydrate layer. The hydrate layer was penetrated at three sites (Sites 859, 860, and 861). Although no frozen gas hydrates were recovered, sediments contained abundant methane at all three sites.

The carbon isotope composition of methane is widely used for the genetic classification of hydrocarbon gases (Rosenfield and Silverman, 1959; Bernard, 1978; Schoell, 1980; Rice and Claypool, 1981). It allows the distinction between bacterial and thermogenic hydrocarbons. Schoell (1980) and Whiticar et al. (1986) have shown additionally that the hydrogen isotope composition of methane in combination with the carbon isotope composition characterizes different pathways of bacterial methane formation. Here, we investigate the genetic characterization of light hydrocarbons by analyses of stable carbon and hydrogen isotope compositions in combination with molecular compositions of gases.

GEOLOGIC SETTING

At the Chile Triple Junction (Fig. 1) an active spreading ridge and adjacent young oceanic crust are being subducted beneath the continent of South America. During ODP Leg 141, Pliocene to Pleistocene sedimentary sequences were recovered at four sites. Three Sites (859, 860, and 861) were drilled along an east-west dip transect about 35 km north of the Chile Triple Junction at water depths ranging from 1652 to 2741 m. Site 863 (2564 m water depth) was drilled at the base

of a trench-slope basin directly above the subducted spreading axis as a strike transect with Site 859.

METHODS

Gas pockets visible in the core through clear plastic core liner were tapped with a hollow punch, and samples were expanded into 20-ml evacuated sample tubes (vacutainers) aboard *JOIDES Resolution*. The molecular compositions of hydrocarbon gases were determined on a Hewlett-Packard 5890a gas chromatograph.

For the isotope analyses the individual gas components were separated by a gas chromatograph and subsequently combusted to CO_2 and H_2O over CuO at 850°C , using a vacuum preparation line (Schoell, 1980). The combustion produced H_2O is reduced to H_2 by reaction with zinc in sealed glass tubes at 480°C (Vennemann and O'Neil, 1993).

The stable carbon and hydrogen isotope values of methane were measured using a VG Isotech Sira Series II mass spectrometer. Enough ethane was available from several samples for carbon isotope measurements. Isotope ratios are reported in the usual δ -notation relative to the PDB (Pee Dee Belemnite) standard for carbon and SMOW (Standard Mean Ocean Water) standard for hydrogen:

$$\delta R_d(\text{‰}) = \left\{ \left[\frac{(R_d/R_b)_{\text{sample}}}{(R_d/R_b)_{\text{standard}}} \right] - 1 \right\} \times 1000, \quad (1)$$

where R_d/R_b is $^{13}\text{C}/^{12}\text{C}$ and D/H , respectively. The reproducibility of isotope values is $\pm 0.15\text{‰}$ for $\delta^{13}\text{C}$ of methane, $\pm 0.3\text{‰}$ for $\delta^{13}\text{C}$ of ethane, and $\pm 3\text{‰}$ for δD of methane.

RESULTS AND DISCUSSION

Vacutainer gas samples from four sites analyzed in this study are listed by depth of burial in Table 1. $\delta^{13}\text{C}$ values of methane and ethane and δD values of methane determined in this study are reported, as well as the shipboard determination of hydrocarbon composition. Gas pockets frequently appeared and high concentrations of methane were consistently observed at Sites 859, 860, and 861 drilled along the east-west dip transect. At Site 863 drilled as the strike transect with Site 859, gas pockets were relatively rare, and concentrations of methane were low in most vacutainer samples. Only two samples had enough methane for isotope analyses at Site 863. Carbon dioxide concentrations are below 0.1% (1000 ppm) in all samples. We could not measure carbon isotope values of CO_2 due to its low concentration.

¹ Lewis, S.D., Behrmann, J.H., Musgrave, R.J., and Cande, S.C. (Eds.), 1995. *Proc. ODP, Sci. Results*, 141: College Station, TX (Ocean Drilling Program).

² JAPEx Research Center, 1-2-1 Hamada, Mihama-ku, Chiba 261, Japan.

³ Empresa Nacional del Petróleo, Refinería de Petróleos Concón S.A., Casilla 28-D, Viña del Mar, Chile.

Table 1. Molecular composition and isotope data of vacutainer gas samples.

Core, section	Depth (mbsf)	Concentration (ppm)*			Ratio			$\delta^{13}\text{C}\text{‰}$			$\delta\text{D}\text{‰}$
		CH_4	C_2H_6	C_3H_8	C_1/C_2	C_1/C_3	$\text{C}_1/(\text{C}_2+\text{C}_3)$	CH_4	C_2H_6	CH_4	
141-859A-											
4H-1	17.5	862,231	56	0	15,397		15,397	-69.9			-183
5H-6	33.5	916,452	58	0	15,801		15,801	-69.8			
141-859B-											
3R-5	78.0	880,897	72	0	12,235		12,235	-66.2			
10R-3	200.0	742,056	156	7	4757	106,008	4552	-66.2			-174
12R-3	220.0	922,939	275	39	3356	23,665	2939	-66.6			-211
13R-4	231.0	944,456	282	53	3349	17,820	2819	-61.7			-206
16R-3	259.0	953,223	373	152	2556	6271	1816	-65.9			-243
20R-1	294.0	925,201	367	127	2521	7285	1873	-65.0			-209
23R-3	325.0	131,681	38	12	3465	10,973	2634	-65.8			
27R-2	362.2	78,759	19	8	4145	9845	2917	-63.9			-189
34R-2	430.0	750,898	320	163	2347	4607	1555	-63.0			-200
141-860B-											
4H-7	30.0	738,541	8	3	92,318	246,180	67,140	-72.5			-191
7H-5	56.0	915,282	11	4	83,207	228,821	61,019	-67.6			-163
14X-2	101.0	578,722	14	3	41,337	192,907	34,042	-66.7			-208
17X-5	133.0	790,414	56	0	14,115		14,115	-65.7			-208
21X-1	153.3	782,189	66	0	11,851		11,851	-65.3			-183
24X-1	184.4	809,063	245	0	3302		3302	-65.2			-222
25X-2	195.5	749,855	371	0	2021		2021	-64.9			-209
38X-2	321.5	889,497	1800	26	494	34,211	487	-64.1	-60.5		-202
41X-5	355.1	960,281	2126	35	452	27,437	444	-63.5	-60.7		-239
43X-2	361.1	863,584	2308	62	374	13,929	364	-62.8	-59.1		-202
48X-4	411.7	856,949	2239	53	383	16,169	374	-63.3	-53.3		-201
51X-2	436.3	685,249	1636	54	419	12,690	405	-64.2	-44.4		-200
53X-2	456.2	620,622	1714	76	362	8166	347	-62.9	-46.8		
60X-2	514.3	818,272	2198	126	372	6494	352	-62.9	-45.9		-223
62X-2	533.1	970,142	2917	166	333	5844	315	-62.8	-47.0		
141-861A-											
1H-6	8.7	67,077	0	0				-85.1			-222
141-861C-											
4H-3	25.6	621,209	0	2		310,605	310,605	-77.5			-249
7H-3	54.3	661,711	10	2	66,171	330,856	55,143	-71.8			
12X-2	92.2	898,750	65	5	13,827	179,750	12,839	-69.9			
15X-2	120.7	929,217	167	4	5564	232,304	5434	-69.3			-201
17X-2	140.3	966,546	287	2	3368	483,273	3344	-68.6			-196
21X-1	171.4	924,548	573	0	1614		1614	-67.7			-201
25X-5	215.2	925,918	1404	8	659	115,740	656	-65.6	-60.9		-206
32X-2	258.7	876,737	1593	8	550	109,592	548	-64.7	-64.7		-181
35X-3	288.3	828,978	1381	9	600	92,109	596	-64.4	-61.4		-211
37X-1	306.2	926,816	1533	12	605	77,235	600	-64.9	-59.1		
141-861D-											
6R-3	392.4	949,058	1340	6	708	158,176	705	-64.0	-62.1		-206
12R-2	450.0	924,212	716	3	1291	308,071	1285	-64.6			-206
141-863A-											
8X-4	70.3	836,885	2118	0	395		395	-79.7	-69.9		-227
14X-1	124.5	24,026	11	0	2184		2184	-66.8			

Note: * = Shipboard measurement. Blanks indicate data not available.

The $\delta^{13}\text{C}$ values of methane range between -86‰ and -61‰ (Table 1). The $\text{C}_1/(\text{C}_2 + \text{C}_3)$ ratios of all vacutainer samples are higher than 300. Those isotope and molecular compositions indicate methane was mainly produced by bacterial activity (Fig. 2). Bacterial methane formation follows two principal pathways (i.e., CO_2 reduction and fermentation; Schoell, 1980; Jenden and Kaplan, 1986; Martens et al., 1986; Whiticar et al., 1986; Burke et al., 1988). The fermentation processes are usually more important in recent freshwater sediments and swamps, while methane formed by CO_2 reduction is most common in marine sediments (Whiticar et al., 1986). Recent studies however revealed that the methanogenic pathway is not controlled by depositional environment but mainly controlled by temperature, organic substrate, and age of sediments (Schoell, 1988). CO_2 reduction-derived methane and fermentation-derived methane can be differentiated by their deuterium concentration. Fermentation-derived methane is characterized by its depletion in deuterium. δD values of vacutainer gas samples in this study range between -249‰ and -163‰ (Table 1), indicating methanes were generated by bacterial CO_2 reduction (Fig. 3). Methanogenic CO_2 -reducing bacteria are generally active after sulfate depletion by sulfate-reducing bacteria (Claypool and Kaplan, 1974). This mechanism of methanogenesis

is consistent with the observation that relatively low sulfate concentrations in interstitial waters accompany with abundant methane at Sites 859, 860, and 861, while high concentrations of sulfate with low concentrations of methane are observed at Site 863 (Behrmann, Lewis, Musgrave, et al., 1992).

Methane isotope profiles with depth at Sites 859, 860, and 861 are compiled in Figure 4. The BSR lies at approximately 100, 200, and 250 mbsf (meters below seafloor) at Sites 859, 860, and 861, respectively. No distinct change of the $\delta^{13}\text{C}$ values of methane or molecular compositions are observed at those depths. The $\delta^{13}\text{C}$ values of methane become heavier with increasing depth in the upper 200 m at all sites. These changes accord with the predictions of the theoretical model, which assumes the bacterial formation of CH_4 by reducing CO_2 under closed-system conditions (Claypool and Kaplan, 1974). When CH_4 is generated in sediments, the ΣCO_2 reservoir becomes depleted in ^{12}C because of preferential removal of ^{12}C -enriched CO_2 to form CH_4 .

The concentrations of ethane range from 0 to 3000 ppm. The decrease of C_1/C_2 ratios with increasing depth in the upper 200 m are observed (Fig. 5). Ethane and higher hydrocarbons generally increase in concentration with depth in other DSDP and ODP cores (Emeis and

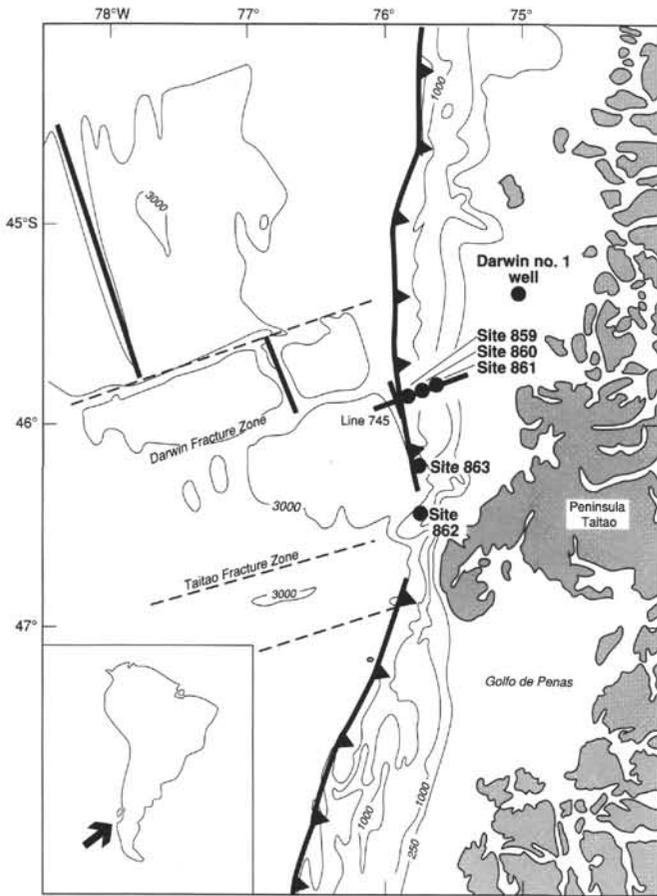


Figure 1. Tectonic sketch map of the Chile Triple Junction and its surroundings showing location of Sites 859, 860, 861, and 863. Solid bold lines indicate spreading segments of the Chile Ridge, separating Nazca Plate (north) and Antarctic Plate (south), barbed line is the frontal thrust of the South American forearc.

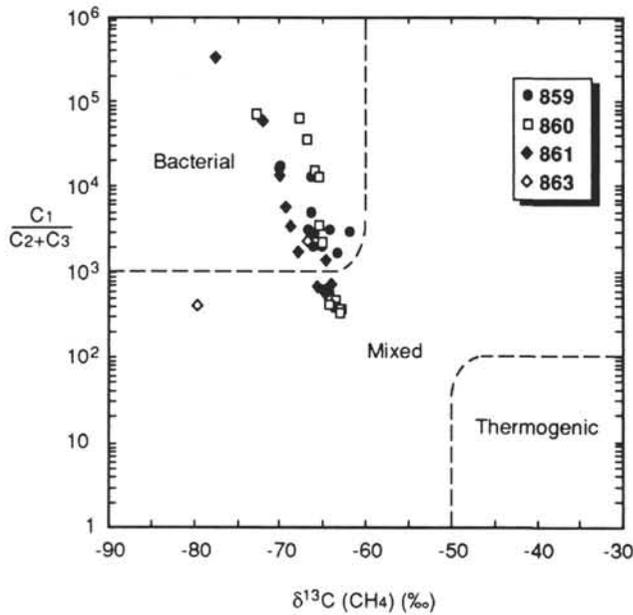


Figure 2. Interpretative plot of molecular ratios vs. carbon isotope compositions of methane from gas pockets, combining Sites 859, 860, 861, and 863 (diagram modified after Bernard, 1978).

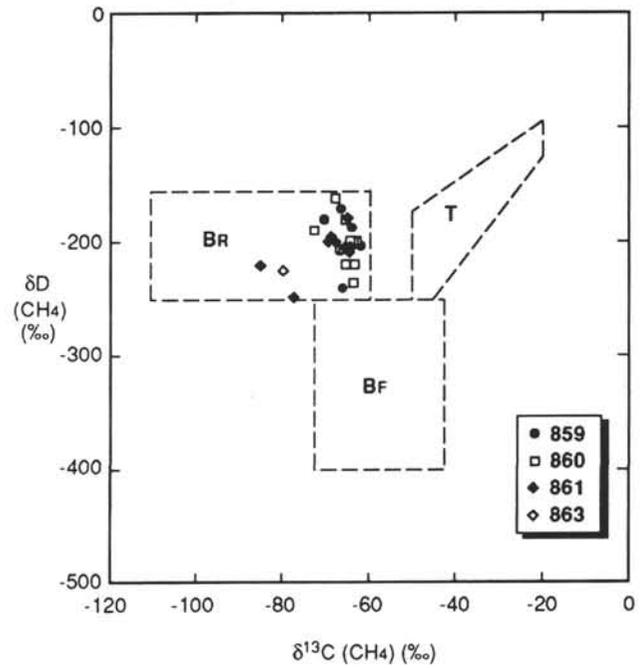


Figure 3. Interpretative plot of hydrogen and carbon isotope compositions of methane from gas pockets, combining Sites 859, 860, 861, and 863 (diagram modified after Schoell, 1988). Fields BR and BF are the areas which encompass bacterial methanes that form by CO₂ reduction and fermentation, respectively. Field T is the area which encompasses methane of thermogenic origin.

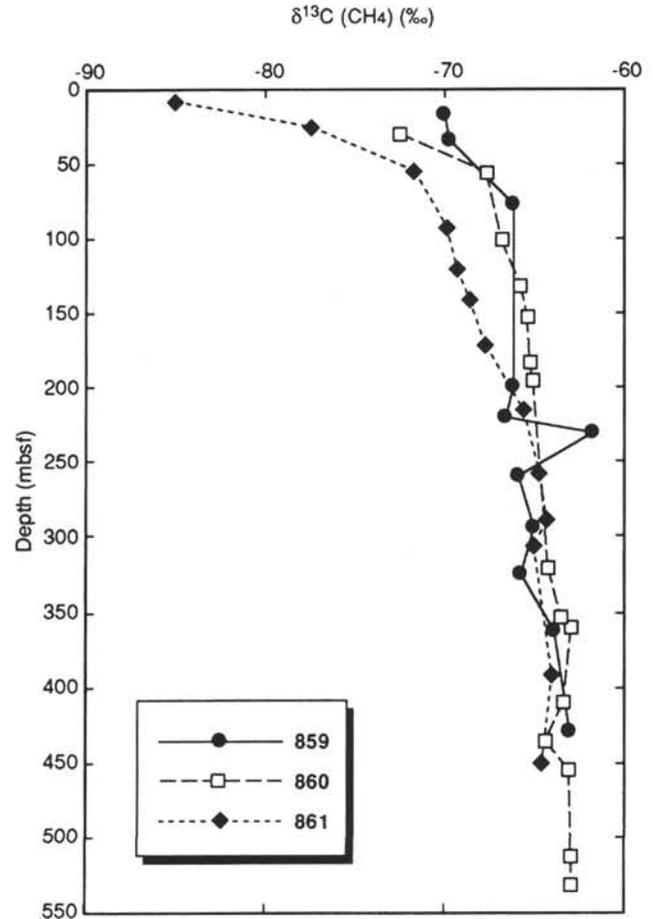


Figure 4. Carbon isotope profile of methanes from gas pockets from Sites 859, 860, and 861.

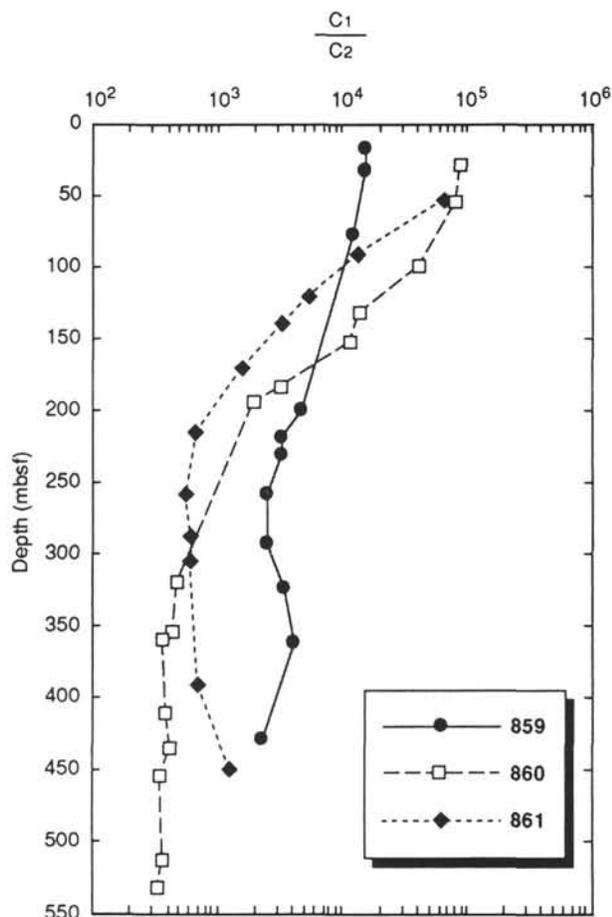


Figure 5. C_1/C_2 ratio profile of hydrocarbons from gas pockets at Sites 859, 860, and 861.

Kvenvolden, 1986). Ethane and higher hydrocarbons are generally interpreted as thermogenic components resulting from both thermal degradation of indigenous organic matter in sediments and/or upward migration from deeper, more mature strata. However, active formation of bacterial higher hydrocarbons has been observed in anaerobic bacterial culture experiments (Hunt et al., 1980) and incubation studies of sediments from different aquatic environments (Vogel et al., 1982; Oremland et al., 1988). This kind of experimental evidence, combined with the common observation of small quantities of ethane and higher hydrocarbons in recent marine sediments, has led some authors to suggest bacterial and low temperature chemical processes as a reasonable source for these hydrocarbons (Hunt et al., 1980; Kvenvolden and Redden, 1980; Whelan et al., 1980).

$\delta^{13}C$ values of ethane were measured on 13 samples below 200 mbsf at Sites 860 and 861, and one sample at 70 mbsf at Site 863, ranging between -70‰ and -44‰ (Table 1). The $\delta^{13}C$ values of ethane of core gases from ODP Leg 84, Site 570 are fairly uniform, ranging from -24‰ to -26‰ in six sections, indicating a thermogenic origin (Jeffrey et al., 1985), and those values measured on sorbed gases from ODP Leg 112, Sites 679, 680, and 682 range from -38‰ to -25‰ for 22 samples except for one data of -48.3‰ , also indicating a thermogenic origin (Whiticar and Suess, 1990). Ethanes of this study are depleted in ^{13}C compared to these data, and the carbon isotope compositions are among the lightest values reported for ethane in natural gas. The $\delta^{13}C$ values of organic matter in the sediments of this region averages about -25‰ (Waseda et al., this volume). The differences between the $\delta^{13}C$ values of ethane and organic matter in this region are approximately 20‰ to 45‰. Such large fractionation can not be explained by thermogenic or low temperature chemical

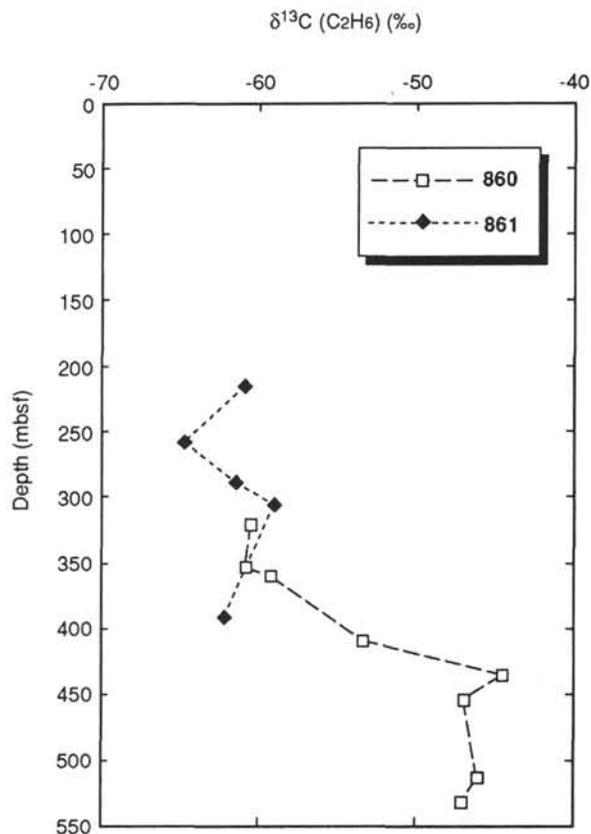


Figure 6. Carbon isotope profile of ethanes from gas pockets at Sites 860 and 861.

reaction. Therefore, we conclude that the origin of this isotopically light ethane is mainly bacterial. Isotopically light (-58‰ to -45‰) biogenic ethane has also been reported in natural gas samples from Italy (Mattavelli et al., 1992).

Propane and higher hydrocarbons can also be generated by bacterial activity (Hunt et al., 1980). However, the detection of heavier hydrocarbons extending up to C_7 in vacutainer and headspace gases in deeper layers below 200 mbsf and presence of well-matured extracted bitumens in some sediment samples strongly suggest the existence of migrated thermogenic hydrocarbons (Behrmann, Lewis, Musgrave, et al., 1992; Didyk et al., this volume). The $\delta^{13}C$ values of ethane become heavier from -60‰ to -45‰ and the C_1/C_3 ratios decrease with increasing depth at the interval of 350 to 450 mbsf at Site 860, while the $\delta^{13}C$ values of ethane are almost constant and the C_1/C_3 ratios are also constant, ranging between 10^5 and 10^6 at Site 861 (Figs. 6 and 7). The $\delta^{13}C$ values of ethane and C_1/C_3 ratios show negative correlation at Site 860 (Fig. 8). If propane is mainly derived from thermogenic decomposition of organic matter, these changes in the $\delta^{13}C$ values of ethane and C_1/C_3 ratios at Site 860 can be explained by the increase of thermogenic hydrocarbon contribution with increasing depth. The low degree of maturation of the organic matter is observed at all sites of Leg 141 in accordance with the shallow depth of burial of the sediments and low bottom hole temperature. We therefore suggest the thermogenic hydrocarbon components are not generated in situ but have migrated from more mature strata.

Since the concentrations of ethane are too low, we could not measure the $\delta^{13}C$ values of ethane at Site 859. In deeper strata below 200 mbsf, C_1/C_2 ratios at Site 859 are higher than those of Sites 860 and 861 (Fig. 5). On the other hand, C_1/C_3 ratios at Site 859 are lowest among three sites (Fig. 7). Judging from these results, at Site 859, we infer bacterial ethane production is least active and thermogenic hydrocarbon contribution in deeper strata below 200 mbsf is highest among

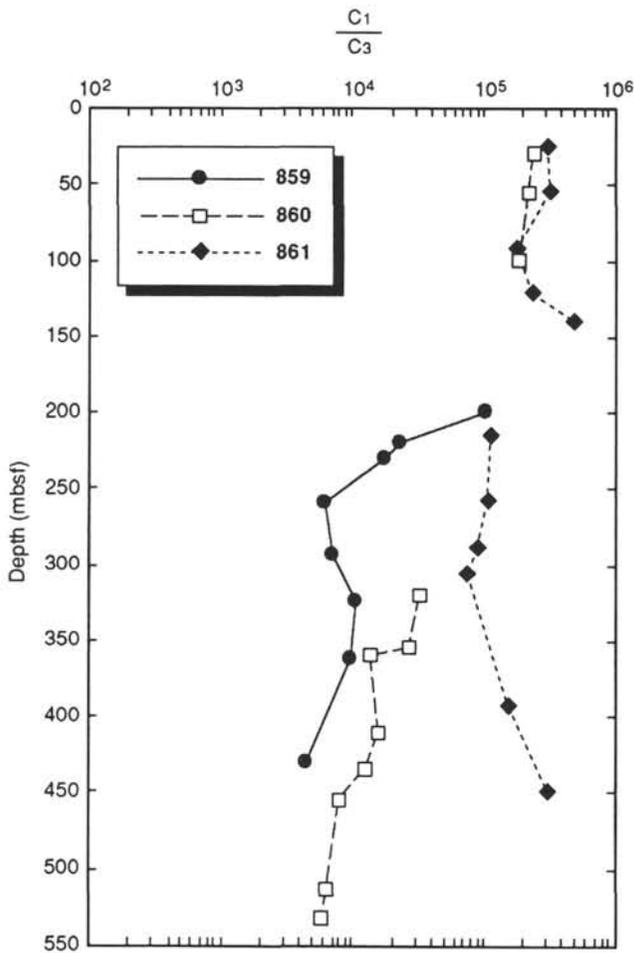


Figure 7. C_1/C_3 ratio profile of hydrocarbons from gas pockets at Sites 859, 860, and 861.

three sites. The methane isotope depth profile at Site 859 is rougher than the profiles at Sites 860 and 861, and a positive spike is observed at 231 mbsf (Fig. 4). The downhole geothermal gradient at Site 859 is extremely nonlinear downhole, showing active lateral fluid flow, and the evaluation of the temperature data recorded at 240 mbsf shows that the borehole fluid at this depth was substantially hotter, indicating the injection of hot fluids into the borehole from an aquifer of limited stratigraphic thickness in the near vicinity (Shipboard Scientific Party, 1992). The depth of this thermal anomaly almost coincides with the depth of the positive spike on the methane isotope depth profile, indicating thermogenic hydrocarbons have migrated with hot fluids.

To calculate the mixing ratio between bacterial and thermogenic gases, we assume that the isotopic compositions of the thermogenic end member are -45‰ (CH_4) and -29‰ (C_2H_6), adopted from the isotope data of gas hydrate recovered in Gulf of Mexico whose origin is clearly classified as thermogenic (Brooks et al., 1984), and the molecular composition is 90% methane, 5% ethane, and 5% other gases. The bacterial end member is assumed to be the composition of Sample 141-861C-32X-2, which has the most ^{13}C -depleted ethane at Sites 860 and 861. The mixing line is shown in Figure 9, indicating the contribution of thermogenic gas does not exceed 5% of total gas in this case.

SUMMARY

Seismic sections across the Chile margin in the forearc region indicate the presence of bottom-simulating reflectors (BSRs) which

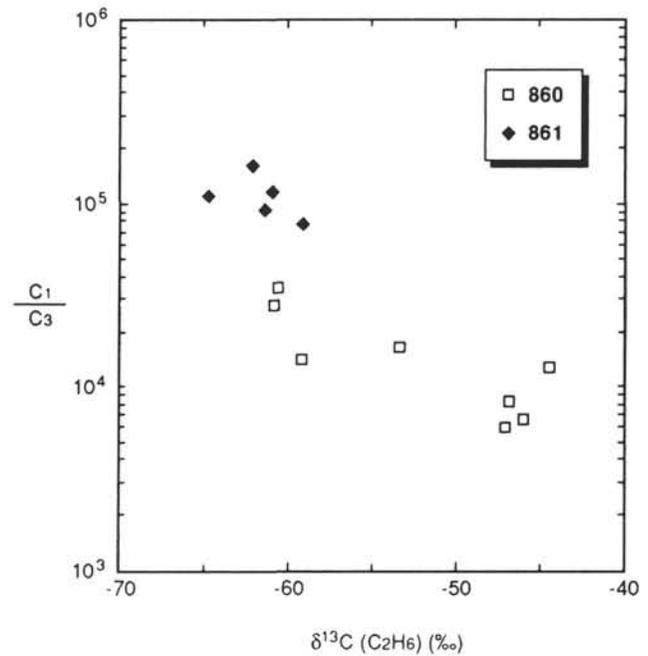


Figure 8. C_1/C_3 ratios and carbon isotope values of ethanes from gas pockets at Sites 860 and 861.

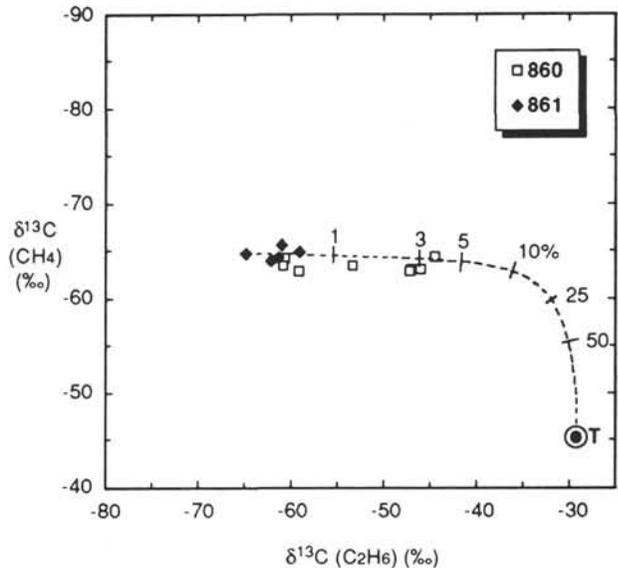


Figure 9. Carbon isotope compositions of methane and ethane from gas pockets at Sites 860 and 861. Dashed line indicates mixing between bacterial and thermogenic gases, supposing carbon isotope compositions of thermogenic end member (T) are -45‰ (methane) and -29‰ (ethane), and molecular composition is 90% methane, 5% ethane, and 5% other gases. The percentages of thermogenic components in total gases are shown with the mixing line.

are thought to mark the base of a layer of gas hydrates. The hydrate layer was penetrated at three sites (Sites 859, 860, and 861). Although no frozen gas hydrates were recovered, sediments contain abundant methane at all three sites. The $\delta^{13}\text{C}$ values of methane range between -86‰ and -61‰ . The δD values of methane range between -249‰ and -163‰ . The $C_1/(C_2 + C_3)$ ratios of all studied samples are higher than 300. These data indicate methane is mainly produced by bacterial activity, and the primary methanogenic pathway is CO_2 reduction.

The $\delta^{13}\text{C}$ values of ethane range between -70‰ and -44‰ , indicating the origin of ethane is also mainly bacterial.

In deeper strata below 200 mbsf at Site 860, the $\delta^{13}\text{C}$ values of ethane become heavier from -60‰ to -45‰ and the C_1/C_3 ratios decrease with increasing depth. This indicates the presence of a small amount of thermogenic hydrocarbons. Judging from C_1/C_3 ratios, the contribution of thermogenic gases is highest at Site 859, located nearest to the spreading ridge, and lowest at Site 861 among three sites drilled on the trench slope of the continental margin. The low degree of maturation of the organic matter suggest the thermogenic hydrocarbon component are not generated in situ but has migrated from more mature strata, possibly driven by active fluid flow in these strata.

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*Abbreviations for names of organizations and publications in ODP reference lists follow the style given in *Chemical Abstracts Service Source Index* (published by American Chemical Society).

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